Seymour/Carraher's

Polymer Chemistry

Seventh Edition

Charles E. Carraher, Jr.

CRC Press
Taylor & Francis Group

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Foreword

Polymer science and technology have developed tremendously over the last few decades, and the production of polymers and plastics products has increased at a remarkable pace. By the end of 2000, nearly 200 million tons per year of plastic materials were produced worldwide (about 2% of the wood used, and nearly 5% of the oil harvested) to fulfill the ever-growing needs of the *plastic age*; in the industrialized world plastic materials are used at a rate of nearly 100 kg per person per year. Plastic materials with over $250 billion per year contribute about 4% to the gross domestic product in the United States. Plastics have no counterpart in other materials in terms of weight, ease of fabrication, efficient utilization, and economics.

It is no wonder that the demand and the need for teaching in polymer science and technology have increased rapidly. To teach polymer science, a readable and up-to-date introductory textbook is required that covers the entire field of polymer science, engineering, technology, and the commercial aspect of the field. This goal has been achieved in Carraher's textbook. It is eminently useful for teaching polymer science in departments of chemistry, chemical engineering, and material science, and also for teaching polymer science and technology in polymer science institutes, which concentrate entirely on the science and technologies of polymers.

This seventh edition addresses the important subject of polymer science and technology, with emphasis on making it understandable to students. The book is ideally suited not only for graduate courses but also for an undergraduate curriculum. It has not become more voluminous simply by the addition of information—in each edition less important subjects have been removed and more important issues introduced.

Polymer science and technology is not only a fundamental science but also important from the industrial and commercial point of view. The author has interwoven discussion of these subjects with the basics in polymer science and technology. Testimony to the high acceptance of this book is that early demand required reprinting and updating of each of the previous editions. We see the result in this new significantly changed and improved edition.

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Preface

As with most science, and chemistry in particular, there is an explosive broadening and importance of the application of foundational principles of polymers. This broadening is seen in ever-increasing vistas allowing the promotion of our increasingly technologically dependent society and solutions to society's most important problems in areas such as the environment and medicine. Some of this broadening is the result of extended understanding and application of already known principles but also includes the development of basic principles and materials known to us hardly a decade ago. Most of the advancements in communication, computers, medicine, air and water purity are linked to macromolecules and a fundamental understanding of the principles that govern their behavior. Much of this revolution is of a fundamental nature and is explored in this seventh edition. The text contains these basic principles and also touches on their application to real-life situations. Technology is the application of scientific principles. In polymers there is little if any division between science and technology.

Polymers are found in the organic natural world as the building blocks for life itself. They are also found as inorganic building blocks that allow construction of homes, skyscrapers, and roads. Synthetic polymers serve as basic building blocks of society now and in the future. This text includes all three of these critical segments of polymeric materials.

A basic understanding of polymers is essential to the training of today's science, biomedical, and engineering students. *Polymer Chemistry* complies with the American Chemical Society's Committee on Professional Training old and revised guidelines as an advanced or in-depth course. It naturally integrates and interweaves the important core areas since polymers are critical to all of the core areas, which in turn contribute to the growth of polymer science. Most of the fundamental principles of polymers extend and enhance similar principles found throughout the undergraduate and graduate training of students. This allows students to integrate their chemical knowledge illustrating the connection between fundamental and applied chemical information. Thus, along with the theoretical information, application is integrated as an essential part of the information. As in other areas such as business and medicine, short case studies are integrated as historical material.

While this text is primarily written as an introductory graduate-level text, it can also be used as an undergraduate text, or as an introductory undergraduate–graduate text. The topics are arranged so that the order and inclusion or exclusion of chapters or parts of chapters will still allow students an adequate understanding of the science of polymers. Most of the chapters begin with the theory followed by application. The most important topics are generally at the beginning of the chapter followed by important, but less critical, sections. Some may choose to study the synthesis-intense chapters first, others the analytical/analysis/properties chapters, and yet others to simply read the chapters as they appear in the book. All of the elements of an introductory text with synthesis, property, application and characterization are present, allowing this to be the only polymer course taken by an individual or the first in a series of polymer-related courses taken by the student.

This edition continues in the "user-friendly" mode with special sections in each chapter containing definitions, learning objectives, questions, and further reading. Application and theory are integrated so that they reinforce one another. There is a continued emphasis on pictorializing, reinforcing, interweaving, and integrating basic concepts. The initial chapter is short, allowing students to become acclimated. Other chapters can be covered in about a week's time or less. Where possible, difficult topics are distributed and reinforced over several topics.

The basic principles that apply to synthetic polymers apply equally to inorganic and biological polymers and are present in each of the chapters covering these important polymer groupings.

The updating of analytical, physical, and special characterization techniques continues. The chapter on biological polymers has been expanded so that it is now two chapters. The chapter on organometallic and inorganic polymers has likewise been greatly upgraded. An additional chapter covering the important area of composites has been added. Topics such as blends, multiviscosity oils, cross-linking, microfibers, protein folding, protein site identification, aerogels, carbon nanotubes, breakage of polymer chains, permeability and diffusion, mass spectroscopy, polyethers and epoxies, synthetic rubbers, poly(methyl methacrylate), polyacrylonitrile, and polyurethanes have been added or greatly enhanced. A number of new selected topics have been added including nonlinear optical behavior, photo physics, drug design and activity, flame retardants, textiles, water-soluble polymers, hydrogels, and anaerobic adhesives. The emphasis on the molecular behavior of materials has been expanded as has been the emphasis on nanotechnology and nanomaterials. The practice of including a number of appendices has continued, including an enlargement of the trade names appendix.

Acknowledgments

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I thank Girish Barot, Amitabh Battin, and Randy Doucette, for their assistance in proofing. I also thank my wife Mary Carraher for her help in proofing and allowing this edition to be written.

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Polymer Nomenclature

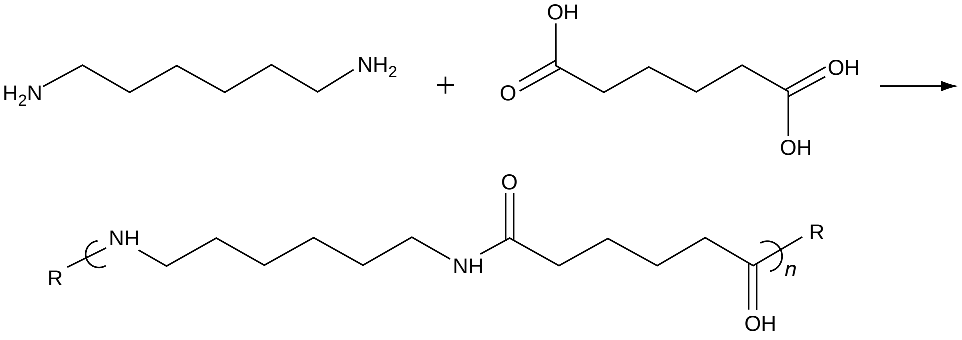
As with most areas, the language of the area is important. Here we will focus on naming polymers with the emphasis on synthetic polymers. Short presentations on how to name proteins and nucleic acids are given in Chapter 10 and for nylons in Chapter 5.

The fact that synthetic polymer science grew in many venues before nomenclature groups were present to assist in standardization of the naming approach resulted in many popular polymers having several names including common names. Many polymer scientists have not yet accepted the guidelines given by the official naming committee of the International Union of Pure and Applied Chemistry (IUPAC), because the common names have gained such widespread acceptance. Although there is a wide diversity in the practice of naming polymers, we will concentrate on the most utilized systems.

COMMON NAMES

Little rhyme or reason is associated with many of the common names of polymers. Some names are derived from the place of origin of the material, such as *Hevea brasilliensis*—literally "rubber from Brazil"—for natural rubber. Other polymers are named after their discoverer, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

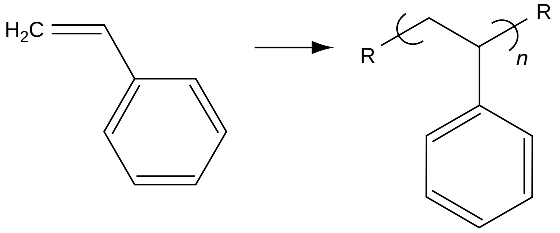
For some important groups of polymers, special names and systems of nomenclature were developed. For instance, the nylons were named according to the number of carbons in the diamine and dicarboxylic acid reactants used in their synthesis. The nylon produced by the condensation of 1,6-hexamethylenediamine (6 carbons) and adipic acid (6 carbons) is called nylon-6,6. Even here, there is no set standard as to how nylon-6,6 is to be written with alternatives including nylon-66 and nylon-6,6.



Nylon-6,6

SOURCE-BASED NAMES

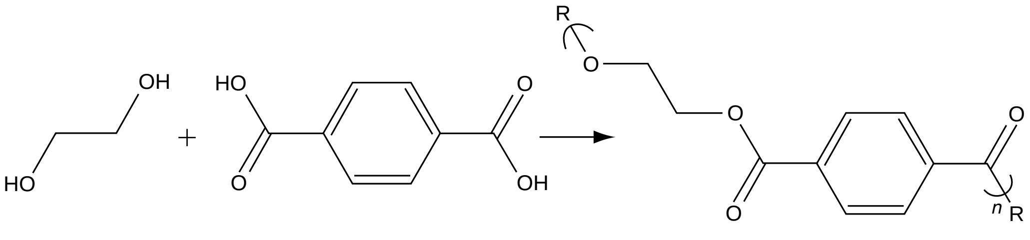
Most common names are source-based, i.e., they are based on the common name of the reactant monomer, preceded by the prefix "poly." For example, polystyrene is the most frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.



Styrene Polystyrene

The vast majority of commercial polymers based on the vinyl group ($H_2C{=}CHX$) or the vinylidene group ($H_2C{=}CX_2$) as the repeat unit are known by their source-based names. Thus, polyethylene is the name of the polymer synthesized from the monomer ethylene; poly(vinyl chloride) from the monomer vinyl chloride, and poly(methyl methacrylate) from methyl methacrylate.

Many condensation polymers are also named in this manner. In the case of poly(ethylene terephthalate), the glycol portion of the name of the monomer, ethylene glycol, is used in constructing the polymer name, so that the name is actually a hybrid of a source-based and a structure-based name.



Poly(ethylene terephthalate)

This polymer is well known by a number of trade names, such as Dacron, its common grouping, polyester, and by an abbreviation, PET.

Although it is often suggested that parentheses be used in naming polymers of more than one word [like poly(vinyl chloride)], but not for single-word polymers (like polyethylene), some authors entirely omit the use of parentheses for either case (like polyvinyl chloride), so even here there exist a variety of practices. We will employ parentheses for naming polymers of more than one word.

Copolymers are composed of two or more monomers. Source-based names are conveniently employed to describe copolymers using an appropriate term between the names of the monomers. Any of half a dozen or so connecting terms may be used depending on what is known about the structure of the copolymer. When no information is known or intended to be conveyed, the connective term “co” is employed in the general format poly(A-co-B), where A and B are the names of the two monomers. An unspecified copolymer of styrene and methyl methacrylate would be called poly[styrene-co-(methyl methacrylate)].

Kraton, the yellow rubber-like material often found on the bottom of running shoes, is a copolymer whose structural information is known. It is formed from a group of styrene units, i.e., a “block” of polystyrene, attached to a group of butadiene units, or a block of polybutadiene, which is attached to another block of polystyrene forming a triblock copolymer. The general representation of such a block might be –AAAAAAAABBBBBBB-AAAAAAAA–, where each A and B represents an individual monomer unit. The proper source-based name for Kraton is polystyrene-block-polybutadiene-block-polystyrene, or poly-block-styrene-block-polybutadiene-block-polystyrene, with the prefix "poly" being retained for each block. Again, some authors will omit the "poly," giving polystyrene-block-butadiene-block-styrene.

STRUCTURE-BASED NAMES

Although source-based names are generally employed for simple polymers, IUPAC has published a number of reports for naming polymers. These reports are being widely accepted for the naming of complex polymers. A listing of such reports is given in the references section. A listing of source- and structure-based names for some common polymers is given in Table 1.

LINKAGE-BASED NAMES

Many polymer "families" are referred to by the name of the particular linkage that connects the polymers (Table 2). The family name is "poly" followed by the linkage name. Thus, those polymers that contain an ester linkage are known as polyesters; those with an ether linkage are called polyethers, etc.

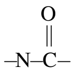
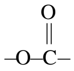
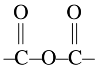
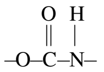
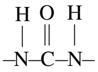
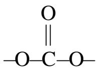
TRADE NAMES, BRAND NAMES, AND ABBREVIATIONS

Trade (and/or brand) names and abbreviations are often used to describe a particular material or a group of materials. They may be used to identify the product of a manufacturer, processor, or fabricator, and may be associated with a particular product or with a material or modified material, or a material grouping. Trade names are used to describe specific groups of materials that are produced by a specific company or under license of that company. Bakelite is the trade name given for the phenol–formaldehyde condensation developed by Baekeland. A sweater whose material is described as containing Orlon contains polyacrylonitrile fibers that are "protected" under the Orlon trademark and produced or licensed to be produced by the holder of the Orlon trademark. Carina, Cobex, Dacovin,

TABLE 1
Source- and Structure-Based Names

Source-Based Names	Structure-Based Names
Polyacrylonitrile	Poly(1-cyanoethylene)
Poly(ethylene oxide)	Polyoxyethylene
Poly(ethylene terephthalate)	Polyoxyethyleneoxyterephthaloyl
Polyisobutylene	Poly(1,1-dimethylethylene)
Poly(methyl methacrylate)	Poly[(1-methoxycarbonyl)-1-metylethylene]
Polypropylene	Poly(1-methylethylene)
Polystyrene	Poly(1-phenylethylene)
Polytetrafluoroethylene	Polydifluoromethylene
Poly(vinylacetate)	Poly(1-acetoxyethylene)
Poly(vinyl alcohol)	Poly(1-hydroxyethylene)
Poly(vinyl chloride)	Poly(1-chloroethylene)
Poly(vinyl butyral)	Poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]

TABLE 2
Linkage-Based Names

Family Name	Linkage	Family Name	Linkage
Polyamide	 $-\mathrm{N}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-$	Polyvinyl	$-\mathrm{C}-\mathrm{C}-$
Polyester	 $-\mathrm{O}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-$	Polyanhydride	 $-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-$
Polyurethane	 $-\mathrm{O}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\overset{\overset{\mathrm{H}}{\vert}}{\mathrm{N}}-$	Polyurea	 $-\overset{\overset{\mathrm{H}}{\vert}}{\mathrm{N}}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\overset{\overset{\mathrm{H}}{\vert}}{\mathrm{N}}-$
Polyether	$-\mathrm{O}-$	Polycarbonate	 $-\mathrm{O}-\overset{\overset{\mathrm{O}}{\Vert}}{\mathrm{C}}-\mathrm{O}-$
Polysiloxane	$-\mathrm{O}-\mathrm{Si}-$	Polysulfide	$-\mathrm{S}-$

Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Pliofex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all trade names for poly(vinyl chloride) manufactured by different companies. Some polymers are better known by their trade name than their generic name. For instance, polytetrafluoroethylene is better known as Teflon, the trade name held by DuPont.

Abbreviations, generally initials in capital letters, are also employed to describe polymers. Table 3 contains a listing of some of the more widely used abbreviations and the polymer associated with the abbreviation.

CHEMICAL ABSTRACTS–BASED POLYMER NOMENCLATURE

The most complete indexing of any scientific discipline is found in chemistry and is done by Chemical Abstracts (CA). Almost all of the modern searching tools for chemicals and

TABLE 3
Abbreviations for Selected Polymeric Materials

Abbreviation	Polymer	Abbreviation	Polymer
ABS	Acrylonitrile–butadiene–styrene terpolymer	CA	Cellulose acetate
EP	Epoxy	HIPS	High-impact polystyrene
MF	Melamine–formaldehyde	PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile	SBR	Butadiene–styrene copolymer
PBT	Poly(butylene terephthalate)	PC	Polycarbonate
PE	Polyethylene	PET	Poly(ethylene terephthalate)
PF	Phenyl–formaldehyde	PMMA	Poly(methyl methacrylate)
PP	Polypropylene	PPO	Poly(phenylene oxide)
PS	Polystyrene	PTFE	Polytetrafluoroethylene
PU	Polyurethane	PVA, PVAc	Poly(vinyl acetate)
PVA, PVAl	Poly(vinyl alcohol)	PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)	SAN	Styrene–acrylonitrile
UF	Urea–formaldehyde		

chemical information are based on CA for at least some information. It is critical for polymer chemists to have some grasp of how CA names chemical compounds. The full description of the guidelines governing the naming of chemical compounds and related properties is given in Appendix IV at the end of the CA *Index Guide*. This description covers about 200 pages. While small changes are made with each new edition, the main part has remained largely unchanged since about 1972. Today, there are computer programs, including that associated with SciFinder Scholar, that name materials once the structure is given. For small molecules this is straight forward, but for polymers care must be taken. Experiments must be carried out with simple polymers before moving to more complex macromolecules. If the Chemical Abstract Service Number (CAS #) is known, this can be entered and names investigated for appropriateness for your use.

CA organizes the naming of materials into 12 major arrangements that tie together about 200 subtopics. These main headings are:

A. Nomenclature systems and general principles
B. Molecular skeletons
C. Principle chemical groups
D. Compound classes
E. Stereochemistry and stereoparents
F. Specialized substances
G. Chemical substance names for retrospective searches
H. Illustrative list of substitute prefixes
J. Selective bibliography of nomenclature of chemical substances
K. Chemical prefixes
L. Chemical structural diagrams from CA Index Names
M. Index

The section dealing with polymers is subtopic 222. Polymers. The subsection dealing with polymers builds on the foundations given earlier, and thus some of the guidelines appear to be confusing and counterproductive to the naming of polymers but the rules were developed for the naming of small molecules. Following is a description of the guidelines that are most important to polymer chemists. Additional descriptions are found in the CA Appendix IV itself and in articles given in the Further reading. Appendix IV concentrates on linear polymers. A discussion of other more complex polymeric materials is also found in articles cited in the Further Reading.

General Rules

In the chemical literature, in particular systems based on CA, searches for particular polymers can be conducted using the CAS # (where known), or by repeat unit. The IUPAC and CAS have agreed upon a set of guidelines for the identification, orientation, and naming of polymers based on the structural repeat unit (SRU). IUPAC names polymers as "poly(constitutional repeat unit)" while CAS utilizes a "poly(structural repeating unit)." These two approaches typically give similar results.

Here we will practice using the sequence "identification, orientation, and naming" first by giving some general principles and finally by using specific examples.

In the identification step, the structure is drawn, usually employing at least two repeat units. Next, in the orientation step, the guidelines are applied. Here we will concentrate on basic guidelines. Within these guidelines are subsets of guidelines that are beyond our scope.

Structures will be generally drawn in the order, from left to right, in which they are to be named.

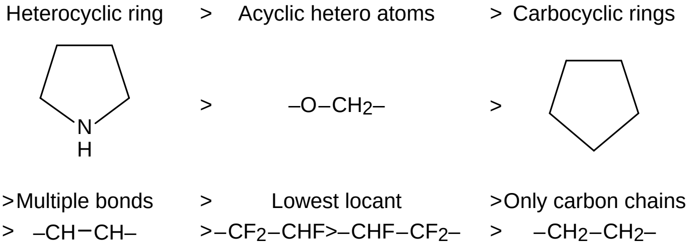
Seniority

The starting point for the naming of a polymer unit involves determining seniority among the subunits.

A. This order is:

Heterocyclic rings>
Greatest number of most preferred acyclic heteroatoms>
Carbocyclic rings>
Greatest number of multiple bonds>
Lowest or closest route (or lowest locant) to these substituents>
Chains containing only carbon atoms

with the symbol ">" indicating "is senior to."
This is illustrated below.



This order is partially derived from guidelines found, for example, in section 133 Compound Radicals, where the following order is given:

Greatest number of acyclic heteroatoms>
Greatest number of skeletal atoms>
Greatest number of most preferred acyclic heteroatoms>
Greatest number of multiple bonds>
Lowest locants or shortest distance to nonsaturated carbons

The lowest locant or shortest distance refers to the number of atoms from one senior subunit to the next most senior subunit when there is only one occurrence of the senior subunit.

This order refers to the backbone and not to substitutions. Thus, polystyrene and poly (vinyl chloride) are contained within the "chains containing only carbon atoms" grouping.

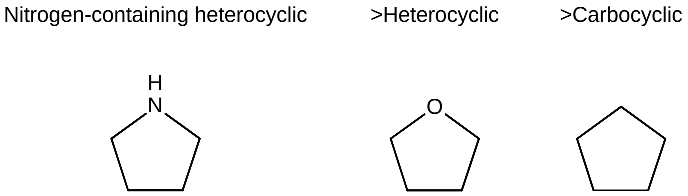
B. For ring systems the overall seniority is

Heterocyclic>
Carbocyclic

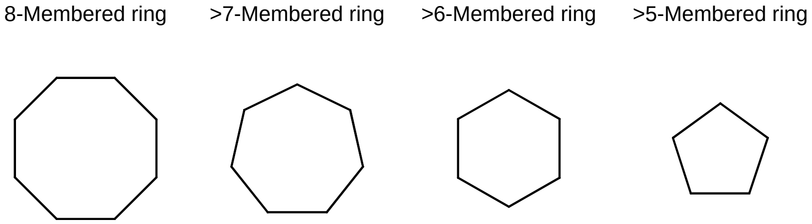
but within the rings there is also an ordering (section 138), which is:

Nitrogenous heterocyclic>
Heterocyclic>
Largest number of rings>
Cyclic system occurring earliest in the following list of systems: spiro, bridges fused, bridges nonfused, fused>
Largest individual ring (applies to fused carbocyclic systems)>
Greatest number of ring atoms

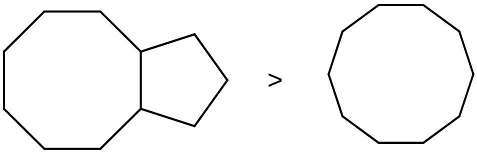
For example,



and



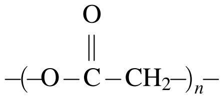
and



C. For heteroatomed linear chains or cyclic rings the order of seniority is O > S > Se > Te > N > P > As > Sb > Bi > Si > Ge > Sn > Pb > B > Hg.

Thus, because $-O-CH_2-$ is senior to $-S-CH_2-$, it would be named first in a polymer that contained both $-O-CH_2-$ and $-S-CH_2-$ segments. Further, a polymer containing these alternating units would not be poly(thiomethyleneoxymethylene) but would be named poly (oxymethylenethiomethylene).

Another example,



$$-\!(\!-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\!)_n-$$

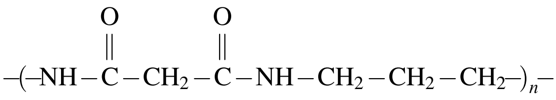
is named poly[oxy(1-oxy-1,2-ethanediyl)] or less preferred poly[oxy (1-oxoethylene)] but not poly[(2-oxo-1,2-ethanediyl)oxy] or poly[(2-oxoethylene)oxy].

D. Unsaturation is senior to saturation. The more the unsaturation, the greater the seniority, with all other items being equal. Thus, 1,4-phenylene is senior to 2,5-cyclohexadiene-1,4-diyl, which is senior to 2-cyclohexene-1,4-diyl, which in turn is senior to cyclohexane-1,4-diyl. For linear chains $-CH{=}CH-CH{=}CH-$ is senior to $-CH{=}CH-CH_2-CH_2-$ which is in turn senior to the totally saturated chain segment.

Route

A. From the senior subunit determined from "seniority" take the shortest path (smallest number of atoms) to another like or identical unit or to the next most preferred subunit. Thus, for the homo polymer poly(oxymethylene) it is simply going from one oxygen to the next oxygen and recognizing that this is the repeat unit. For a more complex ether this means going on in the shortest direction from the senior unit or atom to the next most senior unit or atom until the chain begins to repeat itself. Thus, $-O-C-C-O-C-C-C-$ is named oxy-1,2-ethanediyloxy-1,3-propanedily rather than oxy-1,3-propanediyloxy-1,2-ethanediyl.

B. Where the paths are equal, such as in some nylons, the repeat unit is named so that the heteroatom "N" appears first and the more highly substituted (carbonyl) unit appears next. Thus nylon 3,3 with the structure



$$-\!\!(\!-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-CH_2-CH_2-)_n-$$

is named poly[imino(1,3-dioxo-1,3-propanediyl)imino-1,3-propanediyl].

C. In otherwise identical subunits, there are three items to be considered in decreasing order of importance:

1. Maximum substitution: thus, 2,3,5-trichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene, which in turn is senior to 2-chloro-*p*-phyenylene.
2. Lowest locants: thus, 2,3-dichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene.
3. Earliest alphabetical order: thus, 2-bromo-*p*-phenylene is senior to 2-chloro-*p*-phenylene, which is senior to 2-iodo-*p*-phenylene.

D. Where there is no conflict with other guidelines, triple bonds are senior to double bonds, which in turn are senior to single bonds; multiple bonds should be assigned the lowest possible locants. Thus, the polymer from 1,3-butanediene polymerized in the "1,4-" mode is usually indicated as $-(-C-C{=}C-C-)-$ but is named as though it were $-(-C{=}C-C-C-)-$ and named poly(1-butene-1,4-diyl) with the appropriate *cis*- or *trans*-designation. Polyisoprene, typically drawn as $-(-CH_2-C(CH_3){=}CH-CH_2-)_n-$ is frequently named poly(2-methyl-1,3-butadiene) but is named as though its structure were $-(C(CH_3){=}CH-CH_2-CH_2-)_n-$ with the name poly(1-methyl-1-butene-1,4-diyl).

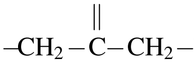
Substituents are named as one of several classes. The most important ones are dealt with here. For monoatomic radicals from borane, methane, silane (and other Group IVA elements) they are named by replacing the "ane" ending by "yl," i.e., "ylene" and "ylidyne," to denote the loss of one, two, or three hydrogen atoms, respectively:

H_2B- boryl H_3C- methyl $H_2C{=}$ methylene $HC\equiv$ methylidyne

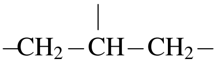
Acyclic hydrocarbon radicals are named from the skeletons by replacing "ane," "ene," and "yne" suffixes with "yl," "enyl," and "ynyl", respectively:

CH_3-CH_2- ethyl $CH_3-CH_2-CH_2-$ propyl $-CH_2-CH_2-$ 1,2-ethanediyl

$-CH{=}CH-$ 1,2-ethenediyl $H_2C{=}CH-CH{=}$ 2-propenylidene



$-CH_2-\overset{\|}{C}-CH_2-$ 1,3-propanediyl-2-ylidene



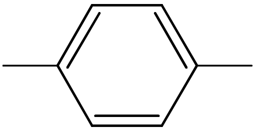
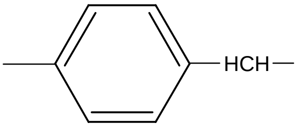
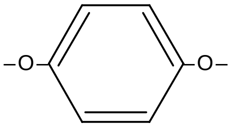
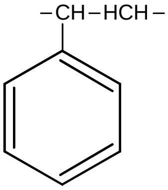
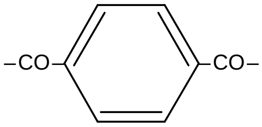
$-CH_2-\overset{|}{CH}-CH_2-$ 1,2,3-propanetriyl

Table 4 contains the names of selected bivalent radicals that may be of use to polymer chemists.

Searching

Searching is made much simpler with computer systems such as SciFinder Scholar where the name or CAS # can be entered, and references related to that compound obtained.

TABLE 4
Names of Select Bivalent Radicals

"Common" or "Trivial" Name	CAS Name	Structure
Adipyl, adipoly	1,6-Dioxo-1,6-hexanediyl	$-CO-(CH_2)_4-CO-$
1,4-Butanediyl	1,4-Butanediyl	$-(CH_2)_4-$
Carbonyl	Carbonyl	$-CO-$
Diglycoloyl	Oxybis(1-oxo-2,1-ethanediyl)	$-CO-CH_2-O-CH_2-CO-$
Ethylene	1,2-Ethanediyl	$-CH_2-CH_2-$
Imino	Imino	$-NH-$
Iminodisulfonyl	Iminobis(sulfonyl)	$-SO_2-NH-SO_2-$
Methene, methylene	Methylene	$-CH_2-$
Oxybis(methylenecarbonylimino)	Oxybis[((1-oxo-2,1-ethanediyl)imino)]	$-NHCO-CH_2-O-CH_2-CO-N-$
Pentamethylene	1,5-Pentanediyl	$-(CH_2)_5-$
Phenylene	1,4-Phenylene	
Phenylenedimethylene	1,4-Phenylenebis(methylene)	
Phenylenedioxy	1,4-Phenylenebis(oxy)	
Sebacoyl	1,10-Dioxo-1,10-decanediyl	$-CO-(CH_2)_8CO-$
Styrenyl	1-Phenyl-1,2-ethanediyl	
Sulfonyl, sulfuryl	Sulfonyl	$-SO_2-$
Tartaroyl	2,3-Dihydroxy-1,4-dioxo-1,4-butanediyl	$-CO-CH(OH)-CH(OH)-CO-$
Terephthaloyl	1,4-Phenylenedicarbonyl	
Thio	Thio	$-S-$
Thionyl	Sulfinyl	$-SO-$
Ureylene	Carbonyldiimino	$-NH-CO-NH-$
Vinylene	1,2-Ethenediyl	$-CH{=}CH-$

Teasing out the particular information you want is more difficult and often requires thinking about associations that might yield the desired information. Thus, if you want to know the solubility of a given polymer, you might look up molecular weight determinations for that polymer since most molecular weight determinations require the polymer be dissolved.

Following is a longer version that can be used if hard copy or electronic version of CA is available.

In searching, polymers from a single monomer are indexed as the monomer name with the term "homopolymer" cited in the modification. Thus, polymers of 1-pentene are listed under the monomer

1-Pentene
    homopolymer

Polymers formed from two or more monomers such as condensation polymers and copolymers, as well as homopolymers are indexed at each inverted monomer name with the modifying term "polymer with" followed by the other monomer names in uninverted alphabetical order. The preferential listing for identical heading parents is in the order: (1) maximum number of substituents; (2) lowest locants for substituents; (3) maximum number of occurrences of index heading parent; and (4) earliest index position of the index heading. Examples are:

1-Pentene
    polymer with 1-hexene

2,5-Furandione
    polymer with 1,4-butanedisulfonic acid

Silane, dichlorodiethyl-
    polymer with dichlorodiphenylsilane

While the percentage composition of copolymers (i.e., the ratio of comonomers) is not given, copolymers with architecture other than random or statistical are identified as "alternating, block, graft, etc." Random or statistical copolymers are not so identified in the CA index. Oligomers with definite structure are noted as dimer, trimer, tetramer, etc.

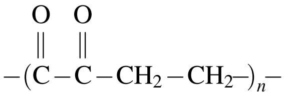
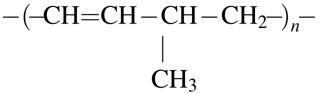
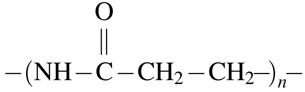
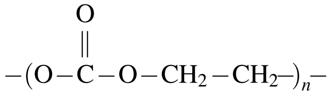
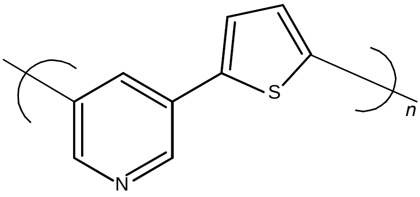
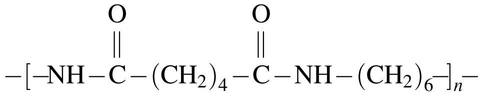
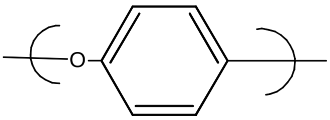
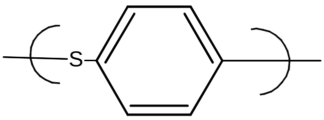
Often similar information is found at several sites. For instance, for copolymers of 1-butene and 1-hexene, information will be listed under both 1-butene and 1-hexene, but the listings are not identical so that both entries should be consulted for completeness.

CA's policy for naming acetylenic, acrylic, methacrylic, ethylenic, and vinyl polymers is to use the source-based method, and source-based representation is used to depict the polymers graphically; thus, a synonym for polyethylene is polyethylene and not poly(1,2-ethanediyl); a synonym for polypropylene is polypropylene, and poly(vinyl alcohol) is named ethenol homopolymer although ethenol does not exist. Thus, these polymers are named and represented structurally by the source-based method, not the structure-based method.

Examples

Following are examples that illustrate CAS guidelines of naming:

$-(CH_2-)_n-$	Poly(methylene)
$-(CH_2-CH_2-)_n-$	Poly(ethylene)
$-(CH{=}CH-)_n-$	Poly(1,2-ethenediyl)

 $-(\overset{\overset{O}{\Vert}}{C}-\overset{\overset{O}{\Vert}}{C}-CH_2-CH_2-)_n-$	Poly1,2-dioxo-1,4-butanediyl
 $-(-CH{=}CH-\underset{\underset{CH_3}{\vert}}{CH}-CH_2-)_n-$	Poly(3-methyl-1-butene-1,4-diyl)
 $-(NH-\overset{\overset{O}{\Vert}}{C}-CH_2-CH_2-)_n-$	Poly[imino(1-oxo-1,3-propanediyl)]
 $-(O-\overset{\overset{O}{\Vert}}{C}-O-CH_2-CH_2-)_n-$	Poly[oxocarbonyloxy(1,2-ethanediyl)]
$-(-CH_2-S-NH-CH_2-CH_2-O-CH_2-S-CH_2-NH-CH_2-)_n-$	Poly(oxymethylenethioimino-1,2-ethanediyloxymethylene thiomethyleneiminomethylene)
$-(-CFH-CH_2-)_n-$	Poly(1-fluoro-1,2-ethanediyl)
$-(-O-CH_2-CH_2-)_n-$	Poly(oxy-1,2-ethanediyl)
$-(-O-CH_2-)_n-$	Poly(oxymethylene)
	Poly(3,5-pyridinediyl-2,5-thiophenediyl)
 $-[-NH-\overset{\overset{O}{\Vert}}{C}-(CH_2)_4-\overset{\overset{O}{\Vert}}{C}-NH-(CH_2)_6-]_n-$	Poly[imino(1,6-dioxo-1,6-hexanediyl)imino-1,6-hexanediyl]
	Poly(oxy-1,4-phenylene)
	Poly(thio-1,4-phenylene)

In this text we will typically employ the more "common" (semisystematic or trivial) names of polymers but it is important in searching the literature using any CA-driven search engine that you are familiar with CA naming for both monomers and polymers.

SUMMARY

While there are several important approaches to the naming of polymers, in this book we will utilize common and source-based names because these are the names that are most commonly utilized by polymer chemists and the general public, and these names, particularly the source-based names, allow a better understanding of the basics of polymers as a function of polymer–structure relationships based on starting materials. Even so, those wishing to do further work in polymers must become proficient in the use of the guidelines used by CA and IUPAC.

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I wish to acknowledge the assistance of Edward S. Wilks for his help in preparing the section on Chemical Abstracts–Based Polymer Nomenclature.

How to Study Polymers

Studying about polymers is similar to studying any science. Following are some ideas that may assist you as you study.

Much of science is abstract. While much of the study of polymers is abstract, it is easier to conceptualize, make mind pictures, of what a polymer is and how it should behave than many areas of science. For linear polymers, think of a string or rope. Long ropes get entangled with themselves and other ropes. In the same way, polymer chains entangle with themselves and with chains of other polymers that are brought into contact with them. Therefore, create mental pictures of the polymer molecules as you study them.

Polymers are real and all around us. We can look at giant molecules on a micro or atomic level or on a macroscopic level. The PET bottles we have may be composed of long chains of poly(ethylene terephthate) (PET) chains. The aramid tire cord is composed of aromatic polyamide chains. Our hair is made up of complex bundles of fibrous proteins, again polyamides. The polymers you study are related to the real world in which we live. We experience these "large molecules" at the macroscopic level everyday of our lives and this macroscopic behavior is a direct consequence of the atomic-level structure and behavior. Make pictures in your mind that allow you to relate to the atomic and macroscopic worlds.

At the introductory level we often examine only the primary factors that may cause particular giant molecule behavior. Other factors may become important under particular conditions. Studies of polymer molecules at times examine only the primary factors that impact polymer behavior and structure. Even so, these primary factors form the basis for both complex and simple structure–property behavior.

The structure–property relationships you will be studying are based on well-known basic chemistry and physical relationships. Such relationships build upon one another and as such you need to study them in an ongoing manner. Understand as you go along. Read the material BEFORE you go to class.

This course is an introductory-level course. Each chapter or topic emphasizes knowledge about one or more area. The science and excitement of polymers has its own language. It is a language that requires you to understand and memorize certain key concepts. Our memory can be short-term or long-term. Short-term memory may be considered as that used by an actor for a television drama. It really does not need to be totally understood, or retained, after the final "take." Long-term memory is required in studying about giant molecules since this concept will be used repeatedly and is used to understand other concepts (i.e., it is built upon). In memorizing, learn how you do this best—time of day, setting, etc. Use as many senses as necessary and be active—read your assignment, write out what is needed to be known, say it, and listen to yourself saying it. Also, look for patterns, create mnemonic devices, avoid cramming too much into too small a time, practice associations in all directions, and test yourself. Memorization is hard work.

While knowledge involves recalling memorized material, to really "know" something involves more than simple recall—it involves comprehension, application, evaluation, and integration of the knowledge. Comprehension is the interpretation of this knowledge—making predictions, applying it to different situations. Analysis involves evaluation of the information and comparing it with other information, and synthesis has to do with integration of this information with other information.

In studying about giant molecules please consider doing the following:

- Skim the text BEFORE the lecture.
- Attend the lecture and take notes.
- Organize your notes and relate information.
- Read and study the assigned material.
- Study your notes and the assigned material.
- Review and self-test.

Learning takes time and effort. Daily skim the text and other study material, think about it, visualize key points and concepts, write down important information, make outlines, take notes, study sample problems, etc. All of these help, but some may help you more than others, so focus on these modes of learning, but not at the exclusion of the other aspects.

In preparing for an exam consider the following:

- Accomplish the above—DO NOT wait until the day before the exam to begin studying; create good study habits.
- Study wisely and see how YOU study best—time of day, surroundings, etc.
- Take care of yourself; get plenty of sleep the night before the exam.
- Attend to last-minute details—is your calculator working, is it the right kind, do you have the needed pencils, review the material once again, etc.
- Know what kind of test it will be if possible.
- Get copies of old exams if possible; talk to others who might have already done the course.

During the test:

- Stay cool, do NOT PANIC.
- Read the directions; try to understand what is being asked for.
- In an essay or similar exam, work for partial credit; plan your answers.
- In a multiple choice or T/F exam, eliminate obviously wrong choices.
- Look over the entire exam; work questions that you are sure of; then go to less sure questions; check answers if time permits.

The study of polymer molecules contains several types of content:

- Facts—the term “polymer” means “many” (*poly*) “units” (*mers*).
- Concepts—linear polymers are long molecules like a string.
- Rules—solutions containing polymer chains are more viscous, slower flowing, than solutions that do not contain polymers.
- Problems—what is the approximate molecular weight of a single polystyrene chain that has 1000 styrene units in it?

These varied types of content are often integrated within any topic, but in this introduction to polymer molecules, the emphasis is often on concepts although all the aspects are important.

1 Introduction to Polymers

1.1 HISTORY OF POLYMERS

Since most chemists, biochemists, and chemical engineers are now involved in some phase of polymer science or technology, some have called this the polymer age. Actually, we have always lived in a polymer age. The ancient Greeks classified all matter as animal, vegetable, and mineral. Minerals were emphasized by the alchemists, but medieval artisans emphasized animal and vegetable matter. All are largely polymeric and are important to life as we know it.

The word "polymer" is derived from the Greek *poly* and *meros*, meaning many and parts, respectively. Some scientists prefer to use the word "macromolecule," or large molecule, instead of polymer. Others maintain that naturally occurring polymers, or biopolymers, and synthetic polymers should be studied in different courses. Others name these large molecules simply "giant molecules." However, the same principles apply to all polymers. If one discounts the end uses, the differences between all polymers, including plastics, fibers, and elastomers or rubbers, are determined primarily by the intermolecular and intramolecular forces between the molecules and within the individual molecule, respectively, by the functional groups present, and, most of all, by their size, allowing a cumulation of these forces.

In addition to being the basis of life itself, protein is used as a source of amino acids and energy. The ancients degraded or depolymerized the protein in meat by aging and cooking, and they denatured egg albumin by heating or adding vinegar to the eggs. Early humans learned how to process, dye, and weave the natural proteinaceous fibers of wool and silk and the carbohydrate fibers from flax and cotton. Early South American civilizations, such as the Aztecs, used natural rubber (NR) (*Hevea brasiliensis*) for making elastic articles and for waterproofing fabrics.

There has always been an abundance of natural fibers and elastomers, but few plastics. Of course, early humans employed a crude plastic art in tanning the protein in animal skins to make leather and in heat-formed tortoise shells. They also used naturally occurring tars as caulking materials and extracted shellac from the excrement of small coccid insects (*Coccus lacca*).

Until Wohler synthesized urea from inorganic compounds in 1828, there had been little progress in organic chemistry since the alchemists emphasized the transmutation of base metals to gold and believed in a vital force theory. Despite this essential breakthrough, little progress was made in understanding organic compounds until the 1850s, when Kekule developed the presently accepted technique for writing structural formulas. However, polymer scientists displayed a talent for making empirical discoveries before the science was developed.

Charles Goodyear grew up in poverty. He was a Connecticut Yankee born in 1800. He began work in his father's farm implement business. Later he moved to Philadelphia, where he opened a retail hardware store that soon went bankrupt. Goodyear then turned to being an inventor. As a child he had noticed the magic material that formed a rubber bottle he had found. He visited the Roxbury India Rubber Company to try to interest them in his efforts to improve the properties of rubber. They assured him that there was no need to do so.

He started his experiments with a malodorous gum from South America in debtor's prison. In a small cottage on the grounds of the prison, he blended the gum, the raw rubber called hevea rubber, with anything he could find—ink, soup, castor oil, etc. While rubber-based products were available, they were either sticky or became sticky in the summer's heat. He found that treatment of the raw rubber with nitric acid allowed the material to resist heat and not to adhere to itself. This success attracted backers who helped form a rubber company. After some effort he obtained a contract to supply the U.S. Post Office with 150 rubber mailbags. He made the bags and stored them in a hot room while he and his family were away. When they returned they found the bags in a corner of the room, joined together as a single mass. The nitric acid treatment was sufficient to prevent surface stickiness, but the internal rubber remained tacky and susceptible to heat.

While doing experiments in 1839 at a Massachusetts rubber factory, Goodyear accidentally dropped a lump of rubber mixed with sulfur on the hot stove. The rubber did not melt, but rather charred. He had discovered vulcanization, the secret that was to make rubber a commercial success. While he had discovered vulcanization, it would take several years of ongoing experimentation before the process was really commercially useful. During this time he and his family were near penniless. While he patented the process, the process was too easily copied and pirated so that he was not able to fully profit from his invention and years of hard work. Even so, he was able to develop a number of items.

Goodyear and his brother, Nelson, transformed NR (hevea rubber) from a heat-"softenable" thermoplastic to a less heat-sensitive product through the creation of cross-links between the individual polyisoprene chain-like molecules using sulfur as the cross-linking agent. Thermoplastics are two-dimensional molecules that may be softened by heat. Thermosets are materials that are three-dimensional networks that cannot be reshaped by heating. Rather than melting, thermosets degrade. As the amount of sulfur was increased, the rubber became harder, resulting in a hard rubber-like (ebonite) material.

The spring of 1851 saw the construction of a remarkable building on the lawns of London's Hyde Park. The building was designed by a maker of greenhouses so it was not surprising that it had a "greenhouse-look." This Crystal Palace was to house almost 14,000 exhibitors from all over the world. It was an opportunity for them to show their wares. Goodyear, then 50 years old, used this opportunity to show off his over two decades' worth of rubber-related products. He decorated his Vulcanite Court with rubber walls, roof, furniture, buttons, toys, carpet, combs, etc. Above it hung a giant 6 ft. rubber raft and assorted balloons. The European public was introduced to the world of new man-made materials.

A little more than a decade later Goodyear died. Within a year of his death, the American Civil War broke out. The Union military used about $27 million worth of rubber products by 1865, helping launch the American rubber industry.

In 1862 Queen Victoria, while in mourning for her recently departed husband, Albert, opened the world's fair in London. One of the exhibitors was Alexander Parks. He was displeased with the limited colors available for rubber products—generally dull and dark. In his workshop in Birmingham, England, he was working with nitrocellulose, a material made from the treatment of cotton with nitric and sulfuric acids. Nitrocellulose solutions were made from dissolving the nitrocellulose in organic liquids such as ethanol and ether. Thin films and coatings were made by simply pouring the nitrocellulose solutions onto the desired item or surface and allowing the solvent to evaporate. He wanted to make solid objects from nitrocellulose. After years of work he developed a material he called Parkensine, from which he made buttons, combs, and in fact many of the items that were made of rubber—except that his materials could be brightly colored, clear, or made to shine like mother-of-pearl. At the London World's Fair he advertised "PATENT PARKESINE of various colours: hard elastic, transparent, opaque, and waterproof.” Even with his work he had not developed a material that could be “worked” or was stable, and even with his hype the material never caught on except within exhibition halls.

At about the same time, John Wesley Hyatt, a printer from Albany, New York, seeking a $10,000 prize for anyone who could come up with a material that was a substitute for ivory billiard balls, developed a material that was stable and could be “worked” from shellac and wood pulp. He then turned to nitrocellulose and discovered that shredded nitrocellulose could be mixed with camphor and heated under pressure to produce a tough white mass that retained its shape. This material, dubbed celluloid, could be made into the usual rubber-like products, as well as solid pieces like boxes, wipe-clean linen, collars, cuffs, and ping-pong balls. Celluloid could also, like the shellac–wood pulp mixture, be worked—cut, drilled, and sawed. But celluloid was flammable, and did not stand up well in hot water. Those who wore celluloid dentures could literally have their “teeth curled” when drinking a hot cup of coffee. One of its best qualities was that it could be made to “look like” other materials—it could be dyed to look like marble, swirled to mimic tortoiseshell and mother-of-pearl, and even look and feel like ivory. It did not make good billiard balls. One account has billiard balls hitting and exploding like a shot that caused cowboys to draw their guns.

Both cellulose and cellulose nitrate (CN) are linear, or two-dimensional, polymers, but the former cannot be softened because of the presence of multitudinous hydrogen bonds between the chain-like molecules. When used as an explosive the CN is essentially completely nitrated, but the material used by Parks and Hyatt was a dinitrate, still potentially explosive, but less so. Parks added castor oil and Hyatt added camphor to plasticize—reduce the effect of the hydrogen bonding—the CN, allowing it some flexibility.

Rubber gained worldwide importance with the invention of the air-filled or pneumatic tires by a Scotsman, John Dunlop, in 1888. He had a successful veterinarian practice in Belfast. In his off time he worked to improve the ride of his son’s tricycle. His invention happened at the right time. The automobile was emerging and the air-filled tires offered a gentler ride. Thus was begun the tire industry.

All of these inventions utilized natural materials at least as one ingredient. After years of work in his chemistry labs in Yonkers, New York, Leo Baekeland in 1907 announced in an American Chemical Society meeting the synthesis of the first truly synthetic polymeric material, later dubbed Bakelite.

Baekeland was born in Belgium in 1863, the son of an illiterate shoe repairman and a maid. He was bright and received his doctorate at the age of 20 with highest honors. He could have spent the rest of his life in academics in Europe, but heeding the words of Benjamin Franklin, he sailed to America. In the 1890s he developed the first photographic paper, called Velox, which could be developed in synthetic light rather than sunlight. George Eastman saw the importance of this discovery and paid Baekeland $750,000 for the rights to use his invention.

It was generally recognized by the leading organic chemists of the 19th century that phenol would condense with formaldehyde. Since they did not recognize the concept of functionality, Baeyer, Michael, and Kleeberg produced useless cross-linked goos, gunks, and messes and then returned to their research on reactions of monofunctional reactants. However, by the use of a large excess of phenol, Smith, Luft, and Blumer were able to obtain a hard, but meltable, thermoplastic material.

With his $750,000, Baekeland set up a lab next to his home. He then sought to solve the problem of making the hard material obtained from phenol and formaldehyde soluble. After many failures, he thought of circumventing the problem by placing the reactants in a mold of the desired shape and allowing them to form the intractable solid material. After much effort he found the conditions under which a hard, clear solid could be made—Bakelite was discovered. Bakelite could be worked, it was resistant to acids and organic liquids, stood up well to heat and electrical charge, and could be dyed to give colorful products. It was used to make bowling balls, phonograph records, telephone housings, gears, and cookware. His materials also made excellent billiard balls. Bakelite also acted as a binder for sawdust, textiles, and paper, forming a wide range of composites including Formica laminates, many of which are still used. It was also used as an adhesive giving us plywood.

There is no evidence that Baekeland recognized what polymers were, but he appeared to have a grasp on functionality and how to "use" it to produce thermoplastic materials that could later be converted to thermosets. Through control of the ratio of phenol to formaldehyde he was able to form a material that was a thermoplastic. He coined the term "A-stage resole resin" to describe this thermoplastic. This A-stage resole resin was converted to a thermoset cross-link, "C-stage Bakelite," by additional heating. Baekeland also prepared thermoplastic resins called "novolacs" by the condensation of phenol with a lesser amount of formaldehyde under acidic conditions. The thermoplastic novolacs were converted to thermosets by addition of more formaldehyde. Although other polymers had been synthesized in the lab, Bakelite was the first truly synthetic plastic. The "recipes" used today differ little from the ones developed by Baekeland, showing his ingenuity and knowledge of the chemistry of the condensation of the trifunctional phenol and difunctional formaldehyde.

Poly(vinyl chloride) (PVC) was initially formed by Baumann in 1872; however, it awaited interest until 1926 when B.F. Goodrich discovered how to make sheets and adhesives from PVC—and the "vinyl age" began. Although polystyrene (PS) was probably first formed by Simon in 1839, it was almost 100 years later, in 1930, that the giant German company I.G. Farben placed PS on the market. PS-molded parts became commonplace. Rohm and Haas bought out Plexiglass from a British firm in 1935 and began the production of clear plastic parts and goods, including replacements for glass as camera lenses, aircraft windows, clock faces, and car taillights.

Till this time, polymer science was largely empirical, instinctive, and intuitive. Several polymers were commercially available prior to World War I: celluloid, shellac, Galalith (casein), Bakelite, and cellulose acetate plastics; hevea rubber, cotton, wool, and silk rayon fibers; Glyptal polyester coatings; bitumen or asphalt, and coumarone–indene and petroleum resins. However, as evidenced by the chronological data shown in Table 1.1, there was little

TABLE 1.1
Chronological Developments of Commercial Polymers (up to 1982)

Before 1800	Cotton, flax, wool, and silk fibers; bitumens caulking materials; glass and hydraulic cements; leather and cellulose sheet (paper); natural rubber (*Hevea brasiliensis*), gutta percha, balata, and shellac
1839	Vulcanization of rubber (Charles Goodyear)
1845	Cellulose esters (Schonbein)
1846	Nitration of cellulose (Schonbein)
1851	Ebonite (hard rubber; Nelson Goodyear)
1860	Molding of shellac and gutta percha
1868	Celluloid (plasticized cellulose nitrate; Hyatt)
1888	Pneumatic tires (Dunlop)
1889	Cellulose nitrate photographic films (Reinchenbach)
1890	Cuprammonia rayon fibers (Despeisses)
1892	Viscose rayon fibers (Cross, Bevan, and Beadle)
1903	First tubeless tire (Litchfield of Goodyear Tire Co.)
1897	Poly(phenylene sulfide)
1901	Glyptal polyesters
1907	Phenol–formaldehyde resins (Bakelite; Baekeland)
1908	Cellulose acetate photographic fibers
1912	Regenerated cellulose sheet (cellophane)

TABLE 1.1 (continued)
Chronological Developments of Commercial Polymers (up to 1982)

1913	Poly(vinyl acetate) (PVAc)
1914	Simultaneous interpenetrating network (SIN)
1920	Urea–formaldehyde resins
1923	Cellulose nitrate automobile lacquers
1924	Cellulose acetate fibers
1926	Alkyd polyester (Kienle)
1927	Poly(vinyl chloride) (PVC) wall covering
1927	Cellulose acetate sheet and rods
1927	Graft copolymers
1928	Nylon (Carothers; DuPont)
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)
1929	Urea–formaldehyde resins
1930	Polyethylene (Friedrich/Marvel)
1931	Poly(methyl methacrylate) (PMMA) plastics
1931	Polychloroprene elastomer (Neoprene; Carothers)
1934	Epoxy resins (Schlack)
1935	Ethylcellulose
1936	Poly(vinyl acetate) (PVAc)
1936	Poly(vinyl butyral) (safety glass)
1937	Polystyrene (PS)
1937	Sytrene–butadiene (Buna-S) and styrene–acrylonitrile (SAN) (Buna-N) copolymer elastomers
1939	Melamine–formaldehyde (MF) resins
1939	Nylon-6 (Schlack)
1939	Nitrile rubber (NR)
1940	Isobutylene–isoprene elastomer (butyl rubber; Sparks and Thomas)
1941	Low-density polyethylene (LDPE)
1941	Poly(ethylene terephthalate) (PET)
1942	Butyl rubber
1942	Unsaturated polyesters (Ellis and Rust)
1943	Fluorocarbon resins (Teflon; Plunket)
1943	Silicones
1945	Styrene–butadiene rubber (SBR)
1946	Polysulfide rubber (Thiokol)
1948	Acrylonitrile–butadiene–styrene (ABS) copolymers
1949	Cyanoacrylate (Goodrich)
1950	Polyester fibers (Winfield and Dickson)
1950	Polyacrylonitrile fibers
1952	Block copolymers
1953	High-impact polystyrene (HIPS)
1953	Polycarbonates (Whinfield and Dickson)
1956	Poly(phenylene ether); poly(phenylene oxide) (PPO) (General Electric)
1957	High-density polyethylene (HDPE)
1957	Polypropylene
1957	Polycarbonate
1958	Poly(dihydroxymethylcyclohexyl terephthate) (Kodel; Eastman Kodak)
1960	Ethylene–propylene monomer (EPM) elastomers
1961	Aromatic nylons (aramids) (Nomex; DuPont)
1962	Polyimide resins
1964	Poly(phenylene oxide)
1964	Ionomers
1965	Polysulfone
1965	Styrene–butadiene block copolymers
1966	Liquid crystals
1970	Poly(butylene terephthalate)
1974	Polyacetylene
1982	Polyetherimide (General Electric)
1991	Carbon nanotubes (Iijima; NEC Lab)

additional development in polymers prior to World War II because of a general lack of fundamental knowledge of polymers. But the theoretical basis was being built. Only a few of the many giants will be mentioned.

Over a century ago, Graham coined the term "colloid" for aggregates with dimensions in the range of 10^{-9}–10^{-7} m. Unfortunately, the size of many macromolecules is in this range, but it is important to remember that unlike colloids, whose connective forces are ionic and/or secondary forces, polymers are individual molecules whose size cannot be reduced without breaking the covalent bonds that hold the atoms together. In 1860 an oligomer, a small polymer, was prepared from ethylene glycol and its structure correctly given as $HO-(-OCH_2CH_2-)_n-OH$. But when poly(methacrylic acid) was made by Fittig and Engelhorn in 1880, it was incorrectly assigned a cyclic structure. Polymers were thought of as being colloids, or cyclic compounds like cyclohexane. By use of the Raoult and van't Hoff concepts, several scientists obtained high molecular weight values for these materials and for a number of other polymeric materials. But since the idea of large molecules was not yet accepted they concluded that these techniques were not applicable to these molecules rather than accepting the presence of giant molecules.

The initial "tire-track in the sand" with respect to tires was the discovery of vulcanization of rubber by Charles Goodyear in 1844. The first rubber tires appeared in the mid-1880s. These tires were solid rubber, with the rubber itself absorbing the bumps and potholes. John Dunlop invented the first practical pneumatic or inflatable tire with his patent granted in 1888. Andre Michelin was the first person to use the pneumatic tire for automobiles. The Michelin brothers, Andre and Edouard, equipped a racing car and drove it in the 1895 Paris–Bordeaux road race. They did not win but it was sufficient advertising to generate interest in pneumatic tires for automobiles. Furthermore, because they did not cause as much damage to the roads, pneumatic tires were favored by legislation. It is interesting to see that the names of these three pioneers still figure prominently in the tire industry. Even so, another inventor had actually been given the first patent for a vulcanized rubber pneumatic tire in 1845 but it did not take off. Thompson was a prolific inventor also having patented a fountain pen in 1849 and a steam traction engine in 1867.

A number of the giant tire companies started at the turn of the century. In America many of these companies centered around Akron, the capital of the rubber tire. In 1898 the Goodyear Tire and Rubber Company started. The Firestone Tire and Rubber Company was started by Harvey Firestone in 1900. Other tire companies shortly followed.

Hermann Staudinger studied the polymerization of isoprene as early as 1910. Intrigued by the difference between this synthetic material and NR, he began to focus more of his studies on such materials. His turn towards these questionable materials, of interest to industry but surely not academically important, was viewed unkindly by his fellow academics. He was told by one of his fellow scientists: "Dear Colleague, leave the concept of large molecules well alone. . . . There can be no such thing as a macromolecule."

Staudinger systematically synthesized a variety of polymers. In the paper "Uber Polymerization" in 1920 he summarized his findings and correctly proposed linear structures for important polymers such as polyoxymethylene (POM) and PS. X-ray studies of many natural and synthetic materials were used as structural proof that polymers existed. Foremost in these efforts were Herman Mark and Linus Pauling. Both of these giants contributed to other important areas of science. Pauling contributed to the fundamental understanding of bonding and the importance of vitamins. Mark helped found the academic and communication (journals, short courses, workshops) basis that would allow polymers to grow from its very diverse roots.

Wallace Hume Carothers is the father of synthetic polymer science. History is often measured by the change in the flow of grains of sand in the hourglass of existence. Carothers is a granite boulder in this hourglass. Carothers was born, raised, and educated in the U.S. Midwest. In 1920 he left Tarkio College with his BS degree and entered the University of Illinois where he received his MA in 1921. He then taught at the University of South Dakota where he published his first paper. He returned to receive his PhD under Roger Adams in 1924. In 1926 he became an instructor in organic chemistry at Harvard.

In 1927 DuPont began a program of fundamental research "without any regard or reference to commercial objectives." This was a radical departure since the bottom line was previously products marketed and not papers published. Charles Stine, director of DuPont's chemical department, was interested in pursuing fundamental research in the areas of colloid chemistry, catalysis, organic synthesis, and polymer formation, and convinced the Board to hire the best chemists in each field to lead this research. Stine visited with many in the academic community including the then president of Harvard, one of my distant uncles, J.B. Conant, an outstanding chemist himself, who told him about Carothers. Carothers was persuaded to join the DuPont group with a generous research budget and an approximate doubling of his academic salary to $6000. This was the birth of the Experimental Station at Wilmington, Delaware.

Up to this point, it was considered that universities were where discoveries were made and industry was where they were put to some practical use. This separation between basic and applied work was quite prominent at this juncture and continues in many areas even today in some fields of work though the difference has decreased. But in polymers, most of the basic research was done in industry, having as its inception the decision by DuPont to bridge this "unnatural" gap between fundamental knowledge and application. In truth, they can be considered as the two hands of an individual, and in order to do manual work both hands are important.

Staudinger believed that large molecules were based on the jointing, through covalent bonding, of large numbers of atoms. Essentially he and fellow scientists like Karl Freudenberg, Herman Mark, Michael Polanyi, and Kurt Myer looked at already existing natural polymers. Carothers, however, looked at the construction of these giant molecules from small molecules forming synthetic polymers. His intention was to prepare molecules of known structure through the use of known organic chemistry and to "investigate how the properties of these substances depended on constitution." Early work included the study of polyester formation through reaction of diacids with diols forming polyesters. But he could not achieve molecular weights greater than about 4000 below the size at which many of the interesting so-called polymeric properties appear.

DuPont was looking for a synthetic rubber (SR). Carothers assigned Arnold Collins to carry out this research. Collin's initial task was to produce pure divinylacetylene. While performing the distillation of an acetylene reaction, in 1930, he obtained a small amount of an unknown liquid, which he set aside in a test tube. After several days the liquid turned to a solid. The solid bounced and eventually was shown to be a SR polychloroprene, whose properties were similar to those of vulcanized rubber but was superior in its resistance to ozone, ordinary oxidation, and most organic liquids. It was sold under its generic name "neoprene" and the trade name "Duprene."

In 1930 Carothers and Julian Hill designed a process to remove water that was formed during the esterification reaction. They simply froze the water as it was removed, using another recent invention called a molecular still (basically a heating plate coupled to vacuum), allowing the formation of longer chains. In April, Hill synthesized a polyester using this approach: he touched a glass stirring rod to the hot mass and then pulled the rod away, effectively forming strong fibers; the pulling helped reorient the mobile polyester chains. The polyester had a molecular weight of about 12,000. Additional strength was achieved by again pulling the cooled fibers. Further reorienting occurred. This process of "drawing" or pulling to produce stronger fibers is now known as "cold drawing" and is widely used in the formation of fibers today. The process of "cold drawing" was discovered by Carothers' group. While interesting, the fibers were not considered to be of commercial use. Carothers and his group then moved to look at the reaction of diacids with diamines instead of diols. Again, fibers were formed but these initial materials were deemed not to be particularly interesting.

In 1934 Paul Flory was hired to work with Carothers to help gain a mathematical understanding of the polymerization process and relationships. Thus, there was an early association between theory and practice or structure–property relationships.

The polyamide fiber project was begun again. One promising candidate was formed from the reaction of adipic acid with hexamethylenediamine, called fiber 66 because each carbon-containing unit had six carbons. It formed a strong, elastic, largely insoluble fiber with a relatively high melt temperature. DuPont chose this material for production. These polyamides were given the name "nylons." Thus was born nylon-6,6, the first synthetic material whose properties equaled or exceeded the natural analog, silk. (Although this may not be so in reality, it was believed at the time to be true.)

As women's hemlines rose in the 1930s, silk stockings were in great demand but were very expensive. Nylon changed this, as it could be woven into sheer hosiery. The initial presentation of nylon hose to the public was by Stine at a forum of women's club members in New York City on October 24, 1938. Nearly 800,000 pairs were sold on May 15, 1940 alone—the first day they were on the market. By 1941 nylon hosiery held 30% of the market but by December 1941 nylon was diverted to make parachutes etc.

From these studies Carothers established several concepts. First, polymers could be formed by employing already known organic reactions but with reactants that had more than one reactive group per molecule. Second, the forces that bring together the individual polymer units are the same as those that hold together the starting materials, namely primary covalent bonds. Much of the polymer chemistry names and ideas that permeate polymer science today were standardized through his efforts.

Representing the true multidisciplinary nature of polymers, early important contributions were also made by physicists, engineers, and academicians from biology, medicine, and mathematics including W.H. Bragg, Peter Debye, Albert Einstein, and R. Simha.

World War II helped shape the future of polymers. Wartime demands and shortages encouraged scientists to seek substitutes and materials that even excelled those currently available. Polycarbonate (Kevlar), which could stop a "speeding bullet," was developed, as was polytetrafluoroethylene (Teflon), which was super slick. New materials were developed spurred on by the needs of the military, electronics industry, food industry, etc. The creation of new materials continues at an accelerated pace brought on by the need for materials with specific properties and the growing ability to tailor-make giant molecules—macromolecules—polymers.

Unlike other areas of chemistry, most of the basic research has been done in industry so that there is often a close tie between discoveries and their commercialization. Table 1.2 lists some of the dates of commercialization for some important polymer discoveries.

A number of Nobel Prizes have been given for polymer work. Table 1.3 highlights winners for advances with synthetic polymers.

Throughout this text advances are placed in some historical setting. This adds some texture to the topics as well as acting as case histories that are so important in some subject areas such as business and medicine.

1.2 WHY POLYMERS?

Polymers are all around us. They serve as the very basis of both plant and animal life as proteins, nucleic acids, and polysaccharides. In construction they serve as the concrete, insulation, and wooden and composite beams. At home they are found as the materials for our rugs, pillows, curtains, coatings, wastepaper baskets, water pipes, window glass, and ice cube trays. In transportation they are present in ever-increasing amounts in our aircraft, automobiles, ships, and trucks. In communication they form critical components in our

TABLE 1.2
Commercialization of Selected Polymers

Polymer	Year	Company
Bakelite	1909	General Bakelite Corp.
Rayon	1910	American Viscose Company
Poly(vinyl chloride)	1927	Goodrich
Styrene–butadiene copolymer	1929	I.G. Farben
Polystyrene	1929/1930	I.G. Farben and Dow
Neoprene	1931	DuPont
Poly(methyl methacrylate)	1936	Rhom & Haas
Nylon-6,6	1939/1940	DuPont
Polyethylene (LDPE)	1939	ICI
Poly(dimethyl siolxane)	1943	Dow Corning
Acrylic fiber	1950	DuPont
Poly(ethylene terephthalate)	1953/1954	DuPont/ICI
Polyurethane block copolymers (Spandex)	1959	DuPont
Poly(phenylene terephthalamide)	1960	DuPont

telephones, televisions, computers, compact discs (CDs), newspapers, optical fibers, and cell phones. Plastics act as favorite materials for our toys such as toy soldiers, plastic models, toy cars, dolls, skip ropes, hula hoops, and corvettes. Our food is polymer-intense as meats, vegetables, breads, and cookies. In history, polymers have been the vehicle for the Magna Carta, the Torah, the Bible, the Koran, and our Declaration of Independence. Outside our homes they are present in our flowers, trees, soil, spiderwebs, and beaches. In fact, it is improbable that a polymer is not involved in your present activity—reading a paper book, holding a plastic-intense writing device, sitting on a cloth-covered chair or bed, and if your eyes need corrective vision, glasses of one variety or another.

Polymers gain their importance because of their size. Many polymers are made from inexpensive and readily available materials allowing vast quantities of products to be made for a high increase in value, but they are typically inexpensive compared to nonpolymer alternatives. They also often have desirable physical and chemical properties. Some polymers are stronger on a weight basis than steel. Most are resistant to rapid degradation and rusting. This text gives more information about these essential materials for life and living.

Polymers are often divided according to whether they can be melted and reshaped through application of heat and pressure. These materials are called “thermoplastics.” The second general classification comprises compounds that decompose before they can be melted or reshaped. These polymers are called “thermosets.” While both thermoset and thermoplastic polymers can be recycled, thermoplastic recycling is easier and more widespread because thermoplastic materials can be reshaped simply by application of heat and pressure.

TABLE 1.3
Nobel Prize Winners for Their Work with Synthetic Polymers

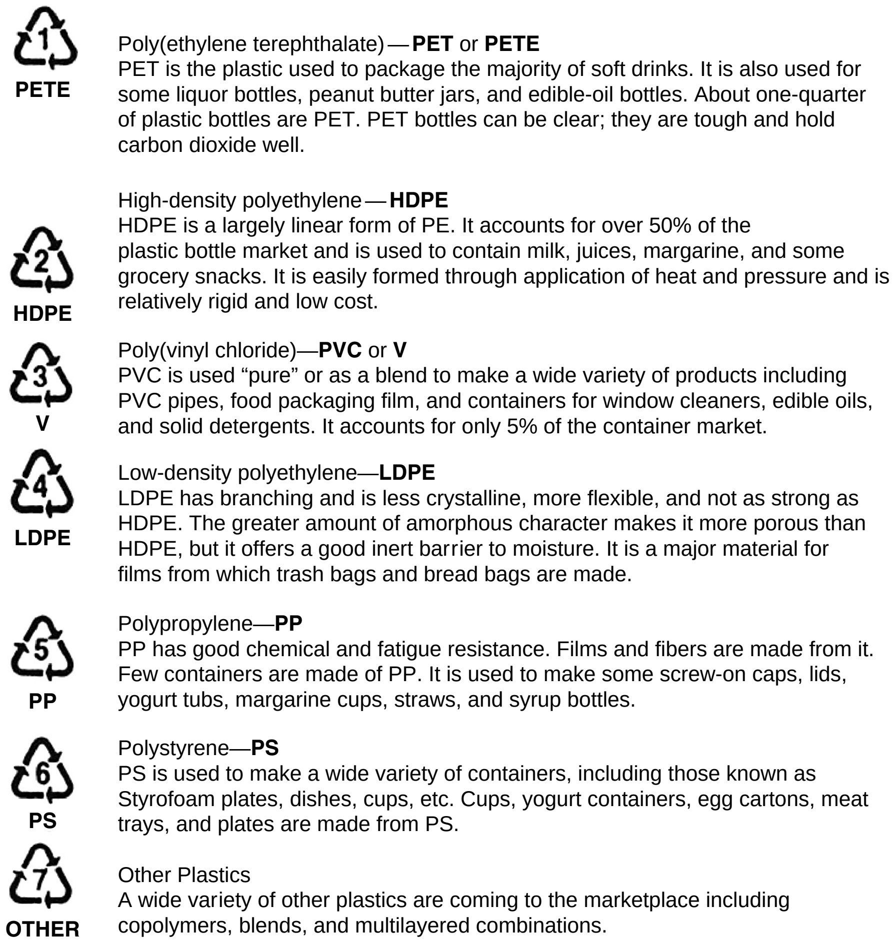
Scientist(s)	Year	Area
Hermann Staudinger	1953	Polymer hypothesis
Karl Ziegler and Giulio Natta	1963	Stereoregulation of polymer structure
Paul Flory	1974	Organization of polymer chains
Bruce Merrifield	1984	Synthesis on a solid matrix
Pierre de Gennes	1991	Polymer structure and control at interfaces
A.J. Heeger, Alan Mac Diarmid, and H. Shirakawa	2000	Conductive polymers

In general groups, synthetic polymers are often described by their "use" and "appearance" as fibers, elastomers, plastics, adhesives, and coatings. A common toothbrush illustrates the three major physical forms of synthetic polymers—the rubbery (elastomeric) grips, plastic shaft, and fibrous bristles. The rubbery grips have a relatively soft touch; the plastic shaft is somewhat flexible and hard; and the bristles are highly flexible. Another illustration of the presence of polymers around us is given in Table 1.4 in which polymers are divided according to source.

To get an idea of the pervasiveness of polymers in our everyday life, we can look at containers. Most containers are polymeric—glass, paper, and synthetic polymer. It is relatively easy to identify each of these general categories. Even within the synthetic polymer grouping, it has become relatively easy to identify the particular polymer used in some applications such as with disposable containers. Most of these synthetic polymers are marked by an "identification code" that is imprinted somewhere on the plastic container, generally on their bottom. The numbers and letters are described in Figure 1.1. The recycling code was developed by the Society of Plastics Industry for use with containers. Today, the "chasing arrows" triangle is being used more widely for recycling by the public. A colorless somewhat hazy water container has a "2" within the chasing arrows and underneath it "HDPE," both indicating that the bottle is made of high-density polyethylene (HDPE). The clear, less flexible soda bottle has a "1" and "PETE" on it, both signifying that the container is made out of poly(ethylene terephthalate) (PET), a polyester. A brownish clear medicine container has a "5" and the letters "PP" on its bottom conveying the information that the bottle is made of polypropylene (PP). Thus, ready identification of some common items is easy.

TABLE 1.4
Common Polymers

Material/Name	Typical Polymer	Chapter
Styrofoam	Polystyrene	6
PVC pipe	Poly(vinyl chloride)	6
Nylon stockings	Polyamide, nylon-6,6	4
Concrete	Cement	12
Meat	Protein	10
Plexiglass	Poly(methyl methacrylate)	6
Automotive bumpers and side panels	Polyethylene and polyethylene/polypropylene blends	5,7
Potatoes	Starch	9
Compact discs (case)	Polycarbonate (polystyrene)	4
Hula hoop	Polypropylene, polyethylene	5
Diamond	Carbon	12
Silicon sealants	Polydimethylsiloxane	11
Bakelite	Phenol–formaldehyde cross-linked	4
Super glue	Poly(ethyl cyanoacrylate)	18
Cotton T-shirt	Cellulose	9
Fiberglass	Composite	8
Saran wrap	PVC copolymer	7
Velcro	Polyamide	4
Rubber band	Natural rubber	9
Soda bottle	Poly(ethylene terephthalate)	4
Teflon	Polytetrafluoroethylene	6
Orlon sweater	Polyacrylonitrile	6
Sand	Silicon dioxide	12
Pillow stuffing	Polyurethane	4
Wood, paper	Cellulose	9
Human genome	Nucleic acids	10



Poly(ethylene terephthalate)—**PET** or **PETE**
PET is the plastic used to package the majority of soft drinks. It is also used for some liquor bottles, peanut butter jars, and edible-oil bottles. About one-quarter of plastic bottles are PET. PET bottles can be clear; they are tough and hold carbon dioxide well.

High-density polyethylene—**HDPE**
HDPE is a largely linear form of PE. It accounts for over 50% of the plastic bottle market and is used to contain milk, juices, margarine, and some grocery snacks. It is easily formed through application of heat and pressure and is relatively rigid and low cost.

Poly(vinyl chloride)—**PVC** or **V**
PVC is used "pure" or as a blend to make a wide variety of products including PVC pipes, food packaging film, and containers for window cleaners, edible oils, and solid detergents. It accounts for only 5% of the container market.

Low-density polyethylene—**LDPE**
LDPE has branching and is less crystalline, more flexible, and not as strong as HDPE. The greater amount of amorphous character makes it more porous than HDPE, but it offers a good inert barrier to moisture. It is a major material for films from which trash bags and bread bags are made.

Polypropylene—**PP**
PP has good chemical and fatigue resistance. Films and fibers are made from it. Few containers are made of PP. It is used to make some screw-on caps, lids, yogurt tubs, margarine cups, straws, and syrup bottles.

Polystyrene—**PS**
PS is used to make a wide variety of containers, including those known as Styrofoam plates, dishes, cups, etc. Cups, yogurt containers, egg cartons, meat trays, and plates are made from PS.

Other Plastics
A wide variety of other plastics are coming to the marketplace including copolymers, blends, and multilayered combinations.

FIGURE 1.1 The Society of Plastics Industry recycling codes utilizing the numbers 1–7 and bold, capital letters to designate the material utilized to construct the container.

However, because of the use of many more complex combinations of polymers for many other items, such identification and identification schemes are not as straightforward. For some items, such as clothing and rugs, labels are present that tell us the major materials in the product. Thus, a T-shirt might have "cotton" on its label signifying that the T-shirt is largely made of cotton. A dress shirt's label may say 55% cotton and 45% polyester meaning it is made from two polymers. Some items are identified by trade names. Thus, a dress advertised as being made from Fortrel (where "Fortrel" is a trade name) means it is made largely of a polyester material, probably the same polyester—PET or PETE—that made our soda bottle. Some everyday items are a complex of many materials of which only some or none are noted. This is true for many running shoes and tires. Tires will often be described as made of polyester (again, probably the same PETE) or nylon (or aramid). This only tells us the composition of the tire cord but not what other materials are included in the tire's composition. Yet, those that deal with tires generally know what is used in the manufacture of the tire in addition to the "stated ingredients." The identification of the main polymers that are present in many everyday items will be introduced gradually through looking at labels, researching on the web, simply knowing what certain items are generally composed of, through the feel and gross physical properties (such as flexibility and stiffness) of the material, etc.

Further, the properties of essentially the same polymer can be varied through small structural changes, thus producing materials with differing properties and uses. There is a match between desired properties and the particular material used. For instance, plastic bags require strength and flexibility. The bag material should be somewhat strong, inexpensive (since most bags are "throwaway" items), and readily available in large quantities. Strength is easily gained from increasing thickness. But with increased thickness comes decreased flexibility, increased cost since more material is needed to make thicker bags, and increased transportation (because of the additional weight) and storage costs. Thus, there is a balance between many competing factors. Plastic bags are typically made from three polymers: HDPE, low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE; actually a copolymer with largely ethylene units). These different polyethylene (PE) polymers are similar, differing only in the amount of branching, which results in differing tendencies to form ordered (crystalline) and less-ordered (amorphous) chain arrangements. Chapter 5 discusses these in greater detail. Grocery bags are generally made from HDPE, which is a largely linear polymer that has a high degree of crystallinity. Here, in comparison to LDPE film with the same strength, the bags are thinner, allowing a decrease in cost of materials, transportation cost, and storage space. The thinness allows good flexibility. LDPE is used for dry cleaning garment bags where simply covering the garments is the main objective rather than strength. The LDPE is less crystalline and weaker, but more flexible, because of the presence of more branching in comparison to HDPE. The thicker glossy shopping bags from malls are LLDPE, which, like HDPE, is largely linear. This increased thickness results in the bags being less flexible. These bags can be used many times.

Thus, most of the common items around us are polymeric. Table 1.4 gives a brief listing of some of these materials along with the chapters that will deal with them in the book.

With the electronic age we can access the Web to gather lots of general information about almost any topic including polymers. This book allows you to have a greater appreciation and understanding of such information and the products around us, including our own bodies.

1.3 TODAY'S MARKETPLACE

Over 100 billion pounds (50 million tons) of synthetic polymers is produced annually in the United States (Tables 1.5 through 1.8), and the growth of the industry is continuing at a fast rate. There is every reason to believe that this polymer age will continue as long as petroleum and other feedstocks are available and as long as consumers continue to enjoy the comfort, protection, and health benefits provided by elastomers, fibers, plastics, adhesives, and coatings. The 100 billion pounds of synthetic polymers consumed each year in the United States translates to over 300 pounds for every man, woman, and child in the United States. This does not include paper and wood-related products, natural polymers such as cotton and wool, or inorganic polymers (Table 1.8).

The soils we grow our foods on are largely polymeric as are the foods we eat. The plants around us are largely polymeric. We are walking exhibits of the widespread nature of polymers—our hair, fingernails, skin, bones, tendons, muscles; clothing such as socks, shoes, undergarments, as well as glasses; the morning newspaper; majority of automobiles, airplanes, trucks, boats, spacecraft; chairs, wastepaper baskets, pencils, tables, pictures, coaches, curtains, glass windows; the roads we drive on, the houses we live in, and the buildings we work in; the tapes and CDs we listen music on; packaging—all are either totally polymeric or contain a large amount of polymeric materials. Table 1.9 provides some general groupings of important polymers. Welcome to the wonderful world of polymer science.

The number of professional chemists directly employed is estimated to be 40%–60% of all employed chemists. The number of chemical industrial employees involved with synthetic

TABLE 1.5
U.S. Production of Plastics (Millions of Pounds)

Year	1995	2000	2005
Thermosetting resins			
Epoxies	570	620	560
Ureas and melamines	1,900	2,800	3,100
Phenolics	3,100	3,900	4,300
Thermoplastics			
Polyethylenes			
Low-density	7,000	6,800	7,200
High-density	10,000	12,600	14,700
Linear low-density	4,700	7,200	10,800
Polypropylene	9,800	14,200	16,400
Polystyrene			
Polystyrene	5,300	6,200	5,800
Acrylonitrile–butadiene–styrene and styrene–acrylonitrile	2,700	2,900	2,900
Polyamides, nylons	900	1,100	1,100
Poly(vinyl chloride) and copolymers	11,000	13,000	14,000
Polyesters			2,400

Source: American Plastics Council.

TABLE 1.6
U.S. Production of Man-Made Fibers (Millions of Pounds)

Year	1995	2000	2005
Noncellulosic			
Acrylics	400	310	120
Nylons	2,400	2,400	2,200
Olefins	2,100	2,900	2,900
Polyesters	3,500	3,500	2,800
Cellulosic			
Acetate and rayon	450	310	120

Source: Fiber Economics Bureau.

TABLE 1.7
U.S. Production of Paints and Coatings (Millions of Gallons)

Year	1995	2000	2005
Architectural	620	650	860
Product	380	450	410
Special	195	180	175

Source: Department of Commerce.

TABLE 1.8
U.S. Production of Synthetic Rubber (Millions of Pounds)

Styrene–butadiene	1,750
Polybutadiene	1,210
Nitrile	180
Ethylene–propylene	540
Other	1,100

Source: International Institute of Synthetic Rubber Producers.

TABLE 1.9
Polymer Classes: Natural and Synthetic

Polymeric Materials				
Inorganic		Organic/Inorganic	Organic	
Natural	Synthetic		Natural	Synthetic
Clays	Fibrous glass	Siloxanes	Proteins	Polyethylene
Cement	Poly(sulfur nitride)	Polyphosphazenes	Nucleic acids	Polystyrene
Pottery	Poly(boron nitride)	Polyphosphate esters	Lignins	Nylons
Bricks	Silicon carbide	Polysilanes	Polysaccharides	Polyesters
Sands		Sol–gel networks	Melanins	Polyurethanes
Glasses			Polyisoprenes	Poly(methyl methacrylate)
Rock-like				Polytetrafluoroethylene
Agate				Polyurethane
Talc				Poly(vinyl chloride)
Zirconia				Polycarbonate
Mica				Polypropylene
Asbestos				Poly(vinyl alcohol)
Quartz				
Ceramics				
Graphite/diamond				
Silicas				

TABLE 1.10
U.S. Chemical Industrial Employment (in Thousands)

Industrial inorganics	98
Drugs	305
Soaps, cleaners, etc.	158
Industrial organics	121
Agricultural	53
Synthetic polymers	1,206

Source: U.S. Department of Labor.

polymers is reported by the U.S. Department of Labor to be over one million, or almost 60% of the chemical industrial workforce (Table 1.10). There are another million employed as production workers in the synthetic polymer sector.

Table 1.11 contains a listing of the major chemical producers in the United States and the world. These producers are involved directly and/or indirectly with some form of synthetic polymers.

Polymeric materials, along with several other chemical industrial products, contribute positively to the balance of trade (Table 1.12). In fact, plastics and resins show the greatest value increase of exports minus imports with over $12 billion net favoring exports. The polymer-intense materials numbers are higher than noted in Table 1.12 since fiber and rubber materials are absent as a separate entry. Even so, the figures demonstrate the positive role polymers play in our balance of trade situation.

TABLE 1.11
Major Chemical Producers Based on (Net) Sales (>2500 Million Dollars; in Millions of U.S. Dollars; 2005)

United States			
Dow	46,300	ExxonMobile	31,200
DuPont	28,100	Lyondell	18,600
Huntsman	13,000	Chevron Phillips	10,700
PPG	7,700	Air Products	7,700
Praxair	7,700	Rhom & Haas	7,100
Eastman Chem.	7,100	General Electric	6,600
Celanese	6,100	Occidental Petroleum	4,600
Hexion Specialty	4,500	Mosaic	4,400
Lubrizol	4,000	Dow Corning	3,900
Nalco	3,300	Honeywell	3,200
Monsanto	3,000	Chemtura	2,900
Cytec Ind.	2,900	Solutia	2,800
Rockwood Specialties	2,800	W.R. Grace	2,600
Europe			
Solvay (Belgium)	10,600	Kemira (Finland)	2,500
Air Liquide (France)	13,000	Rhodia (France)	6,300
BASF (Germany)	53,200	Bayer (Germany)	34,100
Degussa (Germany)	14,600	Lanxess (Germany)	8,900
Merck (Germany)	7,300	Akzo Nobel (The Netherlands)	16,200
DSM (The Netherlands)	10,200	Ciba (Switzerland)	6,000
Clariant (Switzerland)	6,600	Syngenta (Switzerland)	8,100
BOC (United Kingdom)	8,400	ICI (United Kingdom)	10,600
Arkema (France)	7,100		
Japan			
Mitsubishi Chem. Inds.	21,900	Asahi Chem. Inds.	13,600
Sumitomo Chem.	14,100	Teijin	8,500
Mitsui Chem.	13,400	Showa Denko	7,400
Dainippon	9,100	Shin-Etsu	8,900
Toray Inds.	13,000	JSR Corp.	3,100
Taiyo Nippon Sanso	3,600		
Canada			
Nova Corp.	5,600	Potash Corp.	3,800
Agrium	3,500		

Source: C & EN.

TABLE 1.12
U.S. Chemical Trade-Imports and Exports (Millions of Dollars)

	1985		1994		2005	
Year	**Exports**	**Imports**	**Exports**	**Imports**	**Exports**	**Imports**
Organic chemicals	6,000	4,600	12,800	10,800	26,800	38,100
Inorganic chemicals	2,000	2,000	4,100	4,100	7,850	10,200
Oils and perfumes	—	—	3,500	2,000	8,400	7,900
Dyes, colorants	—	—	2,300	1,900	5,000	2,970
Medicinals/pharmaceuticals	2,700	1,080	6,100	4,700	26,000	39,000
Fertilizers	2,160	1,000	2,700	1,300	3,200	3,700
Plastics and resins	3,800	1,600	8,500	3,300	29,450[b]	17,390[b]
Others	5,300	4,220	7,600	2,700	16,400	8,950
Total chemicals[a]	22,000	14,500	51,600	33,400	123,100	128,300
Total	213,000	345,000	502,800	669,100	1,259,000	1,4670,000

Source: Department of Commerce.

[a] Includes nonlisted chemicals.

[b] Includes both plastics in primary and nonprimary forms but does not include rubber and rubber products.

Essentially, all of the industrially advanced countries of the world have major chemical producers. Table 1.11 contains a partial listing of these companies.

Thus, polymers play a critical role in our everyday lives, actually forming the basis for both plant and animal life, and represent an area where chemists continue to make important contributions.

1.4 SUMMARY

After reading this chapter, you should understand the following concepts:

1. Polymers or macromolecules are giant molecules with large structures and high molecular weights. In spite of their varieties they are governed by the same laws that apply to small molecules.
2. If we disregard metals and some inorganic compounds, practically everything else in this world is polymeric. Polymers form the basis for life itself and for our communications, transportation, buildings, food, etc. Polymers include protein and nucleic acids in our bodies, the fibers (natural and synthetic) we use for clothing, protein and starch we eat, elastomers in our automotive tires, paint, plastic wall and floor coverings, foam insulation, dishes, furniture, pipes, etc.
3. There are some systems in place that allow us to readily identify the nature of many polymeric materials including clothing and containers.
4. Early developments in polymers were largely empirical because of a lack of knowledge of polymer science. Advancement in polymers was rapid in the 1930s and 1940s because of the theories developed by Staudinger, Carothers, Mark, and many other scientists.
5. This is truly the age of the macromolecule. Essentially every important problem and advance comprises polymers, including synthetic (such as carbon nanotubes) and biological (such as the human genome and proteins). There are more chemists working with synthetic polymers than in all of the other areas of chemistry combined.

GLOSSARY

ABS Polymer produced by the copolymerization of acrylonitrile, butadiene, and styrene.
Bakelite Polymer produced by the condensation of phenol and formaldehyde.
cellulose Naturally occurring carbohydrate polymer.
elastomer Rubber.
filament Individual extrudate emerging form the holes in a spinneret; forms fibers.
functionality Number of reactive groups.
intermolecular forces Secondary forces between macromolecules.
intramolecular forces Secondary forces within the same macromolecular chain.
linear Continuous chain.
macromolecule Polymer; large chained molecular structure.
natural rubber (NR) Polyisoprene obtained form rubber plants; *Hevea brasiliensis*.
nylon-6,6 Polyamide produced from the condensation of adipic acid and 1,6-hexanediame.
oligomer Low molecular weight polymer with generally 2–10 repeat units.
plasticizer Additive that reduces intermolecular forces in polymers making it more flexible.
polymer Giant molecule, macromolecule, made up of multiple repeating units where the backbone is connected by covalent bonds.
protein Natural polyamide composed of many amino acid–derived repeat units.
rayon Regenerated cellulose in the form of filaments.
thermoplastic Linear polymer that softens when heated.
thermoset Network polymer containing cross-linked molecules that does not soften when heated.
vital force concept Hypothesis that organic compounds can be produced only by natural processes and not in the lab.
vulcanization Process in which elastomers such as natural rubber (NR) are cross-linked by heating with sulfur.

EXERCISES

1. Name six polymers that you encounter daily.
2. Why are there more chemists working with polymers than with other areas?
3. Why are there so many outstanding polymer chemists alive today?
4. Which of the following are polymeric or contain polymers as major components? (a) water; (b) wood; (c) meat; (d) cotton; (e) tires; (f) paint.
5. Name three inorganic polymers.
6. Name three synthetic polymers.
7. Identify what the bottles are made of from the following recycling codes found on their bottoms: (a) 4 with the letters LDPE; (b) 6 with the letters PS; (c) 5 with the letters PP.
8. Why is there a time delay between discovering a new polymer and commercializing it?
9. What are some advantages of polymers over metals?
10. It has been said that we are walking exhibits of the importance of polymers. Explain.
11. Why are there often concentrations of polymer-intense industries?
12. Why might simple identification codes such as those employed for containers fail for objects such as sneakers and tires?

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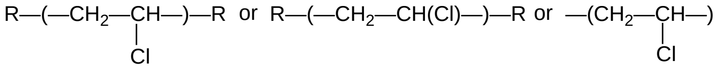
2 Polymer Structure (Morphology)

The size and shape of polymers are intimately connected to their properties. The shape of polymers is also intimately connected to the size of the various units that comprise the macromolecule and the various primary and secondary bonding forces that are present within the chain and between chains. This chapter covers the basic components that influence polymer shape or morphology.

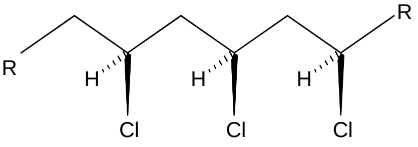
We generally describe the structure of both synthetic and natural polymers in terms of four levels of structure: primary, secondary, tertiary, and quaternary. The primary structure describes the precise sequence of the individual atoms that compose the polymer chain. For polymers that have only an average structure, such as proteins, polysaccharides, and nucleic acids, a representative chain structure is often given.

The structure can be given as a single repeat unit such that the full polymer structure can be obtained by simply repeating that unit 100, 500, 1000 times depending on the precise number of repeat units in the polymer chain. For PVC, this is:



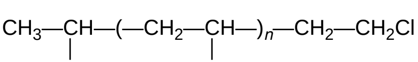
$$\mathrm{R{-}({-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}){-}R}\ \text{or}\ \mathrm{R{-}({-}CH_2{-}CH(Cl){-}){-}R}\ \text{or}\ \mathrm{{-}(CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-})} \tag{2.1}$$

Or some fuller description of the primary structure may be given such as that in Equation 2.2 for three repeat units of PVC where the particular geometry around each chiral carbon is given:



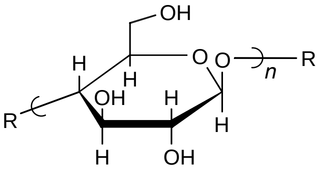
(2.2)

The ends may or may not be given depending on whether they are important to the particular point being made. Thus, for the single PVC repeat unit given above the end groups may be as follows:



$$\mathrm{CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}({-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-})_{\mathit{n}}{-}CH_2{-}CH_2Cl} \tag{2.3}$$

Natural polymers also have general repeat units such as for cellulose:



(2.4)

The secondary structure describes the molecular shape or conformation of the polymer chain. For most linear polymers this shape approaches a helical or "pleated skirt" (or sheet) arrangement depending on the nature of the polymer, treatment, and function. Examples of secondary structures appear in Figure 2.13.

The tertiary structure describes the shaping or folding of the polymer. Examples of this are given in Figures 2.16b, 2.17 left, and 2.17 right.

Finally, the quaternary structure represents the overall shape of groups of the tertiary structures where the tertiary structures may be similar or different. Examples are found in Figures 2.15, 2.16a, and 2.17 middle.

2.1 STEREOCHEMISTRY OF POLYMERS

The terms "memory" and "to remember" are similar and used by polymer chemists in similar, but different ways. The first use of the terms "memory" and "to remember" involves reversible changes in the polymer structure usually associated with stress–strain deformation of a rubber material where the dislodged, moved polymer segments are connected to one another through chemical and physical cross-links so that once the particular stress–strain is removed the polymer returns to its original, prestress–prestrain arrangement of the particular polymer segments. Thus, the polymer "remembers" its initial segmental arrangement and returns to it through the guiding of the cross-links.

The second use involves nonreversible changes of polymer segments and whole chain movements also brought about through stress–strain actions or other means to effect nonreversible changes. These changes include any synthetic chain and segmental orientations as well as postsynthesis changes including fabrication effects. These changes involve "permanent" differences in chain and segmental orientation and in some ways these changes represent the total history of the polymer materials from inception (synthesis) through the moment when a particular property or behavior is measured. These irreversible or nonreversible changes occur with both cross-linked and non-cross-linked materials and are largely responsible for the change in polymer property as the material moves from being synthesized, processed, fabricated, and used in whatever capacity it finds itself. Thus, the polymeric material "remembers" its history with respect to changes and forces that influence chain and segmental chain changes. The ability of polymers to "remember" and have a "memory" is a direct consequence of their size.

We can get an idea of the influence of size in looking at the series of methylene hydrocarbons as the number of carbon atoms increases. For low numbers of carbons, methane, ethane, propane, and butane are gases at room temperature. For the following groupings (Table 2.1) the materials are liquids. The individual hydrocarbon chains are held together by dispersion forces that are a sum of the individual methylene and end group forces. There is a gradual increase in boiling point and total dispersion forces for the individual chains until the materials become waxy solids such as found in bees' waxes and finally where the total dispersion forces are sufficient to be greater than individual carbon–carbon bond strengths so that the chains decompose prior to their evaporation. As the chain growth increases, the chain lengths are finally sufficient to give tough solids we call linear PE. These linear long-chain hydrocarbons are often crystalline and, as with most other crystalline materials such as

TABLE 2.1
Typical Properties of Straight Chain Hydrocarbons

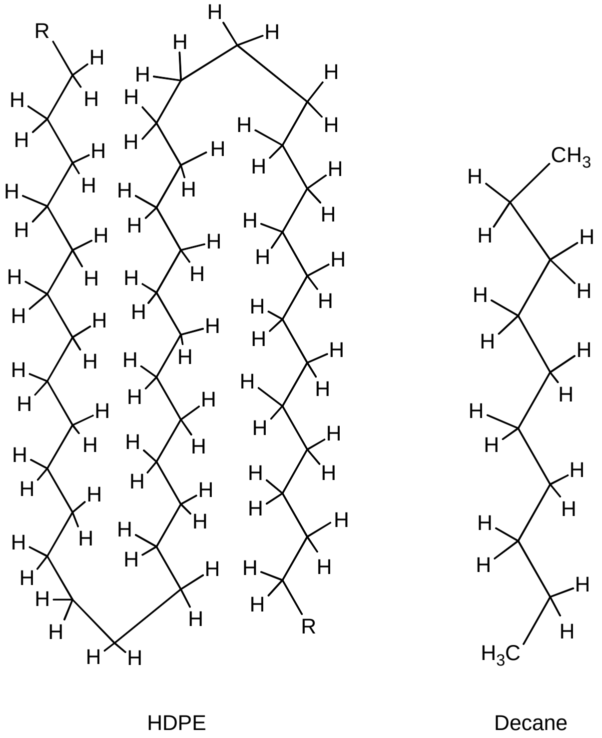
Average Number of Carbon Atoms	Boiling Range (°C)	Name	Physical State at Room Temperature	Typical Uses
1–4	<30	Gas	Gas	Heating
5–10	30–180	Gasoline	Liquid	Automotive fuel
11–12	180–230	Kerosene	Liquid	Jet fuel, heating
13–17	230–300	Light gas oil	Liquid	Diesel fuel, heating
18–25	305–400	Heavy gas oil	Viscous liquid	Heating
26–50	Decomposes	Wax	Waxy	Wax candles
50–1000	Decomposes		Tough waxy to solid	Wax coatings of food containers
1000–5000	Decomposes	Polyethylene	Solid	Bottles, containers, films
>5000	Decomposes	Polyethylene	Solid	Waste bags, ballistic wear, fibers, automotive parts, truck liners

many rocks and diamonds, they are strong but brittle. Fortunately, synthetic PE contains crystalline regions where the polymer chains are both arranged in orderly lines and not arranged in as orderly lines. These latter arrangements are imposed on the PE because of the presence of some branching in the linear polymer backbone and the need for long chains to be present in several crystalline structures with less-ordered regions present between the crystalline portions. These noncrystalline regions are referred to as amorphous regions and are responsible for allowing the PE to have some flexibility. Thus, most polymers contain amorphous as well as crystalline regions that provide both flexibility and strength.

The result of cumulative secondary forces can be readily seen by looking at the properties of linear alkanes as the number of methylene units increases. As noted before, methane, ethane, and propane are gases. As the number of methylene units increases to hexane, heptane, and octane, the alkanes become liquids. Further increases give a variety of waxes including ones that make birthday candles. These materials are solid but not strong. As the number of methylene units increase to several hundred the material is referred to as low molecular weight PE and has some strength; it now feels and acts more like a plastic material. Increasing the chain size gives eventually ultra-high molecular weight polyethylene (UHMWPE), which is very strong and used in applications where strength is important such as in the construction of ballistic resistant body armor (i.e., bulletproof vests). As a side note, low molecular weight PE with appreciable side branching has a melting range generally below 100°C, whereas high molecular weight PE with few branches has a melting range approaching the theoretical value of about 145°C.

HDPE, formerly called low-pressure PE $[H(CH_2CH_2)_nH]$, like other alkanes $[H(CH_2)_nH]$, may be used to illustrate several polymer structures. As in introductory organic chemistry, we can understand the properties and chemical activities of most complex organic compounds if we understand their basic chemistry and geometry. HDPE, like decane $[H(CH_2)_8H]$ or paraffin $[H(CH_2)_{\text{about }50}H]$, is a largely linear chainlike molecule consisting of catenated carbon atoms bonded covalently. The carbon atoms in all alkanes, including HDPE, are joined at characteristic tetrahedral bond angles of approximately 109.5°. While decane consists of 10 methylene groups, HDPE may contain more than 1000 methylene units (Figure 2.1). While we use the term normal or linear to describe nonbranched chains, we know that the chains are zigzag-shaped with many possible structural variations because of the tetrahedral bond angles and their ability for twisting.

The distance between the carbon atoms is 1.54 Å or 0.154 nm. The apparent zigzag distance between carbon atoms in a chain of many carbon atoms is 0.126 nm. Thus, the length



HDPE

Decane

FIGURE 2.1 Simulated structure of linear high-density polyethylene (HDPE) contrasted with the structural formula of linear or normal decane.

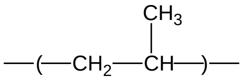
of an extended nonane chain is 8 units times 0.126 nm/units = 1.008 nm. For PE, the repeat unit has two methylenes so that the apparent zigzag distance is 2 × 0.126 nm or 0.252 nm for each "ethylene" unit. The zigzag or contour length of an HDPE chain 1000 units long (effectively 2000 methylenes) $[H(CH_2CH_2)_{1000}H]$ is 1000 units times 0.252 nm/units or 252 nm. However, because of rotations around the carbon atoms, chains seldom extend to their full extended contour length but are present in many different shapes or conformations.

The full contour length of a polymer is obtained by multiplying the apparent repeat unit length (l), which is the length of each mer or unit, by the number of units (n); contour length $= nl$. Even so, it is important to know the average end-to-end distance of polymer chains. The statistical method for this determination, called the random flight technique, was developed by Lord Raleigh in 1919. The classical statistical approach may be used to show the distance traveled by a blindfolded person taking n number of steps of length l in a random walk or the distance flown by a confused moth, bird, or bee.

The distance traveled from start to finish is not the straight-line path measured as nl (the contour length) but the root-mean-square (RMS) distance $(\langle r^2\rangle^{1/2})$, which is equal to $ln^{1/2}$. Thus, the RMS length of a flexible PE chain with 1000 units is 0.252 nm times $(1000)^{1/2} = 7.96$ nm or about 3% of the contour length. Nobel laureate Paul Flory and others have introduced several corrections so that this random flight technique could be applied to polymer chains approaching a full contour length of nl; i.e., rigid rod structures.

Each specific protein molecule has a specific chain length, like classical small molecules, and is said to be monodisperse with respect to chain length or molecular weight. However, most synthetic commercial polymers such as HDPE are composed of molecules of different lengths. Thus, the numerical value for the number of repeat units, n, or the degree of polymerization (DP) should be considered an average DP or average molecular weight. This average notion is often noted by a bar over the top, $\overline{DP}$ or $\overline{M}$. Accordingly, the average molecular weight of a polydisperse polymer will equal the product of the average $\overline{DP}$ times the molecular weight of the repeating unit or mer.

In organic chemistry, it is customary to call a nonlinear molecule, like isobutane, a branched chain. However, polymer scientists use the term “pendant group” to label any group present on the repeat unit. Thus, PP



$$—(—CH_2—\overset{\overset{\displaystyle CH_3}{|}}{CH}—)— \qquad (2.5)$$

has a methyl group as a pendant unit, but PP is designated as a linear polymer. In contrast, LDPE, formally called high-pressure PE, is a branched polymer because chain extensions or branches of methylene units are present coming off a branch point along the typically linear backbone chain (Figure 2.2). For LDPE the frequency of this branching is about 1.5/20 methylene units to 1/2000 methylene units. This branching, like branching in simple alkanes, increases the specific volume and thus reduces the density of the polymer. The linearity provides strength since it increases the opportunity of forming a regular crystalline structure while the branching provides flexibility and toughness since this encourages the formation of amorphous regions. Recently, low-pressure processes have been developed that produce LLDPE that is largely linear but with much less branching (Table 2.2).

Both linear and branched polymers are typically thermoplastics, meaning they can be melted before they undergo decomposition. However, cross-linked three-dimensional or network polymers are thermosets, meaning they decompose before they melt. The cross-link density can vary from low, such as found in a rubber band, to high, such as found in ebonite (Figure 2.3).

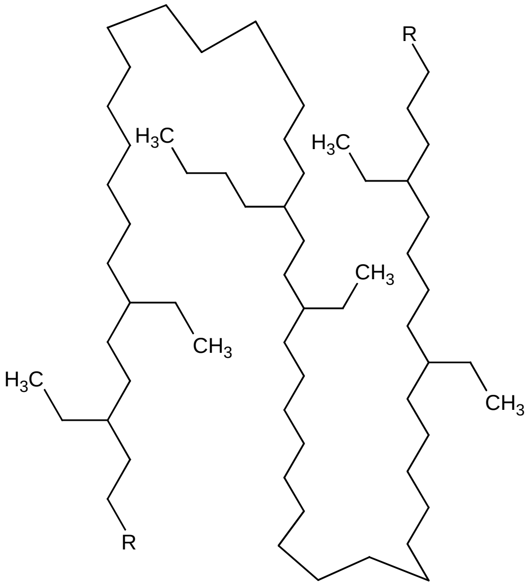


FIGURE 2.2 Simulated structural formula for branched low-density polyethylene (LDPE); compare with Figure 2.1 for HDPE.

TABLE 2.2
Types of Commercial Polyethylene (PE)

	General Structure	Crystallinity (%)	Density (g/cc)
LDPE	Linear with branching	50	0.92–0.94
LLDPE	Linear with less branching	50	0.92–0.94
HDPE	Linear with little branching	90	0.95

While there is only one possible segment arrangement for the repeat units in HDPE, there are two possible repeat units in PP and most other polymers. The units can be connected using what is called a head-to-tail or head-to-head arrangement (Figure 2.4). The usual arrangement by far is the head-to-tail so that pendant methyl groups appear on alternate backbone carbons.

The polymerization of monosubstituted vinyl compounds that give polymers like PS and PP produces polymer chains that possess chiral sites on every other carbon in the polymer backbone. Thus, the number of possible arrangements within a polymer chain is staggering since the number of possible isomers is 2^n where n is the number of chiral sites. For a relatively short chain containing 50 propylene units the number of isomers is about 1×10^{15}. While the presence of such sites in smaller molecules can be the cause of optical activity, these polymers are not optically active since the combined interactions with light are negated by other similar, but not identical, sites contained on that particular and other polymer chains. Further, it is quite possible that no two polymer chains produced during a polymerization will be exactly identical because of chiral differences.

The particular combinations of like and mirror image units within a polymer chain influence the polymer properties on a molecular level. On the bulk level, the average individual chain structure influences properties.

In the early 1950s Nobel laureate Giulio Natta used stereospecific coordination catalysts to produce stereospecific isomers of PP. Natta used the term “tacticity” to describe the different possible structures. As shown in Figure 2.5, the isomer corresponding to the arrangement DDDDDD or LLLLLL is called “isotactic” (same). The isomer corresponding to the DLDLDLDL alternating structural arrangement around carbon is called “syndiotactic”

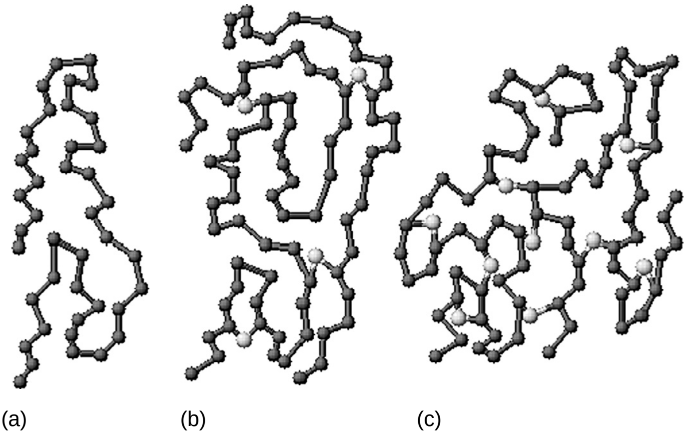


FIGURE 2.3 Skeletal structural formulas of a linear polymer (a) and a network (cross-linked) polymer with low cross-linking density (b) and high cross-linking density (c).

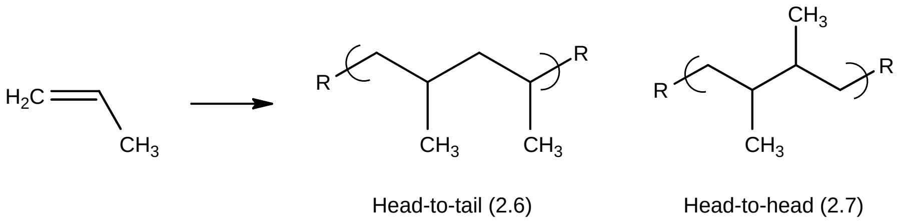


FIGURE 2.4 Simulated structural formulas showing the usual head-to-tail and unusual head-to-head configurations of polypropylene (PP).

(alternating). The isomer arrangement that corresponds to some mix of stereo arrangement around the chiral carbons is called "atactic" (having nothing to do with). The differences in stereoregularity around the chiral carbon influence the physical properties of the polymers. Thus, those with isotactic or syndiotactic arrangements are more apt to form compact crystalline arrangements and those with atactic stereoregularity are more apt to form amorphous arrangements. The melting point (T_m) of isotactic polypropylene (iPP) is of about 160°C and it is highly crystalline, whereas atactic polypropylene (aPP) melts at about 75°C and is amorphous. The term "eutectic" is used to describe either an isotactic or syndiotactic polymer, or a mixture of both.

While most polymers contain only one chiral or asymmetrical center in each repeat unit, it is possible to have diisotacticity where two different substituents are present at chiral centers. These isomers are labeled erythro- and threodiisotactic and erythro- and threosyndiotactic isomers (Figure 2.6). This topic is further described in Appendix J.

The many different conformers resulting from rotation around the carbon–carbon bonds in simple molecules like ethane and *n*-butane may be shown by Newman projections (Figure 2.7). The most stable is the anti or *trans* projection where the steric hindrance is minimized. There are a number of eclipsed and gauche arrangements of which only one of

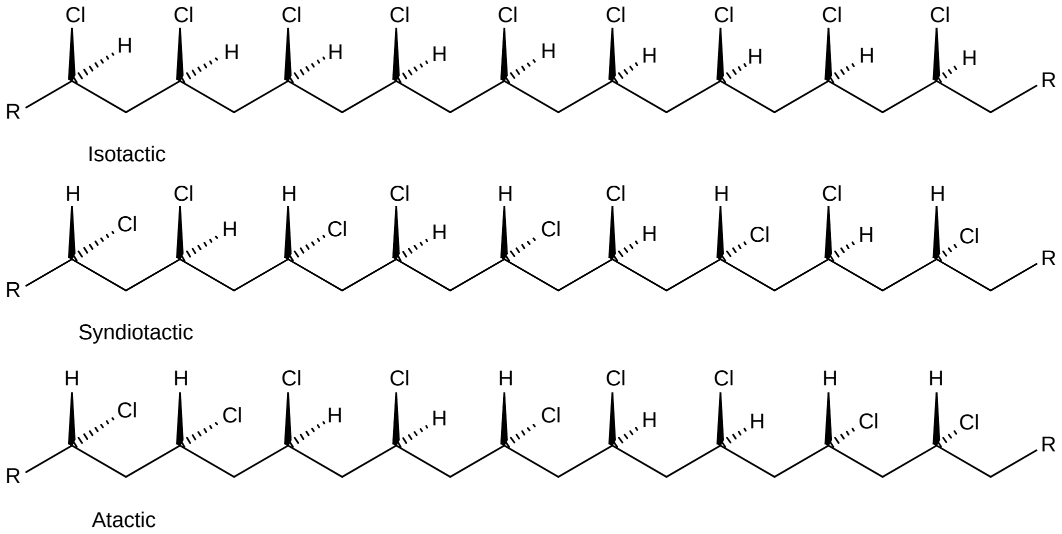


FIGURE 2.5 Skeletal formulas of isotactic, syndiotactic, and atactic poly(vinyl chloride) (PVC).

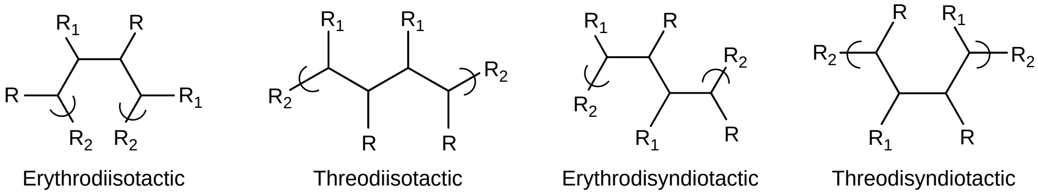


FIGURE 2.6 Simulated formulas of ditactic isomers where R_2 are chain extensions and R and R_1 are not hydrogen.

each is shown in Figure 2.7. The energy difference between the anti and eclipsed, the least stable form, is about 12 kJ/mol.

The ease in going from one conformer to the other decreases as the pendant groups increase in size and in secondary bonding. Thus, PMMA is hard at room temperature because

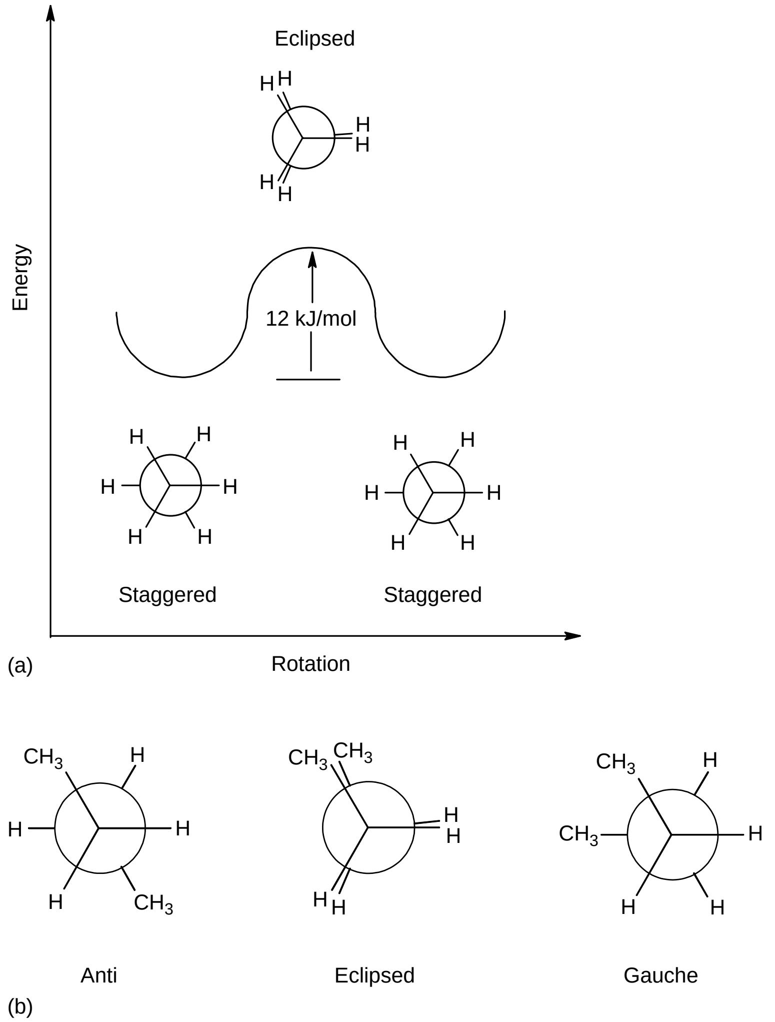


FIGURE 2.7 (a) potential energy profile illustrating the potential energy changes associated with rotation around a C–C bond of ethane; (b) Newman projections of designated conformers of *n*-butane.

of the polar groups and steric hindrance. By comparison, polyisobutylene (PIB), which offers only a small amount of steric hindrance, is flexible at room temperature.

2.2 MOLECULAR INTERACTIONS

Forces in nature are often divided into primary forces (typically greater than 200 kJ/mol) and secondary forces (typically less than 40 kJ/mol). Primary bonding forces can further be subdivided into ionic (characterized by a lack of directional bonding; occurs between atoms of large differences in electronegativity; normally not found in polymer backbones), metallic (the number of outer, valence electrons is too small to provide complete outer shells; often considered as charged atoms surrounded by a potentially fluid sea of electrons; lack of bonding direction), and covalent (including dative and coordinate) bonding (the major bonding in organic compounds and polymers; directional). The bonding length of primary bonds is generally about 0.1–0.22 nm. The carbon–carbon bond length is about 0.15–0.16 nm. Atoms in individual polymer chains are joined to one another by covalent bonds with bonding energies of about 320–370 kJ/mol for single bonds.

Polymer molecules are also attracted to one another through secondary forces. Secondary forces, often called van der Waals forces because they are the forces responsible for the van der Waals corrections to the ideal gas relationships, have longer distance of interaction, in comparison to primary forces. Secondary bonding distances are generally on the order of 0.25–0.5 nm. The force of these interactions is inversely proportional to some power of the distance, generally 2 or greater (i.e., force is proportional to $1/(\text{distance})^r$). Thus, many physical properties are sensitive to the polymer conformation (arrangements related to rotation around single bonds) and configuration (arrangements related to the actual chemical bonding around a given atom), since both affect the proximity of one chain to another. Thus, amorphous PP is more flexible than crystalline PP because the crystalline PP has the units closer to one another, allowing the secondary bonding to be stronger (Figure 2.8).

These intermolecular forces are also responsible for the increase in boiling points within a homologous series such as the alkanes, for the higher-than-expected boiling points of polar molecules such as alkyl chlorides, and for the abnormally high boiling points of water, alcohols, amines, and amides. While the forces responsible for these increases in boiling points are all van der Waals forces, they can be further subdivided in accordance to their source and intensity. Secondary forces could be London dispersion forces, induced permanent forces, and dipolar forces including hydrogen bonding.

Nonpolar molecules such as heptane and PE are attracted to each other by weak London or dispersion forces that result from induced dipole–dipole interactions. The temporary or transient dipoles are due to instantaneous fluctuations in the electron cloud density. The energy range of these forces is fairly constant and about 8 kJ/mol. This force is independent of temperature and is the major force between chains in largely nonpolar polymers, for example, those in classical elastomers and soft plastics such as PE.

It is interesting to note that methane, ethane, and ethylene are all gases; hexane, octane, and nonane are all liquids (at room conditions); while low molecular weight PE is a waxy solid. This trend is primarily due to an increase in the mass per molecule and to an increase in the London forces per polymer chain. The London force interaction between methylene units is about 8 kcal/mol. Thus, for methane molecules the attractive forces are 8 kJ/mol; for octane it is 64 kJ/mol; and for PE with 1000 ethylene (or 2000 methylenes) it is 2000 methylene units × 8 kJ/mol per methylene unit = 16,000 kJ/mol, which is well sufficient to make PE a solid and to break backbone bonds before it boils. (Polymers do not boil because the energy necessary to make a chain volatile is greater than the primary backbone bond energy.)

Polar molecules such as ethyl chloride and PVC are attracted to each other by both the London forces, but also by dipole–dipole interactions resulting from the electrostatic

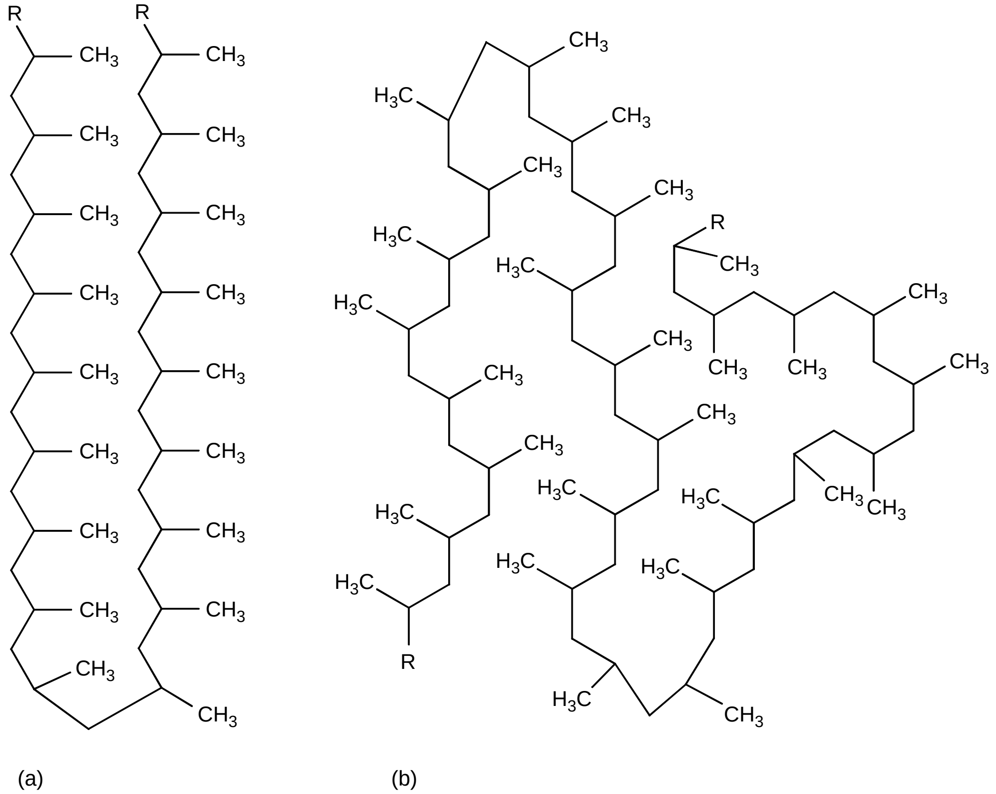


FIGURE 2.8 Representation of (a) a crystalline portion from isotactic polypropylene (iPP), and (b) an amorphous portion from atactic polypropylene (aPP).

attraction of a chlorine atom in one molecule to a hydrogen atom in another molecule. These dipole–dipole forces are of the order of 8–25 kJ/mol, generally greater than the London forces, and they are temperature-dependent. Hard plastics, such as PVC, have these dipole–dipole forces present between their chains.

Strong polar molecules such as ethanol, poly(vinyl alcohol) (PVA), cellulose, and proteins are attracted to each other by a special type of dipole–dipole force called hydrogen bonding. Hydrogen bonding occurs when a hydrogen molecule present on a highly electronegative element, such as nitrogen or oxygen, comes close to another highly electronegative element. This force is variable but for many molecules it is about 40 kJ/mol and for something like hydrogen fluoride, which has particularly strong hydrogen bonding, it is almost as strong as primary bonding. Intermolecular hydrogen bonding is usually present in classical fibers such as cotton, wool, silk, nylon (Figure 2.9), polyacrylonitrile, polyesters, and polyurethanes (PUs). Intramolecular hydrogen bonds are responsible for the helices observed in starch and globular proteins.

It is important to note that the high melting point of nylon-6,6 (265°C) (Figure 2.9) is a result of a combination of dipole–dipole, London, and hydrogen bonding forces. The relative amount of hydrogen bonding decreases as the number of methylene groups increases and a corresponding decrease is seen in the melting point for nylon-6,10 in comparison with nylon-6,6. PUs, polyacrylonitrile, and polyesters are characterized by the presence of strong hydrogen and polar bonding and form strong fibers. In contrast, iPP, which has no hydrogen bonding, is also a strong fiber because of the ability of the similar chains to fit closely

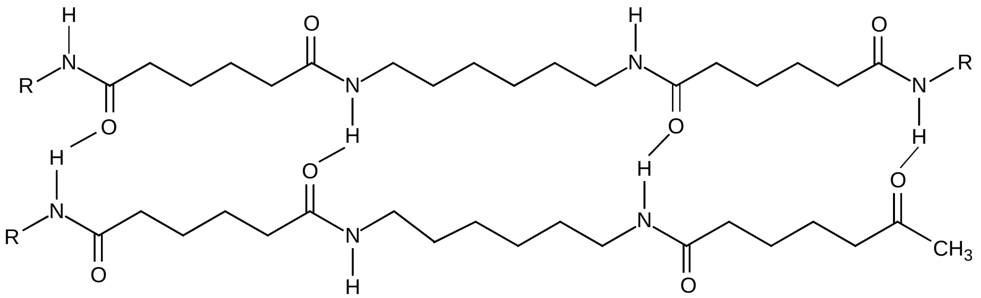


FIGURE 2.9 Typical hydrogen bonding (shown as "–" between hydrogen on nitrogen and oxygen for nylon-6,6.

together. Thus, both secondary bonding between chains and ability to tightly fit together, steric factors, are important in determining polymer properties.

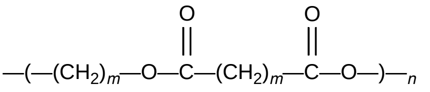
In addition to the contribution of intermolecular forces, chain entanglement is also an important contributory factor to the physical properties of polymers. While paraffin wax and HDPE are homologs with relatively high molecular weights, the chain length of paraffin is too short to permit chain entanglement, and hence lacks the strength and other characteristic properties of HDPE.

Chain entanglement allows long chains to act as though they were even longer because entanglement causes the entangled chains to act together. The critical chain length (z) required for the onset of entanglement is dependent on the polarity and shape of the polymer. The number of atoms in the critical chain lengths of PMMA, PS, and PIB are 208, 730, and 610, respectively.

Viscosity is a measure of the resistance to flow. The latter is a result of cooperative movement of the polymer segments from vacate location, hole, to another vacate location in a melted state. This movement is impeded by chain entanglement, high intermolecular forces, the presence of reinforcing agents, and cross-links. The melt viscosity (η) is often found to be proportional to the 3.4 power of the critical chain length, as shown in the following equation, regardless of the polymer. The constant K is temperature-dependent:

$$\log \eta = 3.4 \ \log \ z + \log \ K \tag{2.8}$$

The flexibility of amorphous polymers above the glassy state, where segmental mobility is possible, is governed by the same forces as melt viscosity and is dependent on a wriggling type of segment motion in the polymer chains. This flexibility is increased when many methylene groups ($-CH_2-$) or oxygen atoms ($-O-$) are present. Thus, the flexibility of aliphatic polyesters usually increases as m is increased:

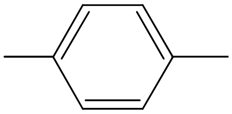


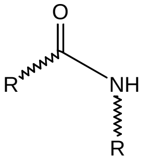
$$-\left(-(CH_2)_m-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_m-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right)-_n \tag{2.9}$$

Aliphatic polyester

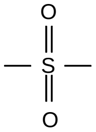
Flexibilizing groups include methylene and ethylene oxides, dimethylsiloxanes, and methylene groups.

In contrast, the flexibility of amorphous polymers above the glass state is decreased when stiffening groups (structures 2.10 through 2.13) are present in the polymer backbone:

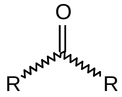

1,4-Phenylene (2.10)



Amide (2.11)

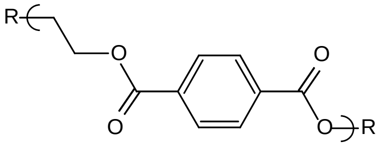


Sulfone (2.12)

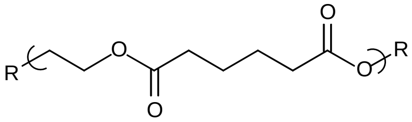


Carboxyl (2.13)

Thus, (PET; 2.14) is stiffer and has a higher melting point than poly(ethylene adipate; 2.15), and the former is stiffer than poly(butylene terephthalate) because of the presence of fewer methylene groups between the stiffening groups



Poly(ethylene terephthalate) (2.14)



Poly(ethylene adipate) (2.15)

These groups act as stiffening units because the groups themselves are inflexible as in the case of 1,4-phenylene or because they form relatively strong bonding, such as hydrogen bonding, between chains as is the case of the amide linkage.

Small molecules such as water can exist in three phases, liquid, solid, and gas. Polymers do not boil, so this phase is missing for polymers, but they do melt. But polymers undergo many other transitions besides melting. The most important of these is the glass transition, which will be discussed below. About 20 transitions have been reported for PE. PS undergoes several transitions, which have been identified. At about −230°C the movement, often described as wagging or oscillation, of the phenyl groups begins. At about −140°C the movement of four-carbon groups in the PS backbone begins. By 50°C torsional vibration of the phenyl groups begins. At about 100°C long-range chain movement begins corresponding to the reported T_g value for PS (Table 2.3). It is important to remember that while small molecules have a precise temperature associated with their transitions, such as 0°C for melting for water, polymer values, while often reported as a specific value, have a temperature range. This temperature range is the result of at least two features. First, there is a variety of polymer chain environments at the molecular level, each with its own energy-associated features. Second, transitions that require large segment or whole chain movement will also have a kinetic factor associated with them because it takes time for chains to untangle or tangle and rearrange themselves. Thus heating and cooling rate affect the temperatures required to effect the changes.

The flexibility of amorphous polymers is reduced drastically when they are cooled below a characteristic transition temperature called the glass transition temperature (T_g). At temperatures below T_g there is no ready segmental motion and any dimensional changes in the polymer chain are the result of temporary distortions of the primary covalent bonds. Amorphous plastics perform best below T_g but elastomers must be used above the brittle point, or they will act as a glass and be brittle and break when bent.

The melting point is the temperature range in which total or whole polymer chain mobility occurs. The melting point (T_m) is called a first-order transition temperature, and T_g is sometimes referred to as a second-order transition. The values for T_m are usually 33%–100% greater than for T_g. Symmetrical polymers like HDPE exhibit the greatest difference between T_m and T_g. The T_g values are low for elastomers and flexible polymers such as PE

TABLE 2.3
Approximate Glass Transition Temperatures (T_g) for Selected Polymers

Polymer	T_g (K)	Polymer	T_g (K)
Cellulose acetate butyrate	323	Cellulose triacetate	430
Polyethylene (LDPE)	148	Polytetrafluoroethylene	160,400[a]
Atactic polypropylene	253	Poly(ethyl acrylate)	249
Isotactic polypropylene	373	Poly(methyl acrylate)	279
Polyacrylonitrile	378	a-Poly(butyl methacrylate)	339
Poly(vinyl acetate)	301	a-Poly(methyl acrylate)	378
Poly(vinyl alcohol)	358	Poly(vinyl chloride)	354
cis-Poly-1,3-butadiene	165	Nylon-6,6	330
trans-Poly-1,3-butadiene	255	Poly(ethylene adipate)	223
Polydimethylsiloxane	150	Poly(ethylene terephthalate)	342
Polystyrene	373		

[a] Two major transitions observed.

and dimethylsiloxane, and relatively high for hard amorphous plastics such as polyacrylonitrile and PET (Table 2.3).

The T_g for iPP is 373 K or 100°C, yet because of its high degree of crystallinity, it does not flow to any great extent below its melting point of 438 K (165°C). In contrast, the highly amorphous PIB, which has a T_g value of 203 K (−70°C), flows at room temperature (Table 2.3). T_g decreases as the size of the ester groups increases in polyacrylates and polymethylacrylates. The effect of the phenylene stiffening groups is also demonstrated, with the T_g of PET (structure 2.14) being about 120°C higher than that of poly(ethylene adipate) (structure 2.15).

The main reasons why amorphous polymers go from a solid glassy state to a more flexible plastic state are the presence of sufficient energy and unoccupied volume. Heating the sample allows the polymer sufficient energy for the chain segments to become separated and begin movement, which in turn creates free or unoccupied volume that allows the chain segments to slip past one another, resulting in the material being more flexible. In order for the chains to begin moving, the secondary forces that hold the chains together must be overcome. As movement begins, additional unoccupied volume is created and this expansion within a complex maze of intertwining chains creates additional free volume. A measure of this expansion is the thermal coefficient of expansion. The temperature range in which the available free volume and energy necessary to overcome segmental chain interactions is available is called the glass transition temperature, T_g. Since the specific volume of polymers increases at T_g in order to accommodate the increased segmental chain motion, T_g values can be estimated from plots of the change in specific volume with temperature (Figure 2.10).

Below the T_g, the chains are "frozen" into place and the material acts as a brittle solid or glass, hence the term "glassy state".

Other properties such as stiffness (modulus), refractive index, dielectric properties, gas permeability, x-ray adsorption, and heat capacity (Figure 2.11) all change at T_g and have been used to determine the T_g. As seen in Figure 2.11 both T_g and T_m are endothermic because energy is absorbed when segmental mobility or melting occurs. This idealized plot of energy as a function of temperature is for a polymer with about a 50:50 mixture of crystalline and amorphous regions. Bringing about wholesale mobility, melting, takes more energy than causing segmental mobility. This is illustrated in Figure 2.11, in which the area under the

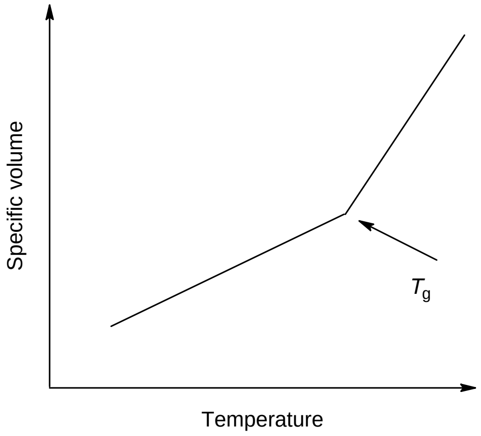


FIGURE 2.10 Determination of T_g by noting the abrupt change in specific volume.

T_g-associated peak is less than the area under the curve for the T_m-associated peak (the area under the peaks is a direct measure of the heat (energy)). While T_g values are most often reported in relation to the onset of segmental motion in the principal polymer backbone, other secondary values may be observed for the onset of motion of large pendant groups, branches, etc.

The number of possible conformers increases with chain length and can be shown statistically to equal 2^{2n} where n is the number of units. Thus, when $n = 1000$, the number of possible conformers of HDPE is 2^{2000} or 10^{600}, more than the grains of sand at all of our beaches combined. Four of these possible conformers are shown in Figure 2.12.

Because there are many possible ends in branched polymers, it is customary to use the radius of gyration (S) instead of r for such polymers. The radius of gyration is actually the RMS distance of a chain end from the polymer's center of gravity. S is less than the end-to-end distance (r), and for linear polymers $r^2 = 6S^2$.

In general, polymers (both natural and synthetic) "emphasize" two general shapes—helical and pleated (Figures 2.9 and 2.13). The intermolecular bonds in many polyamides, including natural polyamides such as β-keratin, where the steric requirements are low,

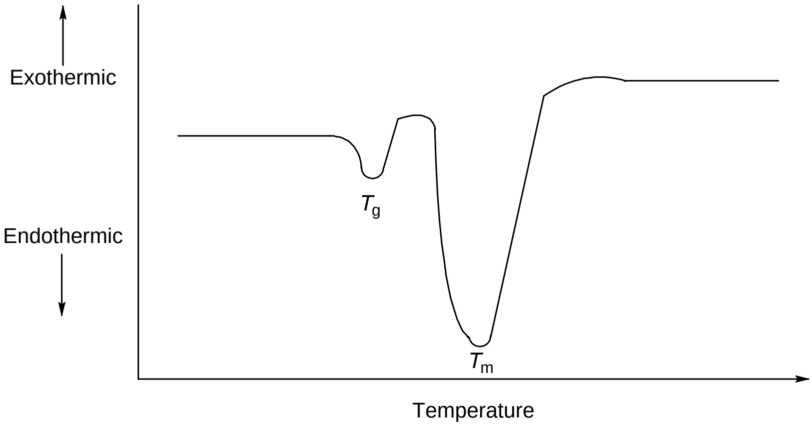


FIGURE 2.11 Typical differential scanning calorimetry (DSC) thermogram of a polymer.

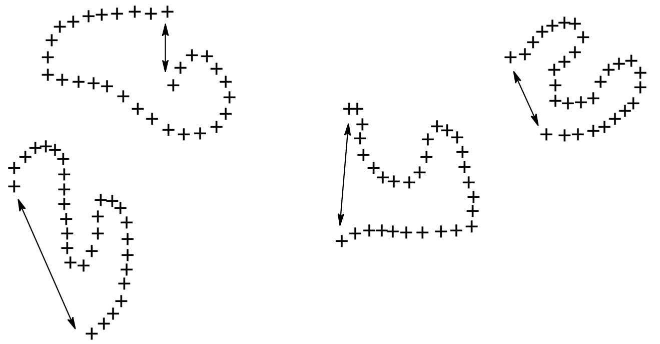


FIGURE 2.12 End-to-end distances for four 30-unit chains.

produce strong pleated sheets. Hair, fingernails and toenails, feathers, and horns have a β-keratin structure. Helical structures are often found where there is high steric hindrance because helical structures allow the minimization of these steric factors by ‘‘radiating’’ them outward from a central (backbone) core, distributing the steric groups around a helical circle. It is important that secondary bonding, generally hydrogen bonding, occurs in both structures. With sheets, bonding occurs between chains and for helical structures bonding occurs within the same chain. Further, some compounds, such as α-keratin, form helical structures within sheet structures.

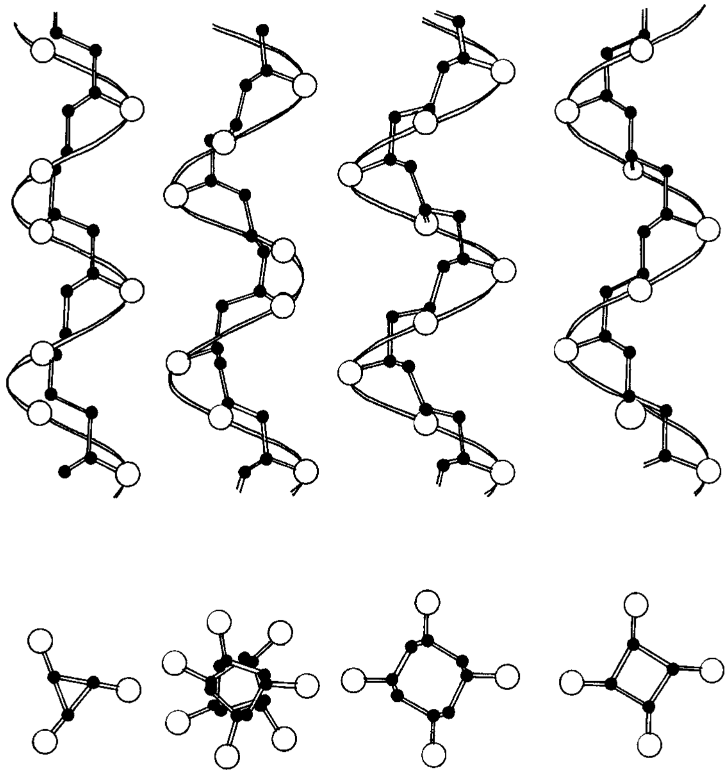


FIGURE 2.13 Helical conformation of isotactic vinyl polymers. (From Gaylord, N., *Linear and Stereoregular Addition Polymers*, Wiley, New York, 1959. With permission.)

α-Keratin (composed of parallel polypeptide α-helices) and most globular proteins are characterized by intramolecular bonds. Section 10.2 discusses more about the structures of the two types of keratin. These, and many other polymers, including nucleic acids, form helices. Ribonucleic acid (RNA) exists as a single-stranded helix, while deoxyribonucleic acid (DNA) exists as a double-stranded helix. For both natural and synthetic polymers these helices vary with respect to the number of backbone carbons per complete cycle. Figure 2.13 contains helical conformations for isotactic vinyl polymers. The "R" groups are designated by the larger open circles. From left to right the nature of the R group varies as expected. For the furthest left R = —CH_3, —CH_2CH_3, —$CH=CH_2$, —OCH_3, —$CH_2CH_2CH(CH_3)_2$, —O—$CH_2CH_2CH(CH_3)_2$, and cyclohexyl. For the next R = —$CH_2CH(CH_3)CH_2CH_3$, —$CH_2CH(CH_3)_2$. For the third from the left R = —$CH(CH_3)_2$, and for the extreme right R = a variety of substituted cyclohexyls including 2-methylcyclohexyl and 4-fluorocyclohexyl.

2.3 POLYMER CRYSTALS

Prior to 1920, leading scientists not only stated that macromolecules were nonexistent, but they also believed that if they did exist, they could not exist as crystals. However, in the early 1920s Haworth used x-ray diffraction techniques to show that elongated cellulose was a crystalline polymer consisting of repeat units of cellubiose. In 1925, Katz, in jest, placed a stretched NR band in an x-ray spectrometer and to his surprise observed an interference pattern typical of a crystalline substance. This phenomenon may be shown qualitatively by the development of opacity when a rubber band is stretched (try it yourself) and by the abnormal stiffening and whitening of unvulcanized rubber when it is stored for several days at 0°C. The opacity noted in stretched rubber and cold rubber is the result of the formation of crystallites, or regions of crystallinity. The latter were first explained by a fringed micelle model, which is now found not consistent with much of the current experimental findings (Figure 2.14).

Amorphous polymers with irregular bulky groups are seldom crystallizable, and unless special techniques are used even ordered polymers are seldom 100% crystalline. The combination of amorphous and crystalline structures varies with the structure of the polymer and the precise conditions that have been imposed on the material. For instance, rapid cooling often decreases the amount of crystallinity because there is not sufficient time to allow the long chains to organize themselves into more ordered structures. The reason linear ordered polymers fail to be almost totally crystalline is largely kinetic, resulting from an inability of

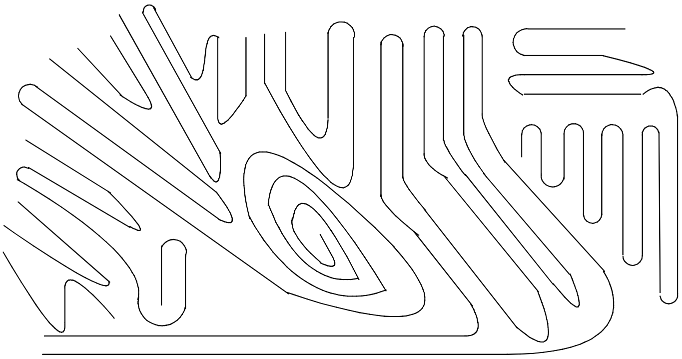


FIGURE 2.14 Schematic two-dimensional representation of a modified micelle model of the crystalline–amorphous structure of polymers.

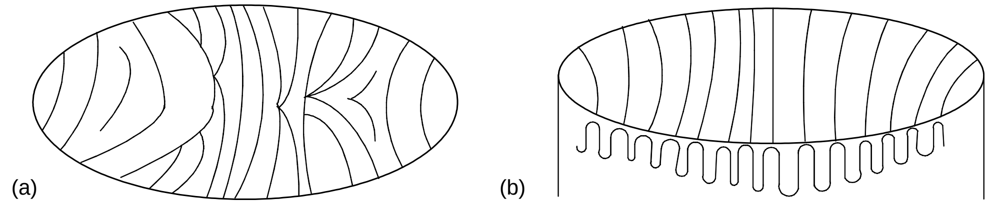


FIGURE 2.15 Structure of a spherulite from the bulk. (b) A slice of a simple spherulite. As further growth occurs, filling in, branch points, etc. occur as shown in (a). The contour lines are simply the hairpin turning points for the folded chains.

the long chains to totally disentangle and perfectly align themselves during the time the polymer chain is cooling and mobile.

Mixtures of amorphous and mini-crystalline structures or regions may consist of somewhat random chains containing some that are parallel to one another forming short-range mini-crystalline regions. Crystalline regions may be formed from large-range ordered platelet-like structures, including polymer single crystals, or they may form even larger organizations such as spherulites, as shown in Figures 2.15 and 2.16. Short- and longer-range ordered structures can act as physical cross-links.

In general, linear polymers form a variety of single crystals when crystallized from dilute solutions. For instance, highly linear PE can form diamond-shaped single crystals with a thickness on the order of 11–14 nm when crystallized from dilute solution. The surface consists of "hairpin-turned" methylene units as pictured in Figures 2.15 and 2.16. The polymer chain axes are perpendicular to the large flat crystal faces. A single polymer chain with 1000 ethylene (2000 methylene) units might undergo about 50 of these hairpin turns on the top surface and another 50 on the bottom with about 20 ethylene units between the two surfaces.

Many polymers form more complex single crystals when crystallized from dilute solution including hollow pyramids that often collapse on drying. As the polymer concentration increases, other structures occur, including twins, spirals, and multilayer dendritic structures with the main structure being spherulites.

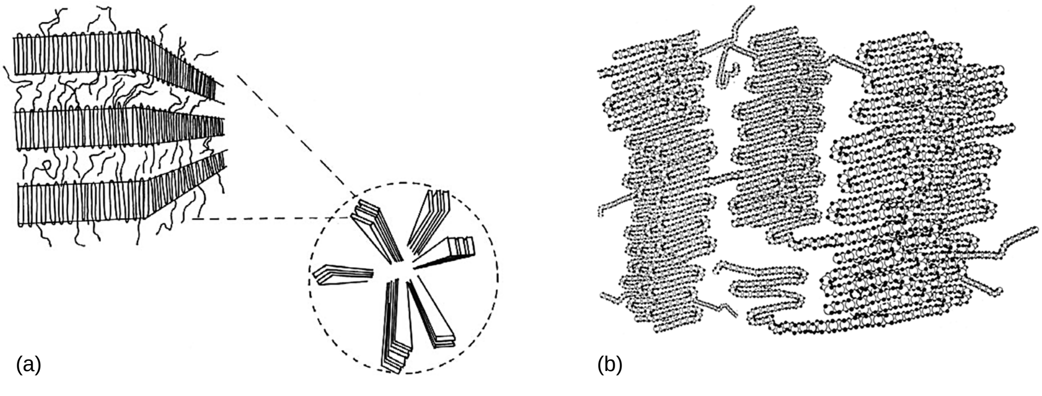


FIGURE 2.16 Spherulite structure showing the molecular-level lamellar chain-folded platelets and tie and frayed chain arrangements (a), and a more complete model of two sets of three lamellar chain-folded platelets formed from polyethylene (PE) (b). Each platelet contains about 850 ethylene units as shown here.

When polymer solids are produced from their melts, the most common structures are these spherulites that can be seen by the naked eye and viewed as Maltese crosslike structures with polarized light and crossed Nicol prisms under a microscope.

For linear PE, the initial structure formed is a single crystal with folded chain lamellae. These quickly lead to the formation of sheaflike structures called axialites or hedrites. As growth proceeds, the lamellae develop on either side of a central reference point. They continue to fan out, occupying increasing volume sections through the formation of additional lamellae at appropriate branch points. The result is the formation of spherulites as pictured in Figures 2.15 and 2.16.

While the lamellar structures present in spherulites are similar to those present in polymer single crystals, the folding of chains in spherulites is less organized. Further, the structures that exist between these lamellar structures are generally occupied by amorphous structures including atactic chain segments, low molecular weight chains, and impurities.

The individual spherulite lamellae are bound together by "tie" molecules that are present in more than one spherulite. Sometimes these tie segments form intercrystalline links, which are threadlike structures, that are important in developing the characteristic good toughness found in semicrystalline polymers. They act to tie together the entire assembly of spherulites into a more or less coherent "package."

Depending upon the particular conditions of crystallization a number of secondary and tertiary structures can be formed. In most cases, crystalline polymers attempt to form crystalline platelets. Under little or no externally applied stress, these platelets organize themselves in spherulites as pictured in Figures 2.15 and 2.16. They start by a nucleating process and begin to radiate outward from the central nucleating site. Amorphous chain segments get trapped between the forming crystalline platelet combinations, giving a kind of fuzzy or frayed exterior. These platelets are generally either planar, as shown in Figure 2.17, or can be helical or twisted. The platelets continue to grow until they butt up against other spherulites.

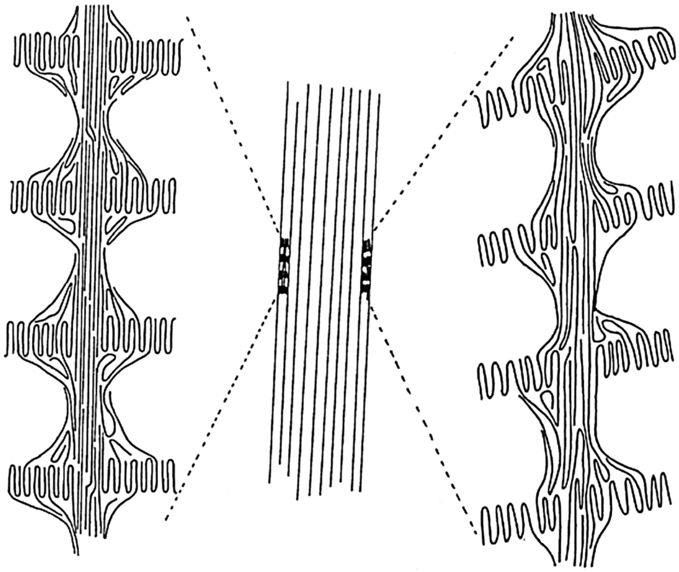


FIGURE 2.17 Crystalline polymer structures formed under applied tension including flow conditions. The center shows the tertiary monofibrillar structure including platelets, the left shows these monofibrillar structures bundled together forming a quaternary structure fibril, and the right shows the distorted shish kebab formed with more rapid flow.

Under externally applied stress, including simple melt flow, the tertiary structure can approach a shish kebab arrangement where there are planes of platelets separated by areas where there exist both crystalline and amorphous regions as pictured in Figure 2.17 (left). These shish kebab structures often organize into quaternary structures consisting of bundles of shish kebab single-stranded filaments forming fibrils. Under more rapid flow conditions the shish kebab itself becomes distorted (Figure 2.17, right).

Interestingly, the amorphous regions within the spherulite confer some flexibility onto the material while crystalline platelets give the material strength, just as in the case with largely amorphous materials. This theme of amorphous flexibility and crystalline strength (and brittleness) is a central idea in polymer structure–property relationships.

It must be remembered that the secondary structure of both the amorphous and crystalline regions typically tends toward a helical arrangement of the backbone for most polymers but not for PE, which forms a crank-shaft structure because of the lack of steric restraints (i.e., lack of pendant groups off the backbone).

The kind, amount, and distribution of polymer chain order or disorder (crystalline or amorphous) is driven by the processing (including pre- and post-) conditions, and thus it is possible to vary the polymer properties through a knowledge of, and ability to, control the molecular-level structures. The crystalline regions may be disrupted by processing techniques such as thermoforming and extrusion of plastics and drawing of fibers. In the last process, which is descriptive of the others, the crystallites are ordered in the direction of the stress, the filament shrinks in diameter, and heat is evolved and reabsorbed as a result of additional orientation and crystallization.

Crystallization often occurs over a wide area or volume almost simultaneously. It is similar to raindrops or grains of sand falling into water and setting up waves that progress outward until they overlap with one another. Avrami and others have studied the rate of crystallization, deriving various relationships to describe and differentiate the various crystallizations. The rate of crystallization can be followed with dilatometry using the Avrami Equation 2.16, which was developed to follow the crystallization of metals. Here, the quotient of the difference between the specific volume V_t at time t and the final specific volume V_f divided by the difference between the original specific volume V_o and the final volume V_f is equal to an experimental expression where K is the kinetic constant related to the rate of nucleation and growth, and n is an integer related to the nucleation and growth of crystals. In theory, the value of n is related to the dimensionality of the growing crystallinity (Table 2.4). It has been calculated using several scenarios.

$$\frac{V_t - V_\mathrm{f}}{V_\mathrm{o} - V_\mathrm{f}} = \mathrm{e}^{-K_t^n} \tag{2.16}$$

TABLE 2.4
Avrami Values for Particular Crystallization Growth for Sporadic and Ordered (or Predetermined) Nucleation

Crystalization Growth Pattern	Sporadic Nucleation	Ordered Nucleation	Overall Dimensionality
Fiber/rod	2	1	1
Disc	3	2	2
Spherulite	4		3
Sheaf	6		

Table 2.4 contains values for two of these scenarios, which are valid for only the initial stages of crystallization.

Noninteger values for n are not uncommon. As noted before, depending on the particular conditions several crystalline formations are possible and found for the same polymer. Sperling has collected a number of Avrami values for some common values given in the literature. The range of values for PE is 2.6–4.0; for poly(decamethylene terephthalate), 2.7–4.0; for PP, 2.8–4.1; for poly(ethylene oxide), 2.0–4.0; and for iPP, 2.0–4.0.

Crystallization of polymers containing bulky groups occurs more slowly than polymers that do not contain bulky substituents. In addition to crystallization of the backbone of polymers, crystallization may also occur in regularly spaced bulky groups even when an amorphous structure is maintained in the backbone. In general, the pendant group must contain at least 10 carbon atoms in order for this side chain crystallization to occur. Ordered polymers with small pendant groups crystallize more readily than those with bulky groups. Rapid crystallization producing films with good transparency may be produced by addition of a crystalline nucleating agent such as benzoic acid and by rapid cooling.

While polymeric hydrocarbons have been used as illustrations for simplicity, it is important to note that the principles discussed apply to all polymers, organic as well as inorganic, and natural as well as synthetic, and to elastomers, plastics, and fibers.

2.4 AMORPHOUS BULK STATE

An amorphous bulk polymer contains chains that are arranged in less than a well-ordered, crystalline manner. Physically, amorphous polymers exhibit a T_g but not a T_m, and do not give a clear x-ray diffraction pattern. Amorphous polymer chains have been likened to spaghetti strands in a pot of spaghetti, but the true extent of disorder that results in an amorphous polymer is still not fully understood.

Chapter 13 contains a discussion of a number of techniques employed in the search for the real structure of the amorphous bulk state. Briefly, evidence suggests that little order exists in the amorphous state with the order being similar to that observed with low molecular weight hydrocarbons. There is evidence that there is some short-range order and for long-range interactions the chains approximate a random coil with some portions paralleling one another. In 1953, Flory and Mark suggested a random coil model whereby the chains had conformations similar to those present if the polymer were in a theta solvent. In 1957, Kargin suggested that amorphous polymer chains exist as aggregates in parallel alignment. Models continue to be developed, but all contain the elements of disorder or order suggested by Flory and Mark and the elements of order suggested by Kargin.

2.5 POLYMER STRUCTURE–PROPERTY RELATIONSHIPS

Throughout the text we will relate polymer structure to the properties of the polymer. Polymer properties are related not only to the chemical nature of the polymer, but also to such factors as extent and distribution of crystallinity, distribution of polymer chain lengths, and nature and amount of additives, such as fillers, reinforcing agents, and plasticizers, to mention a few. These factors influence essentially all the polymeric properties to some extent including hardness, flammability, weatherability, chemical stability, biological response, comfort, flex life, moisture retention, appearance, dyeability, softening point, and electrical properties.

Materials must be varied to perform the many tasks required of them in today's society. Often they must perform them repeatedly and in a "special" manner. We get an ideal of what materials can do by looking at some of the behavior of giant molecules in our body. While a plastic hinge must be able to work thousands of times, the human heart, a complex muscle largely composed of protein polymers (Section 10.6), provides about 2.5 billion beats within a lifetime, moving oxygen (Section 16.8) throughout the approximately 144,000 km of the circulatory system with (some) blood vessels the thickness of hair, and delivering about 8,000 L of blood every day with little deterioration of the cell walls. The master design allows nerve impulses to travel within the body at the rate of about 300 m/min; again polymers are the "enabling" material that allows this rapid and precise transfer of nerve impulses. Human bones, again largely polymeric, have a strength about five times that of steel (on a weight basis). Genes, again polymeric (Sections 10.10 and 10.11), appear to be about 99.9% the same between humans, with the 0.1% functioning to give individuals the variety of size, abilities, etc. that confer uniqueness. In the synthetic realm, we are beginning to understand and mimic the complexities, strength, preciseness, and flexibility that are already present in natural polymers.

Here we will briefly deal with the chemical and physical nature of polymeric materials that permit their division into three broad groups: elastomers or rubbers, fibers, and plastics. Elastomers are high polymers possessing chemical and/or physical cross-links. For industrial application the "use" temperatures must be above T_g (to allow for ready "chain" mobility), and its normal state (unextended) must be amorphous. The restoring force, after elongation, is largely due to entropy. On release of the applied force the chains tend to return to a more random state. Gross, actual mobility of chains must be low. The cohesive energy forces between chains should be low, permitting rapid, easy expansion. In its extended state a chain should exhibit a high tensile strength, whereas at low extensions it should have a low tensile strength. Cross-linked vinyl polymers often meet the desired property requirements. The material, after deformation, should return to its original shape because of the cross-linking. This property is often referred to as an elastic "memory." Figure 2.18 illustrates force versus elongation for a typical elastomer. As the elastomer is pulled, the largely random chain segments become "stretched out," forming microcrystalline domains resulting in a decreased entropy or increased order. Eventually, most of the chains are part of these microcrystalline domains resulting in further elongation requiring much increased force (stress). This microcrystallinization, physical cross-linking, also confers a greater brittleness to the elastomer, eventually resulting in the rubber breaking as additional stress is applied.

Fiber properties include high tensile strength and high modulus (high stress for small strains). These properties can be obtained from high molecular symmetry and high cohesive energies between chains, both requiring a fairly high degree of polymer crystallinity. Fibers are normally linear and drawn (oriented) in one direction, producing higher mechanical

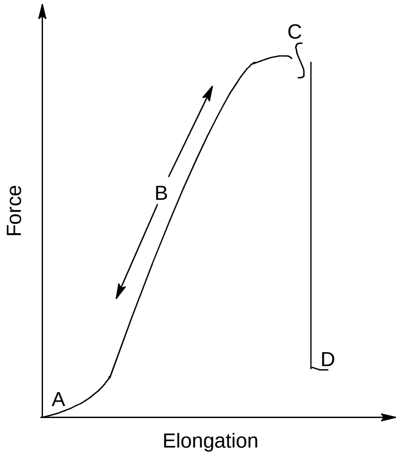


FIGURE 2.18 Elongation of an elastomer as a function of applied force, stress, where A is the original "relaxed" state, B represents movement to full extension, C is the point at which the elastomer "breaks," and D represents the force necessary to pull two separate pieces of elastomer apart.

properties in that direction. Typical condensation polymers, such as polyesters and nylons, often exhibit these properties. If the fiber is to be ironed, its T_g should be above 200°C, and if it is to be drawn from the melt, its T_g should be below 300°C. Branching and cross-linking are undesirable since they disrupt crystalline formation, even though a small amount of cross-linking may increase some physical properties, if effected after the material is drawn and processed. Permanent-press garments often have some cross-linking, ensuring a "remembrance" of the "permanent press."

Products with intermediate properties between elastomers and fibers are grouped together under plastics. Plastics typically have some flexibility and have dimensional stability, i.e., they act as somewhat flexible solids. Many polymers can act as members of two of these three categories depending on the treatment of the material. Thus, nylon-6,6 is fibrous in behavior when it is treated so that the chains have good alignment and are stretched both to increase this alignment and to form fibers. Nylon-6,6 is plastic when it has less alignment, i.e., it is more amorphous, and used as a bulk material rather than as a fiber. Polyesters also can be either fibers or plastics under the same conditions as given for nylon-6,6. Other materials, such as PVC and siloxanes, can be processed to act as plastics or elastomers.

Selected property–structure relationships are summarized in Tables 2.5 and 2.6. As noted before, some polymers can be classified in two categories, with properties varying greatly by molecular weight, end group, processing, cross-linking, plasticizer, etc. Nylon-6,6 in its more crystalline form behaves as a fiber, whereas less crystalline forms of nylon-6,6 are generally classified as plastics.

TABLE 2.5
Selected Property–Structure Relationships

Glass Transition Temperature
- Increases with the presence of:
  - bulky pendant groups
  - stiffening groups as 1,4-phenylene
  - chain symmetry
  - polar groups
  - cross-linking
- Decreases with the presence of:
  - additives like plasticizers
  - flexible main chain groups
  - nonpolar groups
  - dissymmetry

Solubility
- Favored by:
  - longer chain lengths
  - low interchain forces
  - disorder and dissymmetry
  - increased temperature
  - compatible solvent

Crystallinity
- Favored by:
  - high interchain forces
  - regular structure; high symmetry
  - decrease in volume
  - increased stress
  - slow cooling from melt
  - homogeneous chain length

TABLE 2.6
General Property Performance–Structure Relationships[a]

	Increased Crystallinity	Increased Cross-Linking	Increased Molecular Weight	Increased Molecular Weight Distribution	Addition of Polar Backbone Units	Addition of Backbone Stiffening Groups
Abrasion resistance	+	+	+	−	+	−
Brittleness	−	M	+	+	+	+
Chemical resistance	+	V	+	−	−	+
Hardness	+	+	+	+	+	+
T_g	+	+	+	−	+	+
Solubility	−	−	−	0	−	−
Tensile strength	+	M	+	−	+	+
Toughness	−	−	+	−	+	−
Yield	+	+	+	+	+	+

[a] + = increase in property; 0 = little or no effect; − = decrease in property; M = property passes through a maximum; V = variable results dependent on particular sample and temperature.

2.6 CROSS-LINKING

Cross-linking is important because this is a major mechanism for retaining shape, which, in turn, influences the physical properties, such as solubility, of polymers. There are three types of cross-linking present in synthetic and natural polymer. Two of the three types are physical and the third is chemical.

Chemical cross-linking is given many names depending on the particular area of application. For instance, for hair, the term "setting" is often associated with the breakage and subsequent reformation of thiol cross-links. For tires, the terms "vulcanization" and "curing" are associated with the formation of sulfur-associated chemical cross-links (Figure 2.19).

Chain entanglement is a physical means of forming cross-links (Figure 2.20). The incidence of chain entanglement is related to both the particular polymer (dependent on such factors as bond angles and substituents) and its length. The longer a polymer is, the more apt that there is one or more chain entanglements. For most linear polymers, chain entanglements occur when chains of 100 units or more are present. Chain entanglements cause the material to act as if its molecular weight is much greater. For instance, if a chain of PE of 100 units is connected to another PE chain of 100 units, which is again connected to another chain of 100 units, the effective chain length is about 300 units.

The third type of cross-linking involves formation of crystalline portions within an amorphous grouping (Figure 2.21). For vinyl polymers, the temperature that allows segmental chain mobility to occur is well below room temperature, but the temperature to disrupt crystalline formations is typically well above room temperature. Within mixtures of crystalline and amorphous structures below the T_m, the crystalline portions act to "tie in" or connect the surrounding areas acting as cross-links.

In some situations, crystalline formation can occur because of addition of physical stress such as the stretching of a rubber band. As the rubber band is stretched, the amorphous random chains become aligned, forming small areas that are crystalline and oppose further stretching. Thus, rubber bands contain chemical cross-links and form crystalline domains on extension (Figure 2.22).

There are a number of consequences to the presence of cross-links. Cross-links impart a material memory to the chains around and those involved with the cross-links that are locked

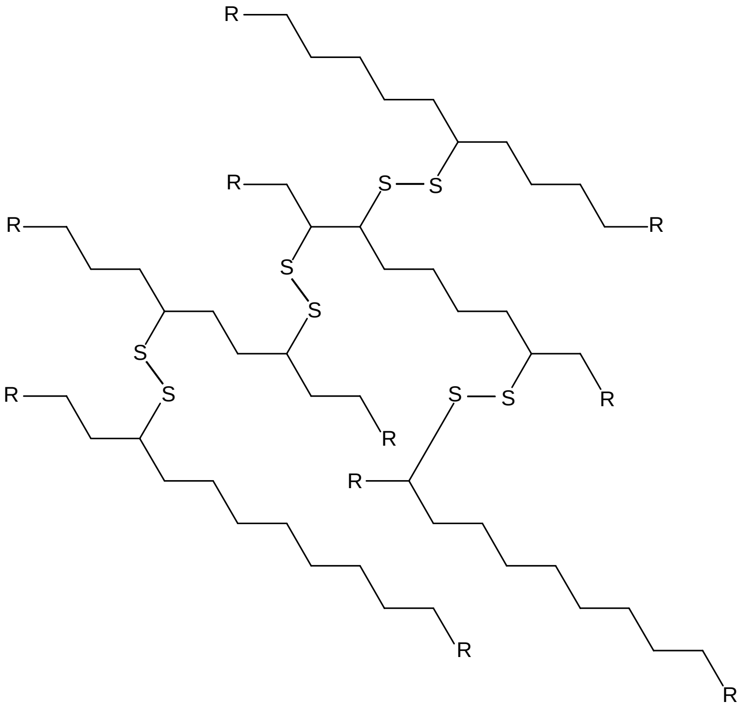


FIGURE 2.19 Chemical cross-linking of polyethylene (PE) chains through formation of disulfide linkages.

into a particular environment. Chemically cross-linked materials are not soluble and do not melt, and are therefore not easily recycled because solubility and melting are often involved in the ready recycling of polymeric materials.

2.7 CRYSTALLINE AND AMORPHOUS COMBINATIONS

Most polymers consist of a combination of crystalline and amorphous regions. Even within polymer crystals such as spherulites (Figures 2.15 through 2.17), the regions between the ordered folded crystalline lamellae are less ordered, approximating amorphous regions.

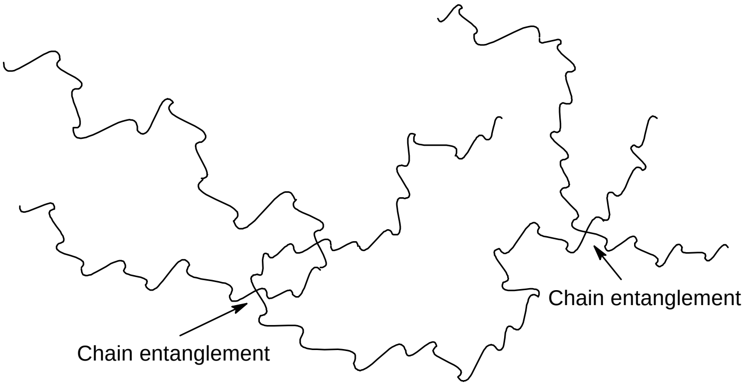


FIGURE 2.20 Physical cross-linking through chain entanglement.

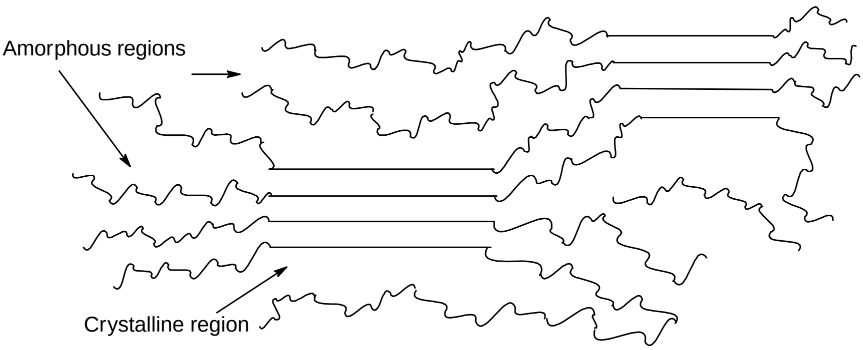


FIGURE 2.21 Crystalline portions that act as physical cross-links.

This combination of crystalline and amorphous regions is important for the formation of materials that have both good strength (contributed largely by the crystalline regions) and some flexibility or "softness" (derived from the amorphous portions). Figure 2.16 contains a space-filled model for PE chains (a total of about 400 units with 5 branches, one longer and four shorter).

This model of PE contains a mixture of amorphous and crystalline regions. Note the cavities within the amorphous regions, with materials containing a majority of amorphous regions having a greater porosity and consequently a greater diffusion and greater susceptibility to chemical and natural attack. As noted before, materials that contain high amounts of the crystalline regions are referred to as being crystalline, are less flexible and stronger, and offer better stability to nature and attack by acids and bases, oils, etc. Also, as noted before, amorphous regions give the material flexibility while the crystalline regions give the material strength. Thus, many materials contain both crystalline and amorphous regions, giving the material a balance between strength and flexibility. The final properties of a material are then dependent on the molecular structure of that material.

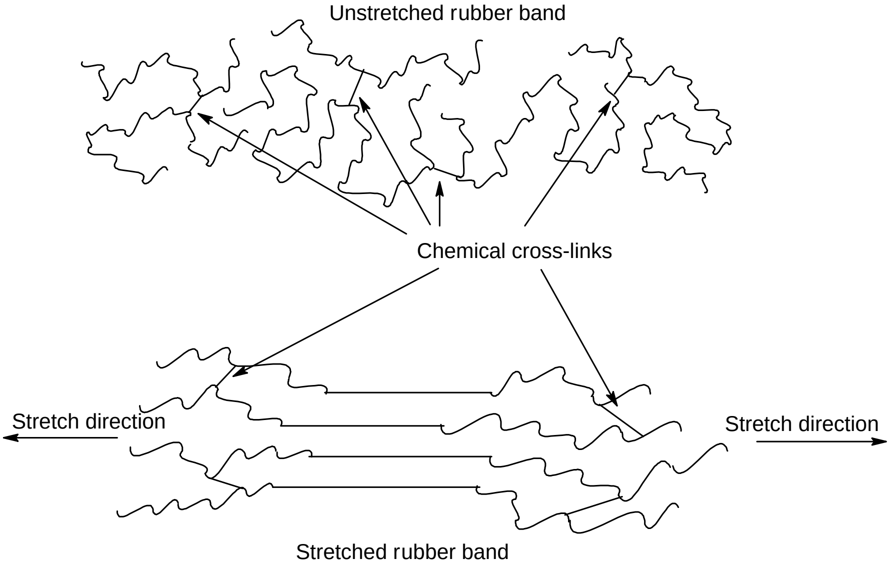


FIGURE 2.22 Chemically cross-linked rubber stretching resulting in the formation of physical crystalline cross-links.

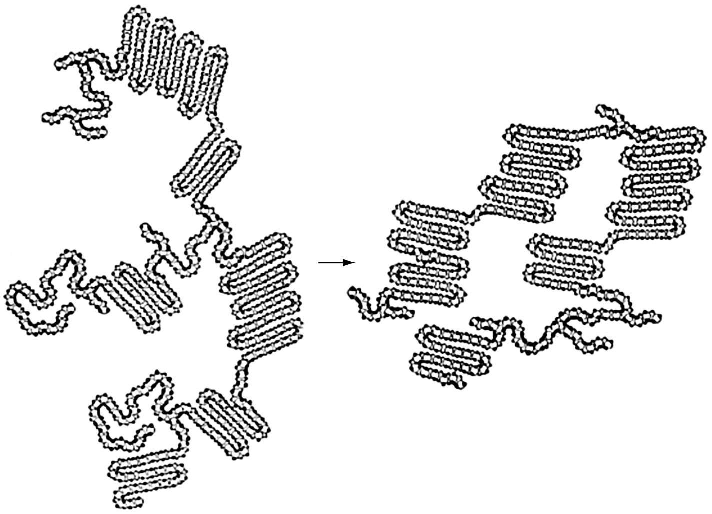


FIGURE 2.23 Idealized structure illustrating crystalline (ordered) and amorphous (nonordered) regions of lightly branched polyethylene (PE) chains for a prestressed and stressed orientation.

Through the use of specific treatment(s) the crystalline and amorphous regions can be largely random to being preferentially oriented in one direction with a greater degree of "crystalline-type" structures when unidirectional stress is applied (Figure 2.23). Here the amount of free space or volume is less, the overall order greater, and properties associated with these changes also changed. The material will be stronger, have a greater ability to resist attack by acids, bases, oils, and other external agents, and the diffusion of gases and other agents through it is would be less. Polymers can be oriented (such as the pulling of fibers or films) in one or two directions. This preferential orientation results in the fiber or film material with anisotropic properties, with the material showing greater strength along the axis of pull.

Figure 2.24 shows the general relationship between material "hardness and softness" and the proportion that is crystalline for largely linear polymers.

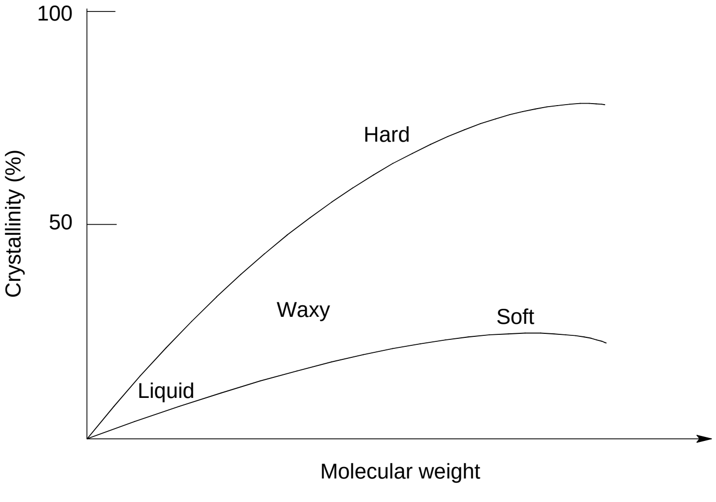


FIGURE 2.24 General physical states of materials as a function of crystallinity and molecular weight.

2.8 SUMMARY

1. Polymers or macromolecules are high molecular weight compounds with chain lengths greater than the critical length required for the entanglement of these chains. There is an abrupt change in melt viscosity and other physical properties of high molecular weight polymers when the chain length exceeds the critical chain length.
2. While some naturally occurring polymers, such as proteins, are monodisperse, i.e., all have the same molecular weight, other natural and synthetic polymers, such as cellulose and PE, are polydisperse, i.e., they consist of a mixture of chains of differing numbers of units. Thus, one uses the term average molecular weight when describing the molecular weight of these polydisperse materials.
3. Many polymers, such as cellulose and HDPE, are linear polymers considering long, continuous, covalently bonded atoms. Others may be branched or cross-linked. Both linear polymers and those with branching are generally thermoplastics that can be remolded by application of heat and pressure. Others that are cross-linked are thermosets that cannot be remolded by application of heat and pressure. Both groups of polymers can be recycled, but it is easier to recycle thermoplastic materials.
4. Functional groups in the polymer backbone, such as the methyl group in PP, are called pendant groups. Such polymers are formed giving a head-to-tail arrangement rather than a head-to-head arrangement.
5. The temperature at which local segmental mobility occurs is called the T_g and that at which wholesale polymer chain mobility occurs is called the T_m.
6. The first-order transition or melting point (T_m) is energywise larger than the T_g. Entirely crystalline polymers will have only a T_m whereas a totally amorphous polymer will have only a T_g. Since most polymers are a combination of amorphous and crystalline regions, they have both a T_g and a T_m.
7. A polymer stretched out to its full contour length is only one of the myriad conformations possible for a polymer at temperatures above T_g, or T_m if the polymer is entirely crystalline. The chain length is expressed statistically as the RMS distance, which is only a fraction of the contour length.
8. Since branched chains like LDPE have many chain ends, it is customary to use the radius of gyration, *S*, as a measure of the distribution of polymer segments. The radius of gyration is the distance of a chain end from the polymer's center of gravity rather than a measure of the RMS. Both measures are statistically related.
9. Fibers and stretched elastomers are translucent because of the presence of ordered crystallites or regions of crystallinity.
10. Crystalline regions of polymers can be represented as combinations of folded chains forming lamellar structures. Amorphous regions are less ordered than crystalline regions. Additional orientation of polymer chains occurs. This results in increased strength in the order of the orientation.
11. The principle differences between elastomers, plastics, and fibers are the presence and absence of stiffening groups, molecular symmetry, and the strength of the intermolecular forces. Elastomers are typically characterized by the absence of stiffening groups, the presence of molecular asymmetry, low amount of crystallinity, and overall absence of strong intermolecular forces. In contrast, fibers are characterized by the presence of stiffening groups, molecular symmetry, high amount of crystallinity, and the presence of strong intermolecular forces. Fibers have a lack of branching and irregularly spaced pendant groups. Plastics have structures and properties that are between elastomers and fibers.
12. There are three types of cross-linking: one is chemical and two physical. Physical cross-linking results from formation of crystalline regions within polymer structures and from chain entanglement. Cross-linked materials have good dimensional memory. Chemically cross-linked materials do not dissolve and do not melt.

GLOSSARY

amorphous Noncrystalline polymer or region in a polymer.

atactic Polymer in which there is a random arrangement of pendant groups on each side of the chain.

backbone Principle chain in a polymer.

branched polymer Polymer having extensions attached to the polymer backbone; not pendant groups.

bulky groups Sterically large groups.

chiral center Asymmetric center such as a carbon atom with four different groups attached to it.

cold drawing Stretching a fiber under room temperature.

configurations Related chemical structures produced by the breaking and remaking of primary covalent bonds.

conformations Various shapes of polymer chains resulting from the rotation around single bonds in the polymer chain.

conformer Shape produced by a change in the conformation of a polymer.

contour length Fully extended length of a polymer chain; equal to the product of the length of a repeat unit times the number of units, or mers.

critical chain length (z) Minimum chain length required for entanglement of polymer chains.

cross-linked density Measure of the relative degree of cross-linking.

crystalline polymer Polymer with ordered structure.

crystallites Regions of crystallinity.

degree of polymerization (DP) Number of repeat units in a chain.

dipole–dipole interactions Moderate secondary forces between polar groups in different or the same polymer chain.

dispersion forces Low-energy secondary forces due to the creation of momentary induced dipoles; also known as London forces.

glass transition temperature (T_g) Temperature range where a polymer gains local or segmental mobility.

glassy state Hard, brittle state; below T_g.

gutta percha Naturally occurring *trans* isomer of polyisoprene.

head-to-tail configuration Normal sequence of mers in which the pendant groups are regularly spaced; for poly(vinyl chloride), PVC, the chlorine atom appears on every other carbon.

intermolecular forces Secondary forces between different molecules.

intramolecular forces Secondary forces within the same molecule.

isotactic Polymer in which the geometry of the pendant groups are all on the same side of the polymer backbone.

lamellar Platelike, or planar (flat), in shape.

linear polymer Polymer with or without chains extending off the backbone.

low-density polyethylene (LDPE) A branched form of PE produced at high pressure by the free-radical-initiated polymerization of ethylene.

maltese cross Cross with arms like arrowheads pointing inward.

melting point (T_m) First-order transition when the solid and liquid phases are in equilibrium.

mer Repeat unit.

modulus Ratio of stress to strain which is a measure of the stiffness of a polymer.

monodisperse Polymer mixture made up of molecules of one specific molecular weight.

pendant groups Groups attached to the main polymer backbone, like methyl groups in PP.

polydisperse Polymer mixture containing chains of varying lengths.

radius of gyration (S) Root-mean-square (RMS) distance of a chain end to a polymer's center of gravity.

root-mean-square (RMS) distance $[(r^2)^{1/2}]$ Average end-to-end distance of polymer chains; $l(n^{1/2})$.

side chain crystallization Crystallization related to that of regularly spaced long pendant groups.

single polymer crystals Lamellar structure consisting of folded chains of a linear polymer.

spherulites Three-dimensional aggregates of polymer crystallites.

stiffening groups Groups in a polymer backbone that decrease the segmental motion of the polymer chain.

syndiotactic Polymer in which the pendant groups are arranged alternately on each side of the carbon backbone.

tacticity Arrangement of the pendant groups in space; i.e., isotactic, syndotactic, atactic.
van der Waals forces Secondary forces based on the attraction between groups.
viscosity Measure of the resistance of a polymer or polymer solution to flow.

EXERCISES

(*To answer some of these questions you may need to look at other parts in the book for structures and specific details.*)

1. Make sketches or diagrams showing (a) a linear polymer, (b) a polymer with pendant groups, (c) a polymer with short branches, (d) a polymer with long branches, and cross-linked polymers with (e) low and (f) high cross-linked density.
2. Which has (a) the greater volume for the same weight of material and (b) the lower softening point: HDPE or LDPE?
3. What is the approximate bond length of the carbon atoms in (a) a linear and (b) a cross-linked polymer?
4. What is the approximate contour length of an HDPE chain with an average DP (chain length) of $n = 2000$ and of a PVC chain of the same number of repeating units?
5. Which of the following are monodisperse polymers with respect to chain length? (a) hevea rubber, (b) corn starch, (c) cellulose from cotton, (d) an enzyme, (e) HDPE, (f) PVC, (g) a specific DNA, (h) nylon 6,6, or (i) a specific RNA?
6. What is the average DP of LDPE having an average molecular weight of 28,000?
7. What is the structure of the repeating unit in (a) PP, (b) PVC, and (c) hevea rubber?
8. Which of the following is a branched chain polymer: (a) HDPE, (b) iPP, (c) LDPE, or (d) amylose starch?
9. Which of the following is a thermoplastic: (a) ebonite, (b) Bakelite, (c) vulcanized rubber, (d) HDPE, (e) celluloid, (f) PVC, or (g) LDPE?
10. Which has the higher cross-linked density: (a) ebonite or (b) soft vulcanized rubber?
11. Do HDPE and LDPE differ in (a) configuration and (b) conformation?
12. Which is a *trans* isomer: (a) gutta percha or (b) hevea rubber?
13. Which will have the higher softening point: (a) gutta percha or (b) hevea rubber?
14. Show (a) a head-to-tail and (b) a head-to-head configuration for PVC.
15. Show the structure of a typical portion of the chain of (a) s-PVC and (b) i-PVC.
16. Show Newman projections of the gauche forms of HDPE.
17. Name polymers whose intermolecular forces are principally (a) London forces, (b) dipole–dipole forces, and (c) hydrogen bonding.
18. Which will be more flexible: (a) poly(ethylene terephthate) or (b) poly(butylene terephthalate)?
19. Which will have the higher glass transition temperature: (a) poly(methylene methacrylate) or (b) poly(butyl methacrylate)?
20. Which will have the higher T_g: (a) iPP or (b) aPP?
21. Which will be more permeable to a gas at room temperature: (a) iPP or (b) aPP?
22. Under what kind of physical conditions are you more apt to form spherulites?
23. What is the full contour length of a molecule of HDPE with a DP of 1500?
24. Which would be more flexible: (a) poly(methyl acrylate) or (b) poly(methyl methacrylate)?
25. Which would you expect to form ‘‘better’’ helical structures: (a) iPP or (b) aPP?
26. Which would you expect to have a higher melting point: (a) nylon-6,6 or (b) an aramide?
27. What type of hydrogen bonds are present in the internal structure of a globular protein?
28. Which would have the greater tendency to ‘‘cold flow’’ at room temperature: (a) PVAc ($T_g = 301$ K) or (b) PS ($T_g = 375$ K)?
29. Which would be least transparent: (a) a combination of amorphous and crystalline PS, (b) entirely crystalline PS, or (c) entirely amorphous PS?
30. Which would be more apt to produce crystallites: (a) HDPE or (b) poly(butyl methacrylate)?
31. Which of the following would you expect to provide strong fibers: (a) nylon-6,6, (b) aPP, or (c) wool.

32. Which would tend to be more crystalline when stretched: (a) unvulcanized rubber or (b) ebonite?
33. Which would be more apt to exhibit side chain crystallization: (a) poly(methyl methacrylate) or (b) poly(dodecyl methacrylate)?

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3 Molecular Weight of Polymers

3.1 INTRODUCTION

The size of macromolecules gives them their unique and useful properties. Size allows polymers to act more as a group so that when one polymer chain moves, surrounding chains are affected by that movement. Size also allows polymers to be nonvolatile since the secondary attractive forces are cumulative (e.g., the London dispersion forces are about 8 kJ/mol of repeat units), and, because of the shear size, the energy necessary to volatilize them is greater than the energy to degrade the polymer.

Generally, the larger the polymer is, the higher is the molecular weight. The average molecular weight ($\overline{M}$) of a polymer is the product of the average number of repeat units or mers expressed as the DP times the molecular weight for the repeating unit. Thus, for PE with a DP of 100 the average molecular weight is simply 100 units times 28 Da/unit = 2800 Da. Note, that atomic mass unit (amu) and dalton (Da) are often used interchangeably as units.

Polymerization reactions, which produce both synthetic and natural (but not for all natural materials such as proteins and nucleic acids) polymers, lead to products with heterogeneous molecular weights, i.e., polymer chains with different numbers of mers. Molecular weight distributions (MWDs) may be rather broad (Figure 3.1), or relatively narrow, or may be mono-, bi-, tri-, or polymodal. A bimodal curve is often characteristic of a polymerization occurring under two different environments. Polymers consisting of chains of differing lengths are called polydisperse while polymers containing only one chain length, such as specific nucleic acids, are called monodisperse.

Some properties, such as heat capacity, refractive index, and density, are not particularly sensitive to molecular weight but many important properties are related to chain length. Figure 3.2 lists three of these. The melt viscosity is typically proportional to the 3.4 power of the average chain length; so η is proportional to $M^{3.4}$. Thus, the melt viscosity increases rapidly as the chain length increases and more energy is required for the processing and fabrication of large molecules. This is due to chain entanglements that occur at higher chain lengths. However, there is a trade-off between molecular weight related properties and chain size such that there is a range where acceptable physical properties are present but the energy required to cause the polymers to flow is acceptable. This range is called the commercial polymer range. Many physical properties, such as tensile and impact strength (Figure 3.2), tend to level off at some point, and increased chain lengths give little increase in that physical property. Most commercial polymer ranges include the beginning of this leveling off threshold.

While a value above the threshold molecular weight value (TMWV; lowest molecular weight where the desired property value is achieved) is essential for most practical applications, the additional cost of energy required for processing extremely high polymer molecular weights is seldom justified. Accordingly, it is customary to establish a commercial polymer range above the TMWV but below the extremely high molecular weight range. However, it should be noted that some properties, such as toughness, increase with chain length. Thus,

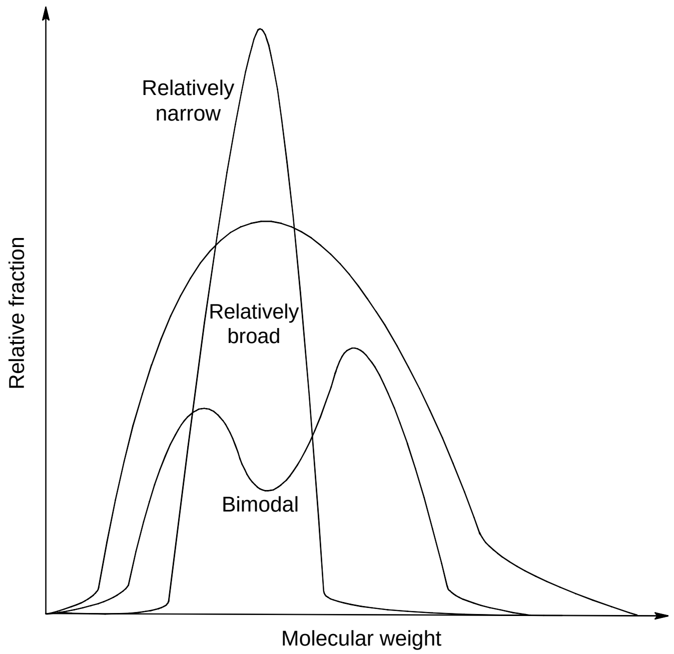

FIGURE 3.1 Relative differential weight distribution curves.

extremely high molecular weight polymers, such as UHMWPE, are used for the production of tough articles such as waste barrels.

Oligomers and other low molecular weight polymers are not useful for applications where high strength is required. The word oligomer is derived from the Greek *oligos*, meaning "a few."

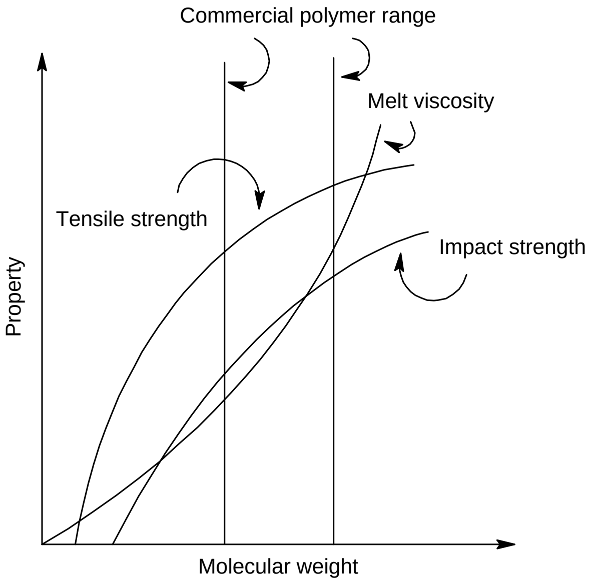

FIGURE 3.2 Relationship between molecular weight and polymer physical properties.

The value of TMWV is dependent on the cohesive energy density (CED) of amorphous polymers, the extent of crystallinity in crystalline polymers, and the effect of reinforcements in polymeric composites. Thus, while a low molecular weight amorphous polymer may be satisfactory for use as a coating or adhesive, a chain length generally above 100 is often required if the polymer is to be used as an elastomer or plastic.

3.2 SOLUBILITY

Polymer mobility is an important aspect to help determine a polymer's physical, chemical, and biological behavior. Lack of mobility, either because of interactions that are too swift to allow the segments within the polymer chain some movement or because there is not sufficient energy (such as a high enough temperature) available to create mobility, results in a brittle material. Many processing techniques require the polymer to have some mobility. This mobility can be achieved through application of heat and/or pressure and through dissolving the polymer. Because of its size, the usual driving force for the mixing and dissolving of materials (entropy) is smaller for polymers in comparison to small molecules. Traditional molecular weight determinations require that the polymer be dissolved. Here, we will focus on the general topic of polymer solubility and factors that influence polymer solubility.

The first attempts at predicting solubility were largely empirical. Paint technologists employed various approaches. In one approach kauri-butanol values were equal to the minimum volume of test solvent that produced turbidity when added to a standard solution of kauri-copal resin in 1-butanol. The aniline point is the lowest temperature where equal volumes of aniline and the test solvent are completely miscible. Both tests are measures of the relative aromaticity of the test solvent.

Mixing can be described in terms of free energy. Free energy has two terms: one related to energy and the other related to order/disorder. The energy-related term is called enthalpy, H, and the order/disorder term is called entropy, S.

In order for mixing and solution to occur, it is essential that the change in free energy, ΔG, which is the driving force in the solution process, decrease to below zero. ΔH and ΔS are equal to the change in enthalpy and change in entropy, and for constant temperature the relationship is the classical Gibbs equation:

$$\Delta G = \Delta H - T\Delta S \tag{3.1}$$

The saying "like likes like the best" reflects the tendency for like molecules to remain together. The energy term works against mixing and solution occurring since it requires a net amount of energy to disrupt the attractive energies of like molecules necessary for mixing and solution to occur. Thus, it is the entropy term that is the driving force for mixing and solubility that is occurring. In general, changes in entropy are greater for the mixing and solubility of smaller molecules because there are a greater number of possible arrangements for smaller molecules that result in a high entropy or randomness when small molecules are involved in the solubility and mixing process. When polymers are involved, the change in entropy is less because the number of arrangements of polymer chains is less than the possible arrangements if the single mer units (small molecules) were involved. This results in (1) polymers generally being soluble in, or miscible with, fewer solvents; and (2) the extent of solubility and mixing generally being less for polymers in comparison with similar smaller molecules.

There have been many attempts to describe the process of mixing and solubility of polymer molecules in thermodynamic terms. By assuming that the sizes of polymer segments are similar to those of solvent molecules, Flory and Huggins derived an expression for the partial molar Gibbs free energy of dilution that included the dimensionless Flory–Higgins interaction parameter $X_1 = Z\Delta H/RT$, where Z is the lattice coordination number. It is now known that X_1 contains enthalpy and entropy contributions. The Flory–Higgins approach has been used to predict the equilibrium behavior between liquid phases containing an amorphous polymer. The theory has also been used to predict the cloud point which is just below the critical solution temperature T_c where two phases coalesce. The Flory–Higgins interaction parameter has been used as a measure of solvent power. In general, the value of X_1 is 0.5 for poor solvents and decreases for good solvents.

Some limitations of the Flory–Higgins lattice theory were overcome by Flory and Krigbaum who assumed the presence of an excluded volume. The excluded volume is the volume occupied by a polymer chain including long-range intramolecular interactions. The long-range interactions were described in terms of free energy by introducing the enthalpy term K_i and entropy term ψ_1. The entropy and enthalpy terms are equal when $\Delta G = 0$. The temperature at which $\Delta G = 0$ is called the theta (θ) temperature. The theta temperature is the lowest temperature at which a polymer of infinite molecular weight is completely miscible with a specific solvent. The coil expands above the theta temperature and contracts at lower temperatures.

Physical properties of polymers, including solubility, are related to the strength of covalent bonds, stiffness of the segments in the polymer backbone, amount of crystallinity or amorphousness, and intermolecular forces between the polymer chains. The strength of the intermolecular forces is directly related to the CED, which is the molar energy of vaporization per unit volume. Since intermolecular attractions of solvent and solute must be overcome when a solute (here the polymer) dissolves, CED values may be used to predict solubility.

When a polymer dissolves, the first step is often a slow swelling process called solvation, in which the polymer molecules swell by a factor δ, which is related to CED. Linear and branched polymers dissolve in a second step, but network polymers remain in a swollen condition. In the dissolving process, external polymers are initially "dissolved," exposing additional polymer chains to the solvent, eventually resulting in the entire polymer mass being dissolved. Thus, polymer solubility often takes considerably longer than the solubility of smaller molecules.

As early as 1926, Hildebrand showed a relationship between solubility and the internal pressure of the solvent, and in 1931 Scatchard incorporated the CED concept into Hildebrand's equation. This led to the concept of a solubility parameter, δ, which is the square root of CED. Thus, as shown below, the solubility parameter δ for nonpolar solvents is equal to the square root of the heat of vaporization per unit volume:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} = (\mathrm{CED})^{1/2} \text{ or } \delta^2 = \mathrm{CED} \tag{3.2}$$

According to Hildebrand, the heat of mixing a solute and a solvent is proportional to the square of the difference in solubility parameters, where ϕ is the partial volume of each component, namely solvent γ_1 and solute ϕ_2. Since typically the entropy term favors solution and the enthalpy term acts counter to solution, the objective is to match solvent and solute so that the difference between their δ values is small, resulting in a small enthalpy acting against solubility:

$$\Delta H_m = \phi_1 \, \phi_2 \, (\delta_1 - \delta_2)^2 \tag{3.3}$$

The solubility parameter concept predicts the heat of mixing liquids and amorphous polymers. It has been experimentally found that generally any nonpolar amorphous polymer will dissolve in a liquid or mixture of liquids having a solubility parameter that generally does not differ by more than $\pm 1.8\ (\mathrm{cal/cc})^{1/2}$. The Hildebrand (H) is preferred over these complex units, giving as a general difference ±1.8 H.

The solubility parameter concept is based on obtaining a negative Gibbs' free energy. Thus, as ΔH_m approaches zero, ΔG will have the negative value required for solution to occur because the entropy term favors solution occurring. As noted before, the entropy (S) increases in the solution process, hence the emphasis is on achieving low values of ΔH_m.

For nonpolar solvents, which were called regular solvents by Hildebrand, the solubility parameter is equal to the square root of the difference between the enthalpy of evaporation (H_v) and the product of the ideal gas constant (R) and the Kelvin (or Absolute) temperature (T) divided by the molar volume (V), as shown in the following equation:

$$\delta = \left(\frac{\Delta E}{V}\right)^{1/2} = \left(\Delta H_v - \frac{RT}{V}\right)^{1/2} \tag{3.4}$$

Since it is difficult to measure the molar volume, its equivalent, the molecular weight (M) divided by density (D), is substituted for V as shown in the following equation:

$$\delta = D\left(\Delta H_v - \frac{RT}{M}\right)^{1/2} \tag{3.5}$$

Because the law of mixtures applies to the solubility parameter, it is possible to easily calculate the solubility parameter of blended liquids forming mixtures that can serve as solvents. For example, an equal molar mixture of *n*-pentane ($\delta = 7.1$ H) and *n*-octane ($\delta = 7.6$ H) will have a solubility parameter value of 7.35 H (simply $(7.1 + 7.6)/2$).

The solubility parameter of a polymer is generally determined by noting the extent of swelling or actual solution of small amounts of polymer in a series of solvents, comparing the solubility values of the ones that swell or dissolve the polymer, and assigning the polymer a solubility parameter value that is close to the solvents that dissolve or swell it. The solubility parameter can also be determined by adding a nonsolvent to a polymer solution and noting the amount of nonsolvent needed to begin to precipitate the polymers.

Since polar forces are present in polar solvents and polar molecules, this must be considered when estimating solubilities with such "nonregular" solvents and polymers. Hydrogen bonding, a special case of secondary polar bonding, is also important for some solvents and polymers and again will influence the solubility parameters. Thus, special solubility values have been developed for polar and hydrogen-bonding solvents (Tables 3.1 and 3.2).

Plasticizers help the flexibility of polymers and are chosen so that they do not dissolve the polymer but rather allow segmental mobility. Through experience, it is found that the solubility parameter differences between the plasticizer and polymer should be less than 1.8 H for there to be compatibility between the plasticizer and polymer.

Because the heat of vaporization of a polymer is not readily obtained, Small determined values for various components of a polymer chain to calculate the solubility parameter. These values are called molar attraction constants and are additive and have been used for estimation of the solubility parameter for nonpolar polymers. In this approach $\delta = D\Sigma G/M$, where D is density, G are the Small molar attraction constants, and M is the molecular weight of the particular repeat unit. As expected, the more polar units have greater G values while the less polar units have smaller G values.

3.3 AVERAGE MOLECULAR WEIGHT VALUES

Small molecules, such as benzene and glucose, have precise structures, such that each molecule of benzene has six carbon atoms and six hydrogen atoms. By comparison,

TABLE 3.1
Solubility Parameters (δ) for Typical Solvents

Poor Hydrogen Bonding		**Moderate Hydrogen Bonding**		**Strong Hydrogen Bonding**	
Dimethylsiloxane	5.5	Diisopropylether	6.9	Diethylamine	8.0
Difluorodichloromethane	5.5	Diethylether	7.4	*n*-Amylamine	8.7
Neopentane	6.3	Isoamyl acetate	7.8	2-Ethylhexanol	9.5
Nitro-*n*-octane	7.0	Diisobutyl ketone	7.8	Isoamyl alcohol	10.0
n-Pentane	7.0	Di-*n*-propylether	7.8	Acetic acid	10.1
n-Octane	7.6	*sec*-Butyl acetate	8.2	*m*-Cresol	10.2
Turpentine	8.1	Isopropyl acetate	8.4	Analine	10.3
Cyclohexane	8.2	Methylamyl ketone	8.5	*n*-Octyl alcohol	10.3
Cymene	8.2	Ethyl acetate	9.0	*t*-Butyl alcohol	10.9
Carbon tetrachloride	8.6	Methyl ethyl ketone	9.3	*n*-Amyl alcohol	10.9
n-Propylbenzene	8.6	Butyl cellosolve	9.5	*n*-Butyl alcohol	11.4
p-Chlorotoluene	8.8	Methyl acetate	9.6	Isopropyl alcohol	11.5
Decalin	8.8	Dichloroethylether	9.8	Diethylene glycol	12.1
Xylene	8.8	Acetone	9.9	Furfuryl alcohol	12.5
Benzene	9.2	Dioxane	10.0	Ethanol	12.7
Styrene	9.3	Cyclopentanone	10.4	*n*-Ethylformamide	13.9
Tetraline	9.4	Cellosolve	10.5	Methanol	14.5
Chlorobenzene	9.5	*n*,*n*-Dimethylacetamide	10.8	Ethylene glycol	14.6
Ethylene dichloride	9.8	1,2-Propylene carbonate	13.3	Glycerol	16.5
p-Dichlorobenzene	10.0	Ethylene carbonate	14.7	Water	23.4
Nitroethane	11.1				
Acetronitrile	11.9				
Nitroethane	12.7				

each molecule of poly-1,4-phenylene may have a differing number of phenylene-derived units, while single molecules (single chains) of PE may vary in the number of ethylene units, the extent and frequency of branching, the distribution of branching, and the length of branching. A few polymers, such as nucleic acids and many proteins, consist of molecules, individual polymer chains that must not vary, so they have a precise molecular weight.

While there are several statistically described averages, we will concentrate on the two that are most germane to polymers—number average and weight average. These are averages based on statistical approaches that can be described mathematically and that correspond to measurements of specific values.

The number average value, corresponding to a measure of chain length average, is called the number-average molecular weight $\overline{M}_n$. Physically, the number-average molecular weight can be measured using any technique that "counts" the molecules, or that is directly dependent on the number of chains. These techniques include vapor phase and membrane osmometry, freezing point lowering, boiling point elevation, and end-group analysis.

We can describe the number average using a jar filled with plastic capsules such as those used to contain tiny prizes (Figure 3.3). Here, each capsule contains one polymer chain. All the capsules are of the same size, regardless of the size of the polymer chain. Capsules are then withdrawn, opened, and the individual chain length measured and recorded. A graph such as shown in Figure 3.4 can be constructed from the data, with the maximum value being the number-average molecular weight. The probability of drawing a particular capsule is dependent on the number of each capsule and not on the size of the chain within the capsule.

TABLE 3.2
Approximate Solubility Parameter Values for Polymers

Polymer	Poor Hydrogen Bonding	Moderate Hydrogen Bonding	Strong Hydrogen Bonding
Polytetrafluoroethylene	5.8–6.4		
Poly(vinyl ethyl ether)	7.0–11.0	7.4–10.8	9.5–14.0
Poly(butyl acrylate)	7.0–12.5	7.4–11.5	
Poly(butyl methacrylate)	7.4–11.0	7.4–10.0	9.5–11.2
Polyisobutylene	7.5–8.0		
Polyethylene	7.7–8.2		
Poly(vinyl butyl ether)	7.8–10.6	7.5–10.0	9.5–11.2
Natural rubber	8.1–8.5		
Polystyrene	8.5–10.6	9.1–9.4	
Poly(vinyl acetate)	8.5–9.5		
Poly(vinyl chloride)	8.5–11.0	7.8–10.5	
Buna N	8.7–9.3		
Poly(methyl methacrylate)	8.9–12.7	8.5–13.3	
Poly(ethylene oxide)	8.9–12.7	8.5–14.5	9.5–14.5
Poly(ethylene sulfide)	9.0–10.0		
Polycarbonate	9.5–10.6	9.5–10.0	
Poly(ethylene terephthate)	9.5–10.8	9.3–9.9	
Polyurethane	9.8–10.3		
Polymethacrylonitrile		10.6–11.0	
Cellulose acetate	11.1–12.5	10.0–14.5	
Nitrocellulose	11.1–12.5	8.0–14.5	12.5–14.5
Polyacrylonitrile		12.0–14.0	
Poly(vinyl alcohol)			12.0–13.0
Nylon-6,6			13.5–15.0
Cellulose			14.5–16.5

The weight-average molecular weight is similarly described, except that the capsule size corresponds to the size of polymer chain contained within it (Figure 3.5). In this approach, the probability of drawing out a particular chain length is dependent on the size of the capsule. Larger chains have a greater probability (at least in this exercise) of being drawn

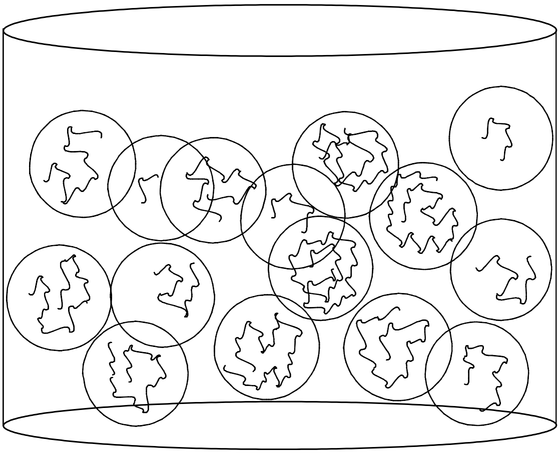

FIGURE 3.3 Jar with capsules, each capsule containing a single polymer chain where the capsule size is the same and independent of the chain size, illustrating the number-average dependence on molecular weight.

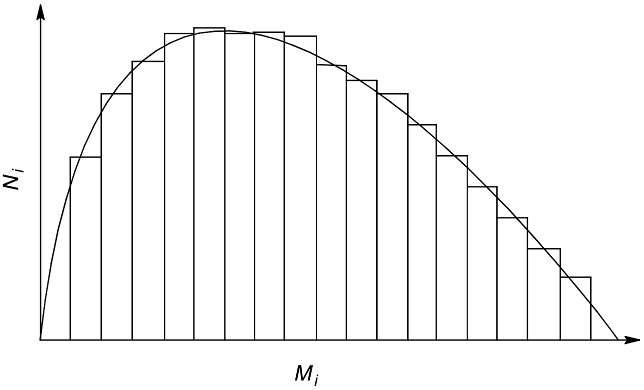

FIGURE 3.4 Molecular weight distribution (MWD) for a polydisperse polymer sample constructed from "capsule-derived" data.

out because they are larger and are contained within larger capsules. Again, a graph is constructed and the maximum value is the weight-average molecular weight.

Several mathematical moments (about a mean) can be described using differential or frequency distribution curves, which can be described by equations. The first moment is the number-average molecular weight $\overline{M}_n$. Any measurement that leads to the number of molecules, functional groups, end groups, or particles that are present in a given weight of sample allows the calculation of $\overline{M}_n$. The value of $\overline{M}_n$ is calculated like any other numerical average by dividing the sum of the individual molecular weight values by the number of molecules. Thus, $\overline{M}_n$ for three molecules having molecular weights of 1×10^5, 2×10^5, and 3×10^5 is $(6 \times 10^5)/3 = 2 \times 10^5$. The general solution is shown mathematically as:

$$\overline{M}_n = \frac{\text{total weight of sample}}{\text{number of molecules of } N_i} = \frac{W}{\Sigma N_i} = \frac{\Sigma M_i N_i}{\Sigma N_i} \tag{3.6}$$

Most thermodynamic properties are related to the number of particles present and are thus dependent on $\overline{M}_n$.

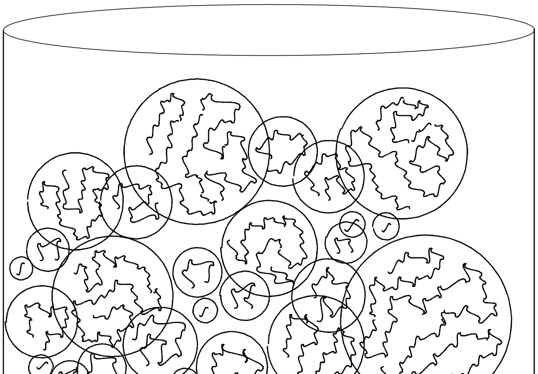

FIGURE 3.5 Jar with capsules, each containing a single polymer chain where the capsule size is directly related to the size of the polymer chain within the capsule.

Colligative properties are dependent on the number of particles present and are thus related to $\overline{M}_n$. $\overline{M}_n$ values are independent of molecular size and are highly sensitive to small molecules present in the mixture. Values of $\overline{M}_n$ are determined by Raoult's techniques, which are dependent on colligative properties such as ebulliometry (boiling point elevation), cryometry (freezing point depression), osmometry, and end-group analysis.

Weight-average molecular weight $\overline{M}_w$ is determined from experiments in which each molecule or chain makes a contribution to the measured result relative to its size. This average is more dependent on the number of longer chains than is the number-average molecular weight, which is dependent simply on the total number of each chain.

The $\overline{M}_w$ is the second moment average and is shown mathematically as:

$$\overline{M}_w = \frac{\Sigma M_i^2 N_i}{\Sigma M_i N_i} \tag{3.7}$$

Thus, the $\overline{M}_w$ of the three chains cited before is:

$$\frac{(1 \times 10^{10}) + (4 \times 10^{10}) + (9 \times 10^{10})}{6 \times 10^5} = 2.23 \times 10^5$$

Bulk properties associated with large deformations, such as viscosity and toughness, are most closely associated with $\overline{M}_w$. The values of $\overline{M}_w$ are most often determined by light-scattering photometry.

However, melt elasticity is more closely related to the third moment known as the z-average molecular weight $\overline{M}_z$. The values of $\overline{M}_z$ are most often determined using either light-scattering photometry or ultracentrifugation. It is shown mathematically as:

$$\overline{M}_z = \frac{\Sigma\, M_i^3 N_i}{\Sigma\, M_i^2 N_i} \tag{3.8}$$

The $\overline{M}_z$ value for the three polymer chains cited above is:

$$\frac{(1 \times 10^{15}) + (8 \times 10^{15}) + (27 \times 10^{15})}{(1 \times 10^{10}) + (4 \times 10^{10}) + (9 \times 10^{10})} = 2.57 \times 10^5$$

While $z + 1$ and higher average molecular weight values can be calculated, the major interests are in $\overline{M}_n$, $\overline{M}_v$, $\overline{M}_w$, and $\overline{M}_z$, which is the order of increasing size for a heterodisperse polymer sample as shown in Figure 3.6. Thus, for heterogeneous molecular weight systems $\overline{M}_z > \overline{M}_w > \overline{M}_n$. The ratio of $\overline{M}_w/\overline{M}_n$ is called the polydispersity index. The most probable polydispersity index for polymers produced by the condensation technique with respect to molecular weight is 2. As the heterogeneity decreases, the various molecular weight values converge until $\overline{M}_z = \overline{M}_w = \overline{M}_n$.

Typical techniques for determining molecular weight are given in Table 3.3. The most popular techniques will be considered briefly. All classical molecular weight techniques require dilute solutions, generally 0.01 g/mL or 1% (1 g/100 mL) solutions. To further minimize solute interactions, extrapolation of the measurements to infinite dilution is normal practice.

For polydisperse polymer samples, measurements that lead directly to the determination of the molecular weight, such as light-scattering photometry and membrane osmometry, are referred to as "absolute molecular weight" methods. Techniques such as viscometry are not absolute molecular weight methods because they require calibration using an absolute molecular weight technique.

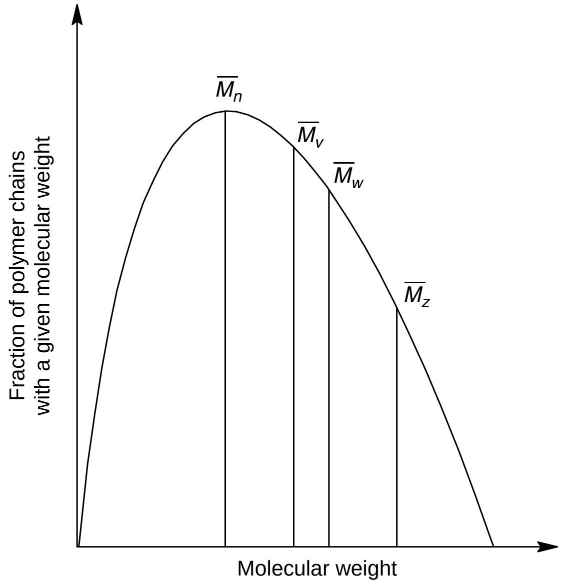

FIGURE 3.6 Molecular weight distributions (MWDs).

TABLE 3.3
Typical Molecular Weight Determination Methods[a]

Method	Type of Molecular Weight Average	Applicable Weight Range	Other Information
Light scattering	M_w	To ∞	Can give other molecular weights and shape
Membrane osmometry	M_n	10^4-10^6	
Vapor phase osmometry	M_n	To 4×10^4	
Electron and x-ray microscopy	M_n, M_w, M_z	10^2 to ∞	
Isopiestic method	M_n	To 2×10^4	
Ebulliometry (BP elevation)	M_n	To 4×10^4	
Cryoscopy (MP depression)	M_n	To 5×10^4	
End-group analysis	M_n	To 2×10^4	
Osmodialysis	M_n	$500-2.5 \times 10^4$	
Centrifugation			
Sedimentation equilibrium	M_z	To ∞	
Archibald model	M_z, M_w	To ∞	
Trautman's method	M_w	To ∞	
Sedimentation velocity gives real M for only monodisperse systems			
Chromatography	Calibrated	To ∞	Gives molecular weight distribution
SAXS	M_w		
MALDI MS		To 10^7	Molecular weight distribution
Viscometry	Calibrated		
Coupled chromatography—LS		To ∞	Molecular weight distribution, shape, M_n, M_w, M_z

[a] "To ∞" means that the molecular weight of the largest particles soluble in a suitable solvent can be, in theory, determined.

3.4 FRACTIONATION OF POLYDISPERSE SYSTEMS

The data plotted in Figure 3.6 were obtained by the fractionation of a polydisperse polymer sample. Polydisperse polymers can be fractionated by a number of techniques. The most widely used technique is chromatography. Other methods include addition of a nonsolvent to a polymer solution, cooling a polymer solution, solvent evaporation, extraction, diffusion, and centrifugation. The molecular weight of the fractions may be determined using any of the classic techniques given in Table 3.3.

Fractional precipitation is dependent on the slight change in the solubility with molecular weight. When a small amount of miscible nonsolvent is added to a polymer solution, the product with the highest molecular weight precipitates first. The procedure is repeated after the precipitate is removed. Molecular weights are run for each fraction and a curve developed that is similar to Figure 3.6.

3.5 CHROMATOGRAPHY

As noted earlier, certain techniques such as colligative methods, light-scattering photometry, special mass spectrometry (MS) techniques, and ultracentrifugation allow the calculation of specific or absolute molecular weights. Under certain conditions some of these also allow the calculation of the MWD.

There are a wide variety of chromatography techniques including paper and column techniques. Chromatographic techniques involve passing a solution containing the to-be-tested sample through a medium that shows selective absorption for the different components in the solution. Ion exchange chromatography separates molecules on the basis of their electrical charge. Ion exchange resins are either polyanions or polycations. For a polycation resin, those particles that are least attracted to the resin will flow more rapidly through the column and be emitted from the column first. This technique is most useful for polymers that contain changed moieties.

In affinity chromatography, the resin contains especially selected molecules that will interact with the particular polymer(s) that is being studied. Thus, for a particular protein, the resin may be modified to contain a molecule that interacts with that protein type. The solution containing the mixture is passed through the column and the modified resin preferentially associates with the desired protein, allowing it to be preferentially removed from the solution. Later, the protein is washed through the column by addition of a salt solution and collected for further evaluation.

In high-performance liquid chromatography (HPLC) pressure is applied to the column that causes the solution to rapidly pass through it, allowing procedures to be completed in a fraction of the time in comparison to regular chromatography.

When an electric field is applied to a solution, polymers containing a charge will move toward either the cathode (positively charged species) or toward the anode (negatively charged species). This migration is called electrophoresis. The velocity at which molecules move is mainly dependent upon the electric field and change on the polymer driving the molecule toward one of the electrodes, and a frictional force dependent on the size and structure of the macromolecule that opposes the movement. In general, the larger and more bulky the macromolecule, the greater the resistance to movement, and the greater the applied field and charge on the molecule, the more rapid the movement. While electrophoresis can be conducted on solutions, it is customary to use a supporting medium of a paper or gel. For a given system, it is possible to calibrate the rate of flow with the molecular weight and/or size of the molecule. Here, the flow characteristics of the calibration material must be similar to those of the unknown.

Generally, though, electrophoresis is often employed in the separation of complex molecules such as proteins, where the primary factor in the separation is the charge on the species.

Some amino acids such as aspartic acid and glutamic acid contain an "additional" acid functional group, while amino acids such as lysine, arginine, and histidine contain "additional" basic groups. The presence of these units will confer to the protein tendencies to move toward the anode or cathode. The rate of movement is dependent on a number of factors including the relative abundance and accessibility of these acid and base functional groups.

Figure 3.7 contains an illustration of the basic components of a typical electrophoresis apparatus. The troughs at either end contain an electrolyte buffer solution. The sample to be separated is placed in the approximate center of the electrophoresis strip.

Gel permeation chromatography (GPC) is based on separation by molecular size rather than by chemical properties. GPC or size exclusion chromatography (SEC) is widely used for molecular weight and MWD determination. In itself, SEC does not give an absolute molecular weight and must be calibrated against polymer samples whose molecular weight has been determined by a technique that does give an absolute molecular weight.

SEC is an HPLC technique whereby the polymer chains are separated according to differences in hydrodynamic volume. This separation is made possible by use of special packing material in the column. The packing material is usually polymeric porous spheres often composed of PS cross-linked by addition of varying amounts of divinylbenzene. Retention in the column is mainly governed by the partitioning (or exchanging) of polymer chains between the mobile (or eluent) phase flowing through the column and the stagnate liquid phase that is present in the interior of the packing material. The column packing is almost spherical. In reality, the packing material has various clefts that ensnare the passing polymer chains such that the progress of smaller chains down the column is preferentially slowed (Figure 3.8).

Through control of the amount of cross-linking, nature of the packing material, and specific processing procedures, spheres of widely varying porosity are available. The motion in and out of the stationary phase depends on a number of factors including Brownian motion, chain size, and conformation. The latter two are related to the polymer chain's hydrodynamic volume—the real, excluded volume occupied by the polymer chain. Since smaller chains preferentially permeate the gel particles, the largest chains are eluted first. As noted above, the fractions are separated on the basis of size.

The resulting chromatogram is then a reflection of the molecular size distribution. The relationship between molecular size and molecular weight depends on the conformation of the polymer in solution. As long as the polymer conformation remains constant, which is

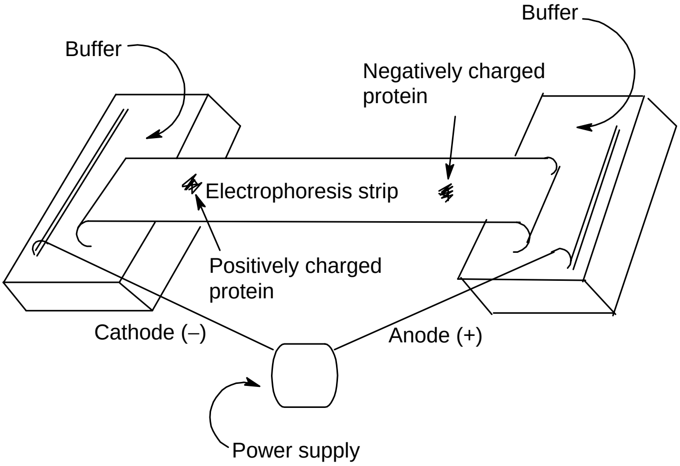

FIGURE 3.7 Basic components of an electrophoresis apparatus.

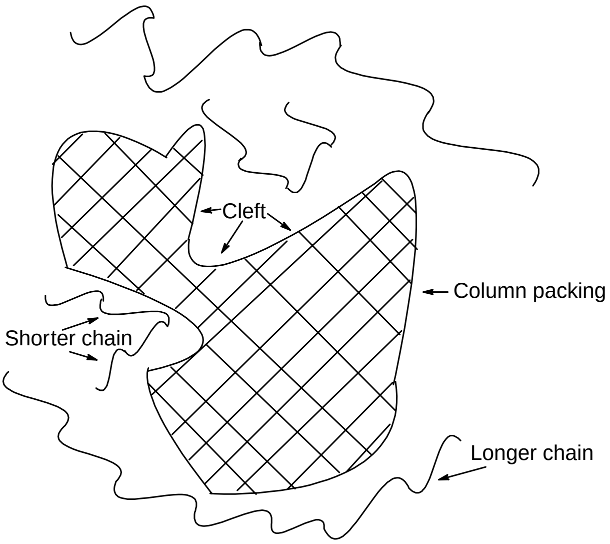

FIGURE 3.8 Illustration of column packing and chains.

generally the case, molecular size increases with molecular weight. The precise relationship between molecular size and molecular weight is conformation-dependent. For random coils, molecular size is measured by the polymer's radius of gyration R, and molecular weight M; R is proportional to M^b, where "b" is a constant depending on the solvent, polymer concentration, and temperature. Such values are known and appear in the literature for many polymers, allowing the ready conversion of molecular size data collected by SEC into molecular weight and MWD.

Figure 3.9 contains the results of a polymer separation using SEC. Here, two different polymer samples are initially added (far left). One polymer sample is a relatively low molecular weight sample with a fairly homogeneous chain size distribution. The second polymer contains longer chains with a broader MWD. As time elapses (second from the left) the two different samples separate, with the sample containing the shorter chains moving

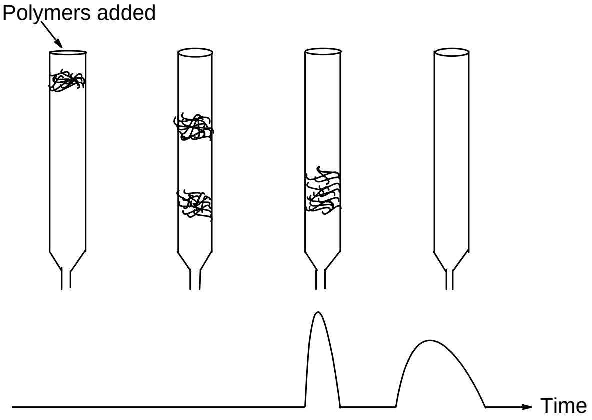

FIGURE 3.9 Illustration of a size exclusion chromatography (SEC) experiment. Column separations are given above with the SEC output given below.

more rapidly down the column. This separation occurs between the samples and within each polymer sample. Then the polymer chains containing the lower molecular weight sample emerge and are recorded as a relatively sharp band (third column). Finally, the sample containing the longer chains emerges, giving a relatively broader band (fourth column).

There is a wide variety of instrumentation ranging from simple manually operated devices to completely automated systems. Briefly, the polymer-containing solution and solvent alone are introduced into the system and pumped through separate columns at a specific rate. The differences in refractive index between the solvent itself and polymer solution are determined using a differential refractometer. This allows calculation of the amount of polymer present as the solution passes out of the column.

The unautomated procedure was first used to separate protein oligomers using Sephadex gels. There are now a wide variety of specialized and general gels used for column packing. The efficiency of these packed columns can be determined by calculating the height (in feet) equivalent to a theoretical plate (HETP), which is the reciprocal of the plate count per feet (*P*). *P* is directly proportional to the square of the elution volume (V_c) and inversely proportional to the height of the column (in feet) and the square of the baseline (*D*) as follows:

$$P = \left(\frac{16}{f}\right)\left(\frac{V_c}{D}\right)^2 \tag{3.9}$$

Conversion of retention volume for a given column to molecular weight can be accomplished using several approaches including peak position, universal calibration, broad standard, and actual molecular weight determination by coupling the SEC to an instrument that gives absolute molecular weight.

In the peak position approach, well-characterized narrow fraction samples of known molecular weight are used to calibrate the column and retention times are determined. A plot of log *M* versus retention is made and used for the determination of samples of unknown molecular weight. Unless properly treated, such molecular weights are subject to error. The best results are obtained when the structures of the samples used in the calibration and those of the test polymers are the same.

The universal calibration approach is based on the product of the limiting viscosity number (LVN) and molecular weight, which is proportional to the hydrodynamic volume. Benoit showed that for different polymers elution volume plotted again the log LVN times molecular weight gave a common line. In one approach molecular weight is determined by constructing a "universal calibration line" through plotting the product of log LVN for polymer fractions with narrow MWDs as a function of the retention of these standard polymer samples for a given column. Molecular weight is then found from retention time of the polymer sample using the calibration line.

Probably the most accurate approach is to directly connect, or couple, the SEC to a device, such as a light-scattering photometer, which directly measures the molecular weight for each elution fraction. Here both molecular weight and MWD are accurately determined.

3.6 COLLIGATIVE MOLECULAR WEIGHTS

3.6.1 OSMOMETRY

A measure of any of the colligative properties involves counting solute (polymer) molecules in a given amount of solvent. The most common technique for polymers is membrane osmometry. The technique is based on the use of a semipermeable membrane through which solvent molecules freely pass, but through which the large polymer molecules are unable to pass. Existing membranes only approximate ideal semipermeability, the chief limitation being the passage of low molecular weight chains through the membrane.

There is a thermodynamic drive toward dilution of the polymer-containing solution with a net flow of solvent toward the cell containing the polymer. This results in an increase in liquid in that cell causing a rise in the liquid level in the corresponding measuring tube. This rise in liquid level is opposed and balanced by a hydrostatic pressure resulting in a difference in the liquid levels of the two measuring tubes. The difference is directly related to the osmotic pressure of the polymer-containing solution. Thus, solvent molecules pass through the semipermeable membrane reaching a "static" equilibrium.

Since osmotic pressure is dependent on the number of particles present, the measurement of this osmotic pressure can be used to determine the M_n of the dissolved polymer. The difference in height (Δh) of the liquids in the columns is converted to osmotic pressure (π) by multiplying the gravity (g) and the density of the solution (ρ), i.e., $\pi = \Delta h \rho g$. In the old static osmometers, it took weeks to months for equilibrium to become established, allowing excessive passage of polymer chains through the membrane. Today, automated osmometers allow molecular weight measurements to occur in minutes, with a minimal of passage of polymer chains through the membrane. The relationship between molecular weight and osmotic pressure is given in the following van't Hoff equation:

$$\pi = \frac{RTC}{\overline{M}_n} + \mathrm{BC}^2 \tag{3.10}$$

Thus, the reciprocal of M_n is the intercept when data for π/RTC versus C are extrapolated to zero concentration (Figure 3.10).

The slope of the lines in Figure 3.10, i.e., the virial constant B, is related to the CED. The value for B would be zero at the theta temperature. Since this slope increases with solvency, it is advantageous to use a dilute solution consisting of a polymer and a poor solvent to minimize extrapolation errors.

In the vapor phase osmometry (VPO) technique, drops of solvent and solution are placed in an insulated chamber close to thermistor probes. Since the solvent molecules evaporate more rapidly from the solvent than from the polymer solution, a temperature difference results that is related to the molarity of the polymer (M), which can be determined if the heat of vaporization per gram of solvent (λ) is known using the following relationship:

$$\Delta T = \frac{RT^2M}{\lambda 100} \tag{3.11}$$

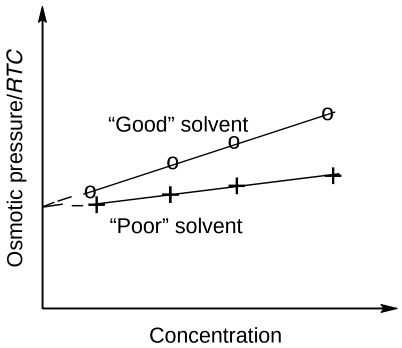

FIGURE 3.10 Plots of osmotic pressure π divided by RTC used to determine $1/\overline{M}_n$ in osmometry.

3.6.2 End-Group Analysis

In cases where the end-groups are known and their concentration can be determined, knowledge of their abundance allows a determination of $\overline{M}_n$. The sensitivity of this method decreases and the chain length becomes greater. Some end-groups can be determined using spectroscopic techniques and others through titration.

3.6.3 Ebulliometry and Cryometry

Raoult's law works for small polymers as well as small molecules. Determination of $\overline{M}_n$ is based for both ebulliometry (boiling point elevation) and cryometry (freezing point lowering) on the Clausius–Clapeyron equation:

$$\overline{M}_n = \left(\frac{RT^2V}{\Delta H}\right)\left(\frac{C}{\Delta T}\right)_{C\to 0} \tag{3.12}$$

By use of sensitive thermocouples and care, molecular weights to about 50,000 Da can be determined.

3.7 LIGHT-SCATTERING PHOTOMETRY

Ever watch a dog or young child chase moonbeams? The illumination of dust particles is an illustration of light scattering, not of reflection. Reflection is the deviation of incident light through one particular angle such that the angle of incidence is equal to the angle of reflection. Scattering is the radiation of light in all directions. Thus, in observing the moonbeam, the dust particle directs a beam toward you regardless of your angle in relation to the scattering particle. The energy scattered per second (scattered flux) is related to the size and shape of the scattering particle and to the scattering angle.

Light is scattered all around us—the fact that the sky above us appears blue, the clouds white, and the sunset shades of reds and oranges is a consequence of preferential scattering of light from air molecules, water droplets, and dust particles. This scattered light carries messages about the scattering objects.

The measurement of light scattering is the most widely used approach for the determination of $\overline{M}_w$. This technique is based on the optical heterogeneity of polymer solutions and was developed by Nobel laureate Peter Debye in 1944.

Modern instruments utilize lasers as the radiation source because they provide a monochromatic, intense, and well-defined light source. Depending upon the size of the scattering object, the intensity of light can be essentially the same or vary greatly with respect to the direction of the oncoming radiation. For small particles the light is scattered equally, independent of the angle of the observer to the incoming light. For larger particles the intensity of scattered light varies with respect to the angle of the observer to the incoming light. For small molecules at low concentrations this scattering is described in terms of the Rayleigh ratio.

In 1871, Rayleigh showed that induced oscillatory dipoles were developed when light passed through gases and that the amount (intensity) of scattered light (τ) was inversely proportional to the fourth power of the wavelength of light. This investigation was extended to liquids by Einstein and Smoluchowski in 1908. These oscillations reradiate the light energy, producing turbidity, i.e., the Tyndall effect. Other sources of energy, such as x-rays or laser beams, may be used in place of visible light sources.

For light-scattering measurements, the total amount of scattered light is deduced from the decrease in intensity of the incident beam I_0 as it passes through a polymer sample. This can be described in terms of Beer's law for the absorption of light as follows:

$$\frac{I}{I_o} = e^{-\tau l} \tag{3.13}$$

where τ is the measure of the decrease of the incident beam intensity per unit length (l) of a given solution and is called the turbidity of the solution.

The intensity of scattered light or turbidity (τ) is proportional to the square of the difference between the index of refraction (n) of the polymer solution and of the solvent (n_o), to the molecular weight of the polymer ($\overline{M}_w$), and to the inverse fourth power of the wavelength of light used (λ). Thus:

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w P_\theta}(1 + 2Bc + Cc^2 + \cdots) \tag{3.14}$$

where the expression for the constant H and for τ is as follows:

$$H = \left[\frac{32\pi^2}{3}\right]\left[n_o^2 \frac{(dn/dc)^2}{\lambda^4 \mathrm{N}}\right] \quad \text{and} \quad \tau = K'n^2\left(\frac{i_{90}}{i_0}\right) \tag{3.15}$$

where n_o = index of refraction of the solvent, n = index of refraction of the solution, c = polymer concentration, the virial constants B, C, etc. are related to the interaction of the solvent, P_θ is the particle-scattering factor, and N is Avogadro's number. The expression dn/dc is the specific refractive increment and is determined by taking the slope of the refractive index readings as a function of polymer concentration.

In the determination of $\overline{M}_w$, the intensity of scattered light is measured at different concentrations and at different angles (θ). The incident light sends out a scattering envelope that has four equal quadrants (Figure 3.11a) for small particles. The ratio of scattering at 45° compared with that at 135° is called the dissymmetry factor or dissymmetry ratio Z. The reduced dissymmetry factor Z_o is the intercept of the plot of Z as a function of concentration extrapolated to zero concentration.

For polymer solutions containing polymers of moderate to low molecular weight P_θ is 1, giving Equation 3.16. At low polymer concentrations Equation 3.16 reduces to Equation 3.17, an equation for a straight line ($y = b + mx$) where the "c"-containing terms beyond the $2Bc$ term are small:

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w}(1 + 2Bc + Cc^2 + \cdots) \tag{3.16}$$

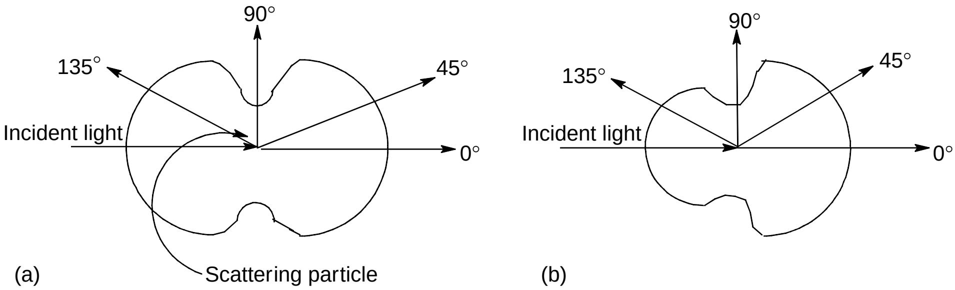

FIGURE 3.11 Light-scattering envelopes. Distance from the scattering particle to the boundaries of the envelope represents an equal magnitude of scattered light as a function of angle for (a) a small scattering particle and (b) a large scattering particle.

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}_w} + \frac{2Bc}{\overline{M}_w} \tag{3.17}$$

Several expressions are generally used in describing the relationship between values measured by light-scattering photometry and molecular weight. One is given in Equation 3.14 and the others, such as Equation 3.18, are exactly analogous except that constants have been rearranged.

$$\frac{Kc}{R} = \frac{1}{\overline{M}_w}(1 + 2Bc + Cc^2 + \cdots) \tag{3.18}$$

When the ratio of the concentration c to the turbidity τ (tau; related to the intensity of scattering at 0° and 90°) multiplied by the constant H is plotted against concentration (Figure 3.12), the intercept of the extrapolated line is the reciprocal of $\overline{M}_w$ and the slope contains the virial constant B. Z_0 is directly related to the particle-scattering factor, and both are related to the size and shape of the scattering particle. As the size of the scattering particle, or the individual polymer chain, approaches about one-twentieth the wavelength of the incident light, scattering interference occurs, giving a scattering envelope that is no longer symmetrical (Figure 3.11b). Here the scattering dependency on molecular weight reverts to the relationship given in Equation 3.14.

The molecular weight for dilute polymer solutions is typically found using one of two techniques. The first is called the dissymmetrical method or approach because it utilizes the determination of Z_0 as a function of the particle-scattering factor as a function of polymer shape. $\overline{M}_w$ is determined from the intercept through substitution of the determined particle-scattering factor. The problem in this approach is the necessity of having to assume a shape for the polymer in a particular solution. For small Z_0 values, choosing an incorrect polymer shape results in a small error, but for larger Z_0 values, the error becomes significant.

The second approach uses multiple detectors (Figure 3.13), allowing a double extrapolation to zero concentration and zero angle with the data forming what is called a Zimm plot (Figure 3.14). The extrapolation to zero angle corrects for finite particle size effects. The radius of gyration, related to polymer shape and size, can also be determined from this plot. The second extrapolation to zero concentration corrects for concentration factors. The intercepts of both plots are equal to $1/\overline{M}_w$.

The Zimm plot approach does not require knowing or having to assume a particular shape for the polymer in solution.

Related to the Zimm plot is the Debye plot. In the Zimm approach, different concentrations of the polymer solution are used. In the Debye approach, one low concentration sample is used with $1/\overline{M}_w$ plotted against $\sin^2(\theta/2)$, essentially one-half of the Zimm plot.

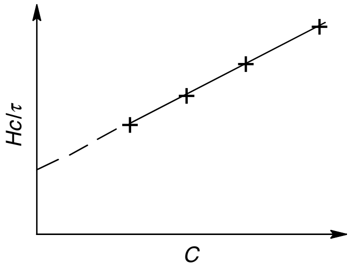

FIGURE 3.12 Typical simple plot used to determine $1/\overline{M}_w$ from scattering data.

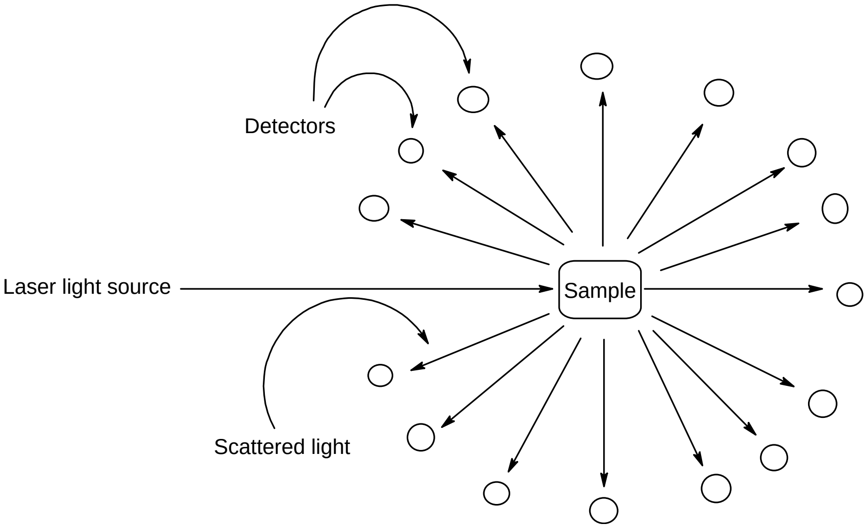

FIGURE 3.13 Multiple detector arrangement showing a sample surrounded by an array of detectors.

Low-angle laser light-scattering (LALLS) photometry and multiangle laser light-scattering (MALLS) photometry take advantage of the fact that at low or small angles, the scattering particle factor becomes one reducing Equation 3.14 to Equation 3.16 and at low concentrations to Equation 3.17.

A number of automated systems exist with varying capabilities. Some internally carry out dilutions and refractive index measurements, allowing molecular weight to be directly determined without additional sample treatment. The correct determination of *dn*/*dc* is very important since any error in its determination is magnified because it appears as the squared value in the expression relating light scattering and molecular weight.

LALLS and MALLS photometers are available that allow not only the determination of $\overline{M}_w$, but also additional values under appropriate conditions. For instance, a Zimm plot as shown in Figure 3.14 allows both $\overline{M}_w$ and $\overline{M}_n$ to be determined as well as the mean radius independent of the molecular conformation and branching.

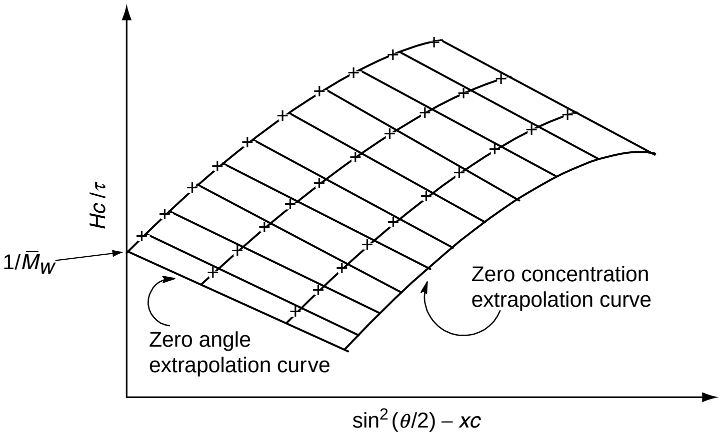

FIGURE 3.14 Zimm plot for a polymer scaled with a negative concentration coefficient (x) to improve data esthetics and accessibility.

These systems may also allow the determination of molecular conformation matching the radius and molecular weight to graphs showing the change in the RMS radius of gyration and molecular weight for different shaped molecules (Figure 3.15). The expression for the mean square radius of gyration is given as

$$r_g^2 = \frac{\Sigma r_i^2 \, m_i}{\Sigma m_i} \tag{3.19}$$

One of the most important advances in polymer molecular weight determination is the "coupling" of SEC and light-scattering photometry, specifically LALLS and MALLS. As noted in Section 3.5, SEC allows the determination of the MWD. In its usual operational configuration, it does not itself allow the calculation of an absolute molecular weight but relies on calibration with polymers of known molecular weight. By coupling HPLC and light-scattering photometry, the molecular weight of each fraction can be determined giving an MWD and various molecular weight values ($\overline{M}_w$, $\overline{M}_z$, $\overline{M}_n$).

The LALLS or MALLS detector measures τ-related values; a differential refractive index (DRI) detector is used to measure concentration, and the SEC supplies samples containing "fractionated" polymer solutions allowing both molecular weight and MWD to be determined. Further, polymer shape can be determined. This combination represents the most powerful one, based on ease of operation, variety of samples readily used, cost, means to determine polymer size, shape, and MWD available today.

A general assembly for a SEC-MALLS instrument is given in Figure 3.16. A typical three-dimensional plot obtained from such an assembly is shown in Figure 3.17.

Dynamic light scattering (DLS) is similar in principle to typical light scattering. When several particles are hit by oncoming laser light, a spotted pattern appears, with the spots originating from the interference between the scattered light from each particle giving a collection of dark (from destructive interference) and light (from constructive interference) spots. This pattern of spots varies with time because of the Brownian motion of the individual

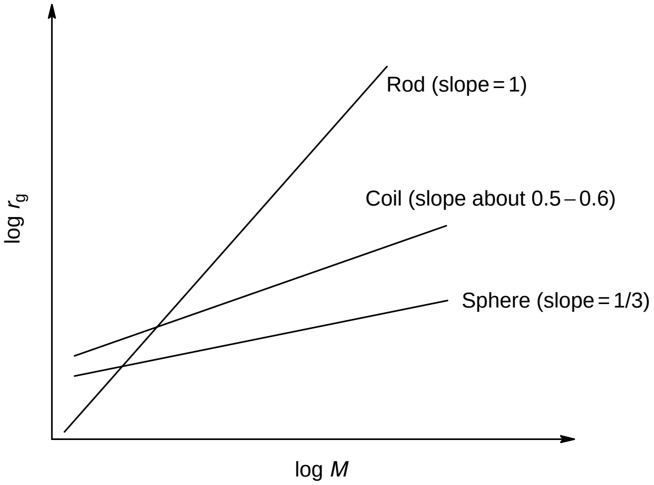

FIGURE 3.15 Standard plot of the log of the mean radium of gyration versus log molecular weight for differently shaped macromolecules. Essentially, for a sphere the radius is proportional to the root-mean-square (RMS) radius, and $M^{1/3}$ with a slope in the log r_g versus log M of 1/3; for rod-shaped polymers, length is proportional to RMS radius and M with a slope of 1; and for random coils the end-to-end distance is proportional to the RMS radius and $M^{1/2}$ with a slope of about 0.5–0.6.

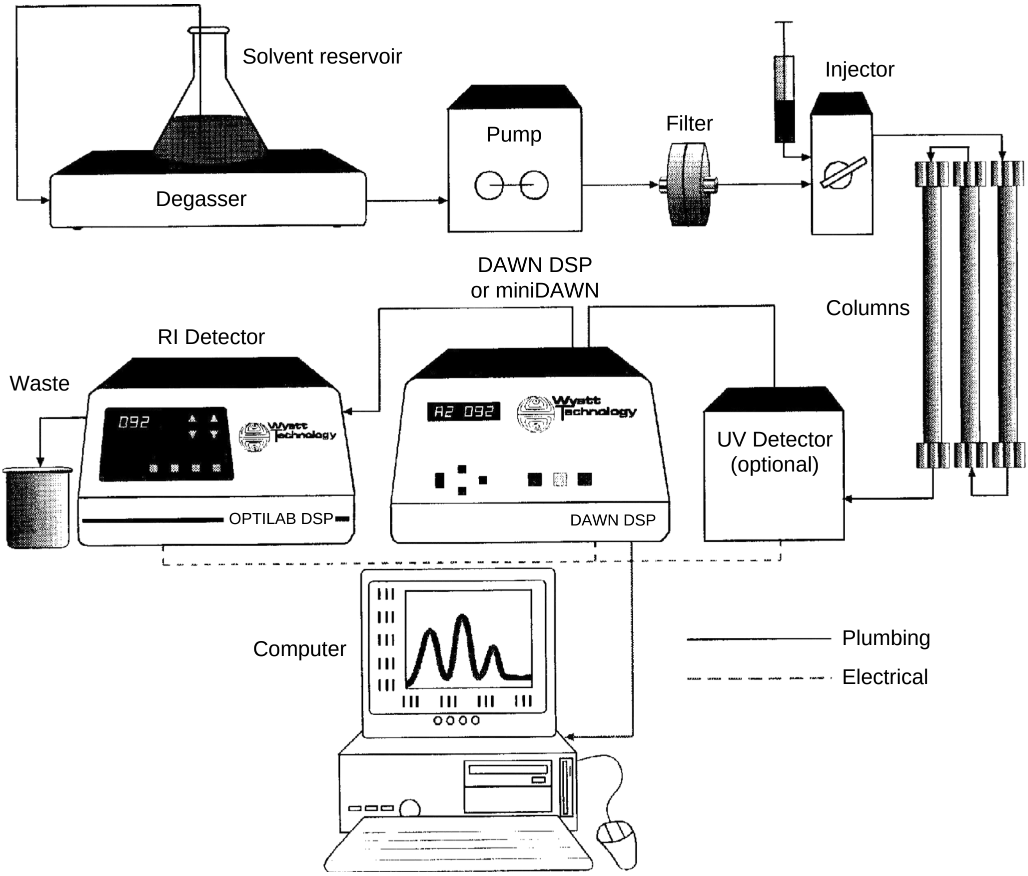

FIGURE 3.16 Typical SEC-MALLS setup including refractive index refractometer. (Courtesy of Wyatt Technology Corporation, Santa Barbara, CA 93117; wyatt@wyatt.com. With permission.)

scattering particles. The rate of change in the pattern of spots is dependent on a number of features including particle size. Generally, the larger the particle, the slower the Brownian motion and, consequently, the slower the change in the pattern. Measurement of these intensity fluctuations with time allows the calculation of the translational diffusion constant of the scattering particles. The technique for this measurement is given several names including DLS, emphasizing the fact that it is the difference in the scattered light with time that is being measured; photon correlation spectroscopy (PCS), with the name emphasizing the particular mathematical technique employed to analyze the light-scattering data; and quasielastic light scattering (QELS), which means that no energy is lost in the collision between the particle and the light photon.

The effect of subtle particle changes as a function of temperature, sample preparation, time, solvent, and other changes can be measured using DLS. Such changes can then be related to performance variations eventually interrelating structure, shape, and biological or physical property.

Another useful variation that employs coupled light scattering is referred to as a triple detection set consisting of three detectors: a light-scattering detector, a differential refractometer detector, and a capillary differential viscometer. It functions in concert with GPC and a light-scattering source. The GPC separates the polymer mixture into molecular weight fractions. According to the Einstein equation the intrinsic viscosity times the molecular

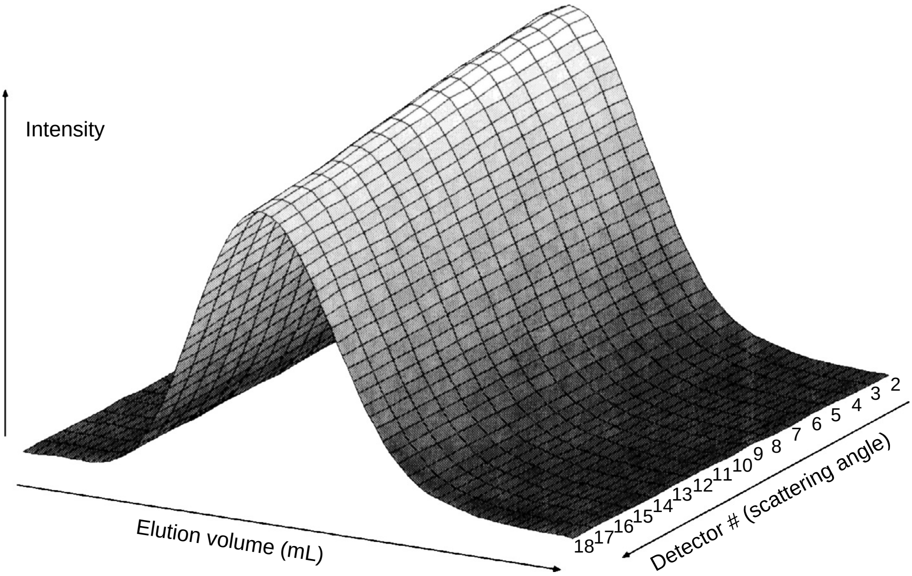

FIGURE 3.17 Three-dimensional plot of scattering intensity as a function of scattering angle and elution volume for a broad molecular weight distribution (MWD) polystyrene (PS) (NITS standard reference 706). (Courtesy of Wyatt Technology Corporation, Santa Barbara, CA 93117; wyatt@wyatt.com. With permission.)

weight is equal to the hydrodynamic volume or size of polymers in solution. Thus, the molecular weight is determined using light-scattering photometry, viscometry gives the intrinsic viscosity, and the equation is solved for size.

Generally, light-scattering photometry has a limit to determining molecular size with the lower limit being about 10 nm. The addition of the viscometer allows molecular sizes to be determined for oligomeric materials to about 1 nm. The assembly allows an independent measure of size and molecular weight as well as additional conformational and aggregation information including small conformational changes. The assembly also allows good molecular determination to occur even when there are small *dn/dc* values, low molecular weight fractions, absorbing and fluorescent polymers, copolymers with varying *dn/dc* values, and chiral polymers that depolarize the incident beam.

Figure 3.18 contains data on myoglobin obtained using a triple detection setup. A molecular weight of 21,100 is found with a viscosity of 0.0247 dl/g, and from this a hydrodynamic radius of 2.06 nm, which is essentially the same as the Stokes value of 2.0 nm reported for myoglobin.

3.8 OTHER TECHNIQUES

3.8.1 ULTRACENTRIFUGATION

Since the kinetic energy of solvent molecules is greater than the sedimentation force of gravity, polymer molecules remain suspended in solution. However, this gravitational field, which permits Brownian motion, may be overcome by increasing this force using high centrifugal forces, such as the ultracentrifugal forces developed by Nobel laureate Theodor Svedberg in 1925.

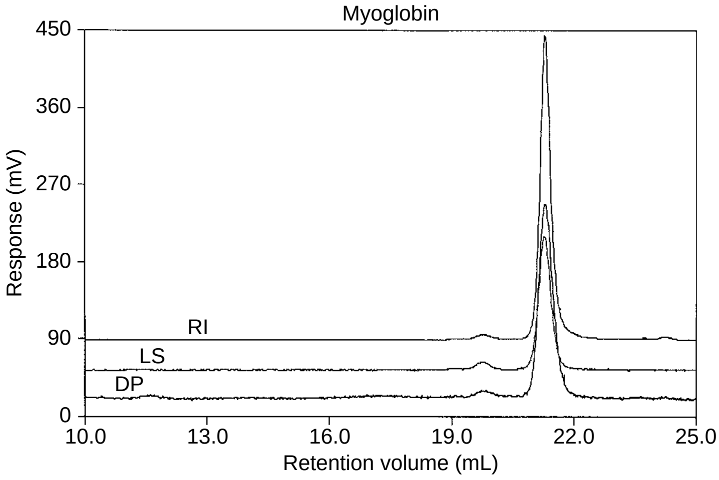

FIGURE 3.18 Response to selected detectors as a function of retention volume for myoglobin (dissolved in PBS buffer at a pH of 6.9). The three detectors are the RI = refractive index signal, LS = light-scattering signal, and DP = differential pressure transducer (viscosity signal). (Courtesy of Viscotek, Houston, TX. With permission.)

Both $\overline{M}_w$ and $\overline{M}_z$ may be determined by subjecting dilute polymer solutions to high centrifugal forces. Solvents with densities and indices of refraction different from the polymers are chosen to ensure polymer motion and optical detection of this motion. In sedimentation velocity experiments, the ultracentrifuge is operated at extremely high rotational speed up to over 70,000 rpm in order to transport the denser polymer molecules through the less dense solvent to the cell bottom or to the top if the density of the solvent is greater than the density of the polymer. The boundary movement during ultracentrifugation can be followed using optical measurement to monitor the sharp change in refractive index (n) between the solvent and solution.

The rate of sedimentation is defined by the sedimentation constant s, which is directly proportional to the polymer mass m, solution density ρ, and specific volume of the polymer V, and inversely proportional to the square of the angular velocity of rotation ω, the distance from the center of rotation to the point of observation in the cell r, and the fractional coefficient f, which is inversely related to the diffusion coefficient D extrapolated to infinite dilution. These relationships are shown in the following equations in which $(1 - V_p)$ is called the buoyancy factor since it determines the direction of macromolecular transport in the cell.

$$s = \frac{(1/\omega^2 r)\mathrm{d}r}{\mathrm{d}t} = \frac{m(1 - V_p)}{f} \tag{3.20}$$

$$D = \frac{RT}{\mathrm{N}f} \quad \text{and} \quad m\mathrm{N} = M \tag{3.21}$$

$$\frac{D}{s} = \frac{RT}{\overline{M}_w(1 - V_p)} \tag{3.22}$$

The sedimentation velocity determination is dynamic and can be completed in a short period of time. The sedimentation equilibrium method gives quantitative results, but long periods of time are required for centrifugation at relatively low velocities to establish equilibrium between sedimentation and diffusion.

TABLE 3.4
Mass Spectrometry (MS) Approaches Used in the Determination of Molecular Weights of Oligomeric and Polymeric Materials

MS-Type	(Typical) Upper Molecular Weight Range (Da)
(Usual) electron impact (EI)	To 2000
Fast atom bombardment (FAB)	To 2000
Direct laser desorption (Direct LD)	To 10^4
Matrix-assisted laser desorption/ionization (MALDI)	To 10^7

The $\overline{M}_w$ is directly proportional to the temperature T and the ln of the ratio of concentration c_2/c_1 at distances r_1 and r_2 from the center of rotation and the point of observation in the cell, and inversely proportional to the buoyancy factor, the square of the angular velocity of rotation, and the difference between the squares of the distances r_1 and r_2 as shown in the following equation:

$$M = \frac{2RT(\ln\, c_2/c_1)}{(1 - V_p)\omega^2(r_2^2 - r_1^2)} \tag{3.23}$$

3.8.2 Mass Spectrometry

Certain MS procedures allow the determination of the molecular weight or molecular mass of oligomeric to polymeric materials (Table 3.4).

In matrix-assisted laser desorption/ionization (MALDI), the polymer is dissolved, along with a “matrix chemical,” and the solution deposited onto a sample probe. The solution is dried. MALDI depends on the sample having a strong ultraviolet (UV) absorption at the wavelength of the laser used. This helps minimize fragmentation since it is the matrix UV-absorbing material that absorbs most of the laser energy. Often employed UV-matrix materials are 2,5-dihydroxybenzoic acid, sinnapinic acid, picplinic acid, and alpha-cyano-4-hydroxy cinnamic acid. The high energy of the laser allows both the matrix material and the test sample to be volatilized. Such techniques are referred to as “soft” since the test sample is not subjected to (much) ionizing radiation and hence little fragmentation occurs.

Mass accuracy on the order of a few parts per million is obtained. Thus, chain content can be determined for copolymers and other chains with unlike repeat units. Polymer MWDs can also be determined using MALDI and related MS techniques. More about MALDI MS and other MS techniques is described in Section 13.4.

Recently, MS combinations have been available including the thermogravimetric analysis–mass spectroscopy (TG–MS) combination developed by Carraher that allows the continuous characterization of evolved materials as a polymer undergoes controlled thermal degradation.

3.9 VISCOMETRY

Viscosity is a measure of the resistance to flow of a material, mixture, or solution. Here we will consider the viscosity of solutions containing small, generally 1 g/100 cc (called 1% solutions) and less, amounts of polymer. The study of such dilute polymer solutions allows a determination of a “relative” molecular weight. The molecular weight is referred to as “relative” since

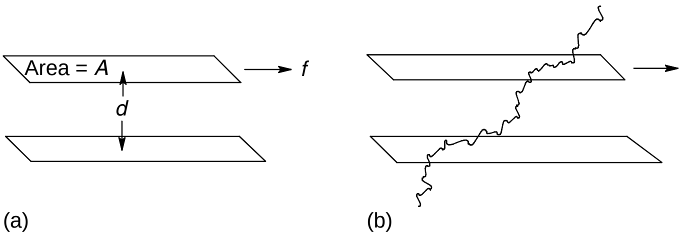

FIGURE 3.19 (a) Representation of Equation 3.24. (b) Illustration of a polymer chain between two flow planes.

viscosity measurements have not been directly related, through rigorous mathematical relationships, to a specific molecular weight. By comparison, measurements made using light-scattering photometry and the other methods covered earlier are relatable to specific molecular weight values, and these techniques are said to give us "absolute" molecular weights.

The relationship between the force f necessary to move a plane of area A relative to another plane a distance d from the initial plane (Figure 3.19), is described as

$$f \propto \left(\frac{A}{d}\right) \tag{3.24}$$

In order to make this a direct relationship a proportionality factor is introduced, which is called the coefficient of shear viscosity or simply viscosity.

$$f = \eta\left(\frac{A}{d}\right) \tag{3.25}$$

Viscosity is then a measure of the resistance of a material to flow. In fact, the inverse of viscosity is given the name fluidicity. A material's resistance to flow increases with its viscosity. Viscosity has been reported using a number of different names. The centimeter–gram–second (CGS) unit of viscosity is called the poise, which is a dyne seconds per square centimeter. Another widely used unit is the pascal (or Pa), which is Newton seconds per square centimeter. In fact, 1 Pa = 10 poise.

Table 3.5 contains the general magnitude of viscosity for some common materials. It is important to note the wide variety of viscosity of materials from gases such as air to viscoelastic solids such as glass.

TABLE 3.5
Viscosities of Selected Common Materials

Substances	General Viscosity (MPa)
Air	0.00001
Water	0.001
Polymer latexes/paints	0.01
PVC plastols	0.1
Glycerol	10
Polymer resins and "pancake" syrups	100
Liquid polyurethanes	1,000
Polymer "melts"	10,000
Pitch	100,000,000
Glass	1,000,000,000,000,000,000,000

TABLE 3.6
Commonly Used Viscosity Terms

Common Name	Recommended Name (IUPAC)	Definition	Symbol
Relative viscosity	Viscosity ratio	η/η_o	$\eta_{rel} = \eta_r$
Specific viscosity	—	$(\eta/\eta_o) - 1$ or $(\eta - \eta_o)\eta_o$	η_{sp}
Reduced viscosity	Viscosity number	η_{sp}/c	η_{red} or η_{sp}/c
Inherent viscosity	Logarithmic viscosity number (LVN)	$\ln(\eta_r/c)$	η_{inh} or $\ln(\eta_r/c)$
Intrinsic viscosity	LVN limit	$(\eta_{sp}/c)_{c\to 0}$ or limit $\ln(\eta_r/c)_{c\to 0}$	LVN

In polymer science we typically do not measure viscosity directly, but rather look at relative viscosity measures by determining the flow rate of one material relative to that of a second material. Viscosity is one of the most widely used methods for the characterization of polymer molecular weight because it provides the easiest and most rapid means of obtaining molecular weight–related data that requires minimal instrumentation. A most obvious characteristic of polymer solutions is their high viscosity, even when the amount of added polymer is small. This is because polymers reside in several flow planes (Figure 3.19b), acting to resist the flow of one plane relative to the flow of another plane.

The ratio of the viscosity of a polymer solution to that of the solvent is called the relative viscosity (η_r). This value minus 1 is called the specific viscosity (η_{sp}), and the reduced viscosity (η_{red}) or viscosity number is obtained by dividing η_{sp} by the polymer concentration c (η_{sp}/c). The intrinsic viscosity, or LVN, is obtained by extrapolating η_{sp}/c to zero polymer concentration. These relationships are given in Table 3.6, and a typical plot of η_{sp}/c and $\ln \eta_r/c$ is shown in Figure 3.20.

Staudinger showed that the intrinsic viscosity or LVN of a solution ($[\eta]$) is related to the molecular weight of the polymer. The present form of this relationship was developed by Mark–Houwink (and is known as the Mark–Houwink equation), in which the proportionality constant K is characteristic of the polymer and solvent, and the exponential a is a function of the shape of the polymer in a solution. For theta solvents, the value of a is 0.5. This value, which is actually a measure of the interaction of the solvent and polymer, increases as the coil expands, and the value is between 1.8 and 2.0 for rigid polymer chains extended to their full contour length and zero for spheres. When a is 1.0, the Mark–Houwink equation (3.26) becomes the Staudinger viscosity equation.

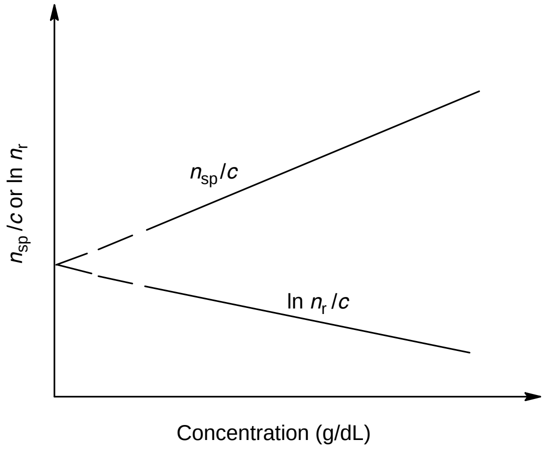

FIGURE 3.20 Reduced and inherent viscosity–concentration lines for a dilute polymer solution.

TABLE 3.7
Typical K Values for the Mark–Houwink Equation

Polymer	Solvent	Temperature (K)	$K \times 10^5$ dL/g
Low-density polyethylene	Decalin	343	39
High-density polyethylene	Decalin	408	68
Isotactic-polypropylene	Decalin	408	11
Polystyrene	Decalin	373	16
Poly(vinyl chloride)	Chlorobenzene	303	71
Poly(vinyl acetate)	Acetone	298	11
Poly(methyl acrylate)	Acetone	298	6
Polyacrylonitrile	Dimethylformamide	298	17
Poly(methyl methacrylate)	Acetone	298	10
Poly(ethylene terephthalate)	*m*-Cresol	298	1
Nylon-6,6	90% Aqueous formic acid	298	110

$$\mathrm{LVN} = KM^a \tag{3.26}$$

Values of a and K have been determined and compiled in several polymer handbooks and are dispersed throughout the literature. Typical values are given in Table 3.7. With known a and K values, molecular weight can be calculated using Equation 3.26. As noted earlier, viscosity is unable to give absolute molecular weight values and must be calibrated, i.e., values of a and K determined using polymer samples where their molecular weights have been calculated using some absolute molecular weight method such as light-scattering photometry. It is customary in determining the a and K values to make a plot of log LVN versus log M since the log of Equation 3.26, i.e., Equation 3.27, is a straight-line relationship where the slope is a and the intercept K. In reality, a is determined from the slope but K is determined by simply selecting a known LVN–M couple and using the determined a value to calculate the K value:

$$\log\ \mathrm{LVN} = a\ \log\ M + \log\ K \tag{3.27}$$

The intrinsic viscosity or LVN, like melt viscosity, is temperature-dependent and decreases as temperature increases as shown in the following equation:

$$\mathrm{LVN} = Ae^{E/RT} \tag{3.28}$$

However, if the original temperature is below the theta temperature, the viscosity will increase when the mixture of polymer and solvent is heated to a temperature slightly above the theta temperature.

Viscosity measurements of dilute polymer solutions are carried out using a viscometer, such as any of those pictured in Figure 3.21. The viscometer is placed in a constant temperature bath and the time taken to flow through a space is measured.

While the description of viscosity is complex, the relative viscosity is directly related to the flow-through times using the same viscometer as shown in Equation 3.29, where t and t_o are the flow times for the polymer solution and solvent, respectively, and the density of the solution (ρ) and solvent (ρ_o) are related as in the following equation:

$$\frac{\eta}{\eta_\mathrm{o}} = \frac{\rho t}{\rho_\mathrm{o} t_\mathrm{o}} = \eta_\mathrm{r} \tag{3.29}$$

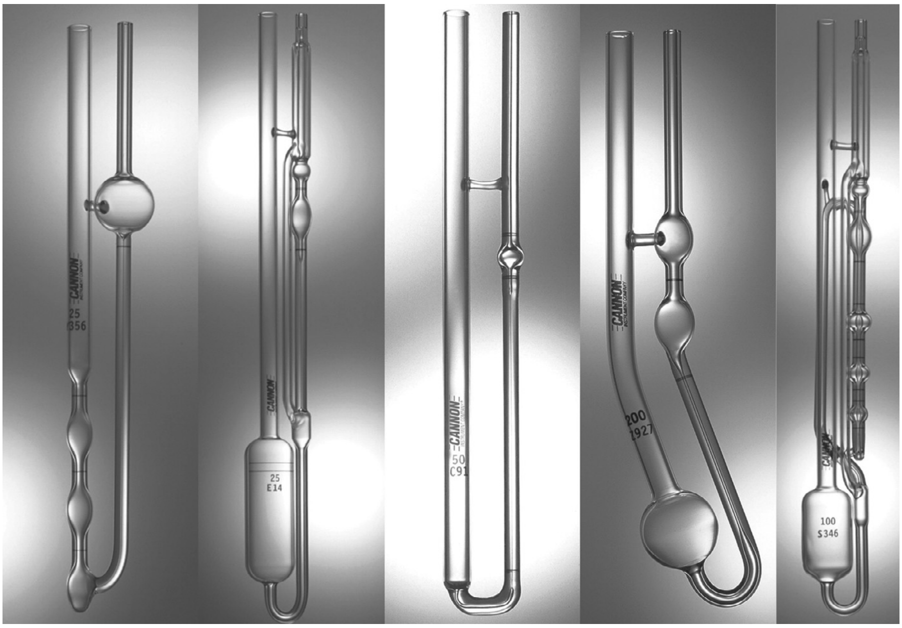

FIGURE 3.21 Common solution viscometers (by permission of Cannon Instrument Company).

Since the densities of the dilute solution and solvent are almost the same, they are normally canceled, giving the following equation:

$$\frac{\eta}{\eta_o} = \frac{t}{t_o} = \eta_r \tag{3.30}$$

Thus, the relative viscosity is simply a ratio of flow times for the polymer solution and solvent. Reduced viscosity is related to the LVN by a virial equation:

$$\frac{\eta_{sp}}{c} = [\eta] + K_1[\eta]^2 c + K'[\eta]^3 c^2 + \cdots \tag{3.31}$$

For most solutions, Equation 3.31 reduces to the Huggins viscosity relationship, Equation 3.32:

$$\frac{\eta_{sp}}{c} = [\eta] + K_1[\eta]^2 c \tag{3.32}$$

which allows $[\eta]$ to be determined from the intercept of the plot of η_{sp}/c versus c and is the basis for the top plot given in Figure 3.20.

Another relationship often used in determining $[\eta]$ is called the inherent viscosity equation and is given in the following equation:

$$\ln \frac{\eta_r}{c} = [\eta] + K_2[\eta]^2 c \tag{3.33}$$

Again, a plot of $\ln \eta_r/c$ versus c gives a straight line with the intercept $[\eta]$ (or LVN) after extrapolation to zero polymer concentration. This is the basis of the lower plot in Figure 3.20. While K_1 and K_2 are mathematically such that

$$K_1 + K_2 = 0.5 \tag{3.34}$$

many systems appear not to follow this relationship.

We will now turn our attention from the viscosity of dilute solutions and look at the viscosity of melted polymers. The viscosity of melted polymers is important in transferring resins and in polymer processing such as determining the correct conditions to have a specific flow rate for injection processing and in determining the optimum conditions to get the necessary dimensions of extruded shapes. Fillers, plasticizers, temperature, solvents, and molecular weight are just some of the variables that influence the viscosity of polymer melts. Here we will look at the dependence of melt viscosity on polymer molecular weight. Polymer melts have viscosities on the order of 10,000 MPa (1 centipoise = 0.001 Pa/sec).

For largely linear polymers such as PS, where there are no particularly bulky side chains, the viscosity or flow is mainly dependent on the chain length. In most polymers the melt viscosity–chain length relationship has two distinct regions where the division occurs when the chain reaches some length called the critical entanglement chain length Z (or simply critical chain length) where intermolecular entanglement occurs. This intermolecular entanglement causes the individual chains in the melt to act as being much more massive because of the entanglement. Thus, the resistance to flow is a combination of the friction and entanglement between chains as they slide past one another. Below the critical entanglement length, where only the friction part is important, the melt viscosity η is related to the weight-average molecular weight by:

$$\eta = K_1 \overline{M}_w^{1.0} \tag{3.35}$$

Above the critical chain length, where both the friction and entanglement are important, the relationship is:

$$\eta = K_h \overline{M}_w^{3.4} \tag{3.36}$$

where K_l is a constant for the precritical entanglement chain length and K_h is for the situation above Z, and where both K values are temperature-dependent. The first power dependence is due to the simple increase in molecular weight as chain length increases, but the 3.4 power relationship is due to a complex relationship between chain movement as related to entanglement and diffusion and chain length.

The critical chain length is often the onset of "strength"-related properties and is generally considered the lower end for useful mechanical properties. The Z value for polymers varies but is typically between 200 and 1000 units in length. For instance, the Z value for PS is about 700; for PIB about 600; for poly(decamethylene sebacate) about 300; for PMMA about 200; and for poly(dimethyl siloxane) about 1000.

A number of techniques have been developed to measure melt viscosity. Some of these are listed in Table 3.8. Rotational viscometers are of varied structures. The Couette cup-and-bob viscometer consists of a stationary inner cylinder, bob, and an outer cylinder, cup, which is rotated. Shear stress is measured in terms of the required torque needed to achieve a fixed rotation rate for a specific radius differential between the radius of the bob and the cup. The Brookfield viscometer is a bob-and-cup viscometer. The Mooney viscometer, often used in the rubber industry, measures the torque needed to revolve a rotor at a specified rate. In the cone-and-plate assemblies the melt is sheared between a flat plate and a broad cone whose apex contacts the plate containing the melt.

A number of capillary viscometers or rheometers have been employed to measure melt viscosity. In some sense, these operate on a principle similar to the simple observation of a trapped bubble moving from the bottom of a shampoo bottle when it is turned upside down. The more viscous the shampoo, the longer it takes for the bubble to move through the shampoo.

TABLE 3.8
Viscosity Measuring Techniques and Their Usual Range

Technique	Typical Range (Poise)
Capillary pipette	0.01–1,000
Falling sphere	1–100,000
Parallel plate	$10{,}000$–10^{9}
Falling coaxial cylinder	$100{,}000$–10^{11}
Stress relaxation	$1{,}000$–10^{10}
Rotating cylinder	1–10^{12}
Tensile creep	100,000–greater than 10^{12}

3.10 SUMMARY

1. Some naturally occurring polymers such as certain proteins and nucleic acids consist of molecules with a specific molecular weight and are called monodisperse. However, many other natural polymers, such as cellulose and NR, and most synthetic polymers consist of molecules with different molecular weights and are called polydisperse. Many properties of polymers are dependent on their chain length. Since the melt viscosity increases exponentially with chain length, the high energy costs of processing high molecular weight polymers are not often justified.
2. The distribution of chain lengths in a polydisperse system may be represented on a typical probability-like curve. The $\overline{M}_n$ is the smallest in magnitude of the typically obtained molecular weights and is a simple arithmetic mean that can be determined using any technique based on colligative properties, such as osmotic pressure, boiling point elevation, freezing point depression, and end-group determination. $\overline{M}_w$ is larger than $\overline{M}_n$ and is referred to as the second power relationship for disperse polymer chains. This value is most often determined by light-scattering photometry. Light-scattering photometry and the colligative related values are referred to as absolute molecular weight values because there is a direct mathematical connection between molecular weight and the particular property used to determine molecular weight.
3. For monodisperse samples, $\overline{M}_n = \overline{M}_w$. For polydisperse samples the ratio of $\overline{M}_w/\overline{M}_n$ is a measure of the polydisparity and is called polydispersity index. The viscosity molecular weight must be calibrated using samples whose molecular weight has been determined with an absolute molecular weight determination technique; thus, it is not an absolute molecular weight determining technique, but it requires simple equipment, and is easy to measure. The Mark–Houwink relationship, $\mathrm{LVN} = KM^{a}$ is used to relate molecular weight and viscosity.
4. The number-average molecular weight is dependent on the number of polymer chains, while the weight-average molecular weight is dependent on the size of the chains. Thus, there is a correlation between the way the molecular weight is obtained and the type of molecular weight obtained.
5. MWD is most often measured using some form of chromatography. In GPC cross-linked polymers are used in a column and act as a sieve, allowing the larger molecules to elute first. After calibration, the molecular weight of the various fractions of the polymer can be determined. Combinations such as chromatography coupled with light-scattering photometry are used to obtain the molecular weight of the various fractions in a continuous manner.
6. While some techniques such as membrane osmometry and light-scattering photometry give absolute molecular weight, other techniques such as viscometry give only relative molecular weights unless calibrated employing a technique that gives absolute molecular weight. After calibration between viscometry values and chain length through some absolute molecular

weight method, viscometry is a fast, inexpensive, and simple method to monitor molecular weight.

7. In general, polymers are soluble in fewer solvents and to a lower concentration than similar smaller molecules. This is because entropy is the driving force for solubility and smaller molecules have larger entropy values when solubility is achieved in comparison to polymers. Polymers also take longer to dissolve since it takes time for the solvent molecules to penetrate the polymer matrix.
8. Flory and Huggins developed an interaction parameter that may be used as a measure of the solvent power of solvents for amorphous polymers. Flory and Krigbaum introduced the idea of a theta temperature, which is the temperature at which an infinitely long polymer chain exists as a statistical coil in a solvent.
9. Hildebrand developed solubility parameters to predict the solubility of nonpolar polymers in nonpolar solvents. The solubility parameter is the square root of the CED. For polar solvents, special solvent–polymer interactions can be incorporated into the solubility parameter approach.

GLOSSARY

affinity chromatography Chromatography in which the resin is designed to contain moieties that interact with particular molecules and/or units within a polymer chain.

bingham plastic Plastic that does not flow until the external stress exceeds a critical threshold value.

Brownian motion Movement of larger molecules in a liquid that results from a bombardment of smaller molecules.

buoyancy factor In ultracentrifugation experiments, it determines the direction of polymer transport under the effect of centrifugal forces in the cell.

chromatography Family of separation techniques based on the use of a medium that shows selective absorption.

cloud point Temperature at which a polymer starts to precipitate when the temperature is lowered.

cohesive energy density (CED) Heat of vaporization per unit volume.

colligative properties Properties of a solution that are dependent on the number of solute molecules present.

commercial polymer range Molecular weight range high enough to have good physical properties but not too high for economical processing.

cryometry Measurement of number-average molecular weight from freezing point depression.

ebulliometry Measurement of number-average molecular weight from boiling point elevation.

effective hydrodynamic volume Cube of the root-mean-square (RMS) end-to-end distance of a polymer chain.

electrophoresis Form of chromatography that uses an electric field to separate molecules.

end-group analysis Determination of number-average molecular weight by determination of end groups.

Flory–Huggins theory Theory used to predict the equilibrium behavior between liquid phases containing polymer.

fractional precipitation Fractionation of polydisperse systems by addition of small amounts of nonsolvent to a solution of polymer.

fractionation of polymers Separation of a polydisperse polymer into fractions of similar molecular weight.

gel permeation chromatography (GPC) Type of liquid–solid elution chromatography which separates solutions of polydisperse polymer solutions into fractions containing more homogeneous chain sizes by means of a sieving action of a swollen cross-linked polymeric gel; also called size exclusion chromatography (SEC).

high-performance liquid chromatography (HPLC) Chromatography in which pressure is applied that causes the solution to pass more rapidly through the column.

Hildebrand (H) Unit used for solubility parameter values.

ion exchange chromatography Chromatography that separates molecules on the basis of their electrical charge employing polyanionic or polycationic resins.

kauri-butanol values Measure of the aromaticity of a solvent.

low-angle laser light-scattering (LALLS) photometry Light scattering that employs low-angle measurements, minimizing the effect of polymer shape on the scattering.

Mark–Houwink equation Relates limiting viscosity number (LVN) to molecular weight; LVN $= KM^a$.

matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) MS in which the sample is placed in a matrix that contains a strong ultraviolet (UV) absorber chosen to match the UV absorption of the laser, which allows the molecules to become volatilized with minimal fragmentation.

melt index Measure of the flow related inversely to melt viscosity.

monodisperse System containing molecules of only one chain length.

multiangle laser light-scattering (MALLS) photometry Similar to LALLS except where the necessary angle ratios are made together; employs low-angle measurements, minimizing the effect of polymer shape on the scattered light.

number-average molecular weight Arithmetical mean value obtained by dividing the sum of the molecular weights by the number of molecules.

oligomer Polymers with 2–10 repeat units; *oligos* means "few."

osmometry Gives number-average molecular weight from osmotic pressure measurements.

polydisperse Mixture of polymer chains of different lengths.

Raoult's law The vapor pressure of a solvent in equilibrium with a solution is equal to the product of the mole fraction of the solvent and the vapor pressure of the pure solvent; this relationship is used in obtaining number-average molecular weights.

SEC-MALLS and SEC-LALLS Coupled chromatography and light-scattering photometry that allows the determination of a number of important values along with chain length distribution.

sedimentation equilibrium experiment Ultracentrifugation technique that allows chain length information to be determined.

semipermeable membrane Membrane that permits the diffusion of solvent molecules but not large molecules.

size exclusion chromatography (SEC) Chromatography in which separation is by molecular size or differences in hydrodynamic volume—also called GPC; can use the universal calibration approach to obtain molecular weight.

solubility parameter A numerical value equal to the square root of the CED which is used to predict polymer solubility.

theta solvent Solvent in which the polymer chain exists as a statistical coil.

theta temperature Temperature at which a polymer of infinite molecular weight begins to precipitate.

ultracentrifuge Centrifuge which increases the force of gravity by as much as 100,000 times, causing a distribution of materials in a solution to separate in accordance with chain length.

vapor pressure osmometry Technique for determining number-average molecular weight by measuring the relative heat of evaporation of a solvent from a solution and a pure solvent.

viscosity Resistance to flow.

intrinsic viscosity The limiting viscosity number (LVN) obtained by extrapolation of the reduced viscosity to zero concentration.

reduced viscosity Specific viscosity divided by the polymer concentration.

relative viscosity Ratio of the viscosity of a solution and that of its solvent.

specific viscosity Difference between the relative viscosity and 1.

weight-average molecular weight Second power average of molecular weight; dependent on the size of the particular chains.

Zimm plot Type of double extrapolation used to determine the weight-average molecular weight in light-scattering photometry.

EXERCISES

1. Which of the following is polydisperse with respect to chain length: (a) casein, (b) commercial PS, (c) paraffin wax, (d) cellulose, or (e) *Hevea brasiliensis*?
2. If the number-average molecular weight for LDPE is 1.4 million, what is the corresponding average chain length?

3. What are the number- and weight-average molecular weights for a mixture of five molecules, each having the following molecular weights: 1.25×10^6; 1.35×10^6; 1.5×10^6; 1.75×10^6; and 2.00×10^6?
4. What is the most probable value for the polydispersity index for (a) a monodisperse polymer and (b) a polydisperse polymer synthesized by a condensation technique?
5. List in increasing values: $\overline{M}_z$, $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_v$.
6. Which of the following provides an absolute measure of the molecular weight of polymers: (a) viscometry, (b) cryometry, (c) osmometry, (d) light-scattering photometry, (e) GCP?
7. What is the relationship between the intrinsic viscosity or LVN and average molecular weight?
8. What molecular weight determination techniques can be used to fractionate polydiserse polymers?
9. Which of the following techniques yields a number-average molecular weight: (a) viscometry, (b) light-scattering photometry, (c) ultracentrifugation, (d) osmometry, (e) ebulliometry, (f) cryometry?
10. What kind of molecular weight do you generally get from light-scattering photometry?
11. What is the value of the exponent a in the Mark–Houwink equation for polymers in theta solvents?
12. How many amino groups are present in each molecule of nylon-6,6 made from an excess of hexamethylenediamine?
13. What is the value of the exponent in the Mark–Houwink equation for a rigid rod?
14. If the values of K and a in the Mark–Houwink equation are 1×10^{-2} cm^3/g and 0.5, respectively, what is the average molecular weight of a polymer whose solution has an intrinsic viscosity of 150 cc/g?
15. Which polymer of ethylene will have the highest molecular weight: (a) a trimer, (b) an oligomer, or (c) UHMWPE?
16. What is a Zimm plot?
17. What type of molecular weight average, $\overline{M}_n$ or $\overline{M}_w$, is based on colligative properties?
18. What principle is used in the determination of molecular weight by vapor pressure osmometry?
19. Why does the melt viscosity increase faster with molecular weight increase than other properties such as tensile strength?
20. In spite of the high cost of processing, UHMWPE is used for making trash cans and other durable goods. Why?
21. Under what conditions are the weight- and number-average molecular weights the same?
22. What is the driving force for polymer solubility?
23. What are colligative methods for measuring molecular weight and what kind of molecular weight do you get?
24. What is the advantage of using viscometry to measure molecular weight?
25. Which will yield the higher apparent molecular weight values in the light-scattering method: (a) a dust-free system or (b) one in which dust particles are present?
26. Does HPLC need to be calibrated before it can give absolute molecular weights?
27. Which of the following does modern liquid chromatography allow the calculation of: (a) weight-average molecular weight; (b) radius of gyration; (c) number-average molecular weight; (d) MWD; or (e) polydispersity index?
28. What is the significance of the virial constant B in osmometry and light-scattering equations?
29. According to Hildebrand, what is a regular solvent?
30. Which of the two steps that occur in the solution process, (a) swelling and (b) dispersion of the polymer particles, can be accelerated by agitation?
31. Define CED.
32. For solution to occur, the change in Gibbs' free energy must be: (a) 0, (b) <0, or (c) >0.
33. Will a polymer swollen by a solvent have higher or lower entropy than the solid polymer?
34. Define the change in entropy in the Gibbs free energy equation.
35. Is a liquid that has a value of 0.3 for its interaction parameter a good or a poor solvent?
36. What is the value of the Gibbs free energy change at the theta temperature?
37. What term is used to describe the temperature at which a polymer of infinite molecular weight precipitates from a dilute solution?
38. At which temperature will the polymer coil be larger in a poor solvent: (a) at the theta temperature; (b) below the theta temperature; or (c) above the theta temperature?

39. If the solubility parameter for water is 23.4 H, what is the CED for water?
40. What is the heat of mixing of two solvents having identical solubility parameters?
41. If the density of a polymer is 0.85 g/cc and the molar volume is 1,176,470 cc, what is the molecular weight?
42. Describe the steps that occur when a polymer is dissolved.
43. Why is it important to determine polymer chain length?
44. Why do δ values decrease as the molecular weight increases in a homologous series of aliphatic polar solvents?
45. Which would be a better solvent for PS: (a) *n*-pentane; (b) benzene; or (c) acetonitrile?
46. Which will have the higher or greater slope when its reduced viscosity or viscosity number is plotted against concentration: a solution of PS (a) in benzene or (b) in *n*-octane?
47. What are general typical values for *a* in the viscosity relationship to molecular weight?
48. When is the Flory equation similar to the Mark–Houwink equation?
49. What is the term used for the cube root of the hydrodynamic volume?
50. Explain why the viscosity of a polymer solution decreases as the temperature increases.
51. Is MALDI restricted to use for natural polymers such as proteins and nucleic acids?

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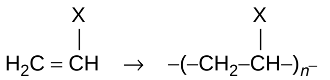
4 Polycondensation Polymers (Step-Reaction Polymerization)

In this chapter we will emphasize condensation polymers. Since most of these are formed from stepwise kinetics, we will also focus on this kinetic process.

4.1 COMPARISON BETWEEN POLYMER TYPE AND KINETICS OF POLYMERIZATION

There is a large, but not total, overlap between the terms condensation polymers and stepwise kinetics and the terms addition (or vinyl) polymers and chain kinetics. In this section we will look at each of these four terms and illustrate the similarities and differences between them.

The terms addition and condensation polymers were first proposed by Carothers and are based on whether the repeat unit of the polymer contains the same atoms as the monomer. An addition polymer has the same atoms as the monomer in its repeat unit:



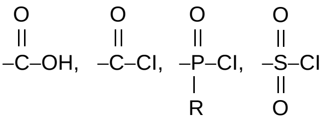
$$H_2C{=}\overset{\overset{X}{|}}{CH} \rightarrow -(-CH_2-\overset{\overset{X}{|}}{CH}-)_n- \qquad (4.1)$$

The atoms in the backbone of addition polymers are almost always only carbon.

Condensation polymers generally contain fewer atoms in the polymer than in the reactants because of the formation of by-products during the polymerization process and the backbone contains noncarbon atoms:

$$X-A-R-A-X + Y-B-R'-B-Y \longrightarrow -(-A-R-A-B-R'-B-)- + XY \qquad (4.2)$$

where A–X can be most Lewis bases such as $-NH_2$, $-SH$, $-OH$, and B–Y can be Lewis acids such as



$$-\overset{\overset{O}{\|}}{C}-OH,\ -\overset{\overset{O}{\|}}{C}-Cl,\ -\underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{P}}-Cl,\ -\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Cl$$

Typically chain polymerizations form addition polymers and stepwise polymerizations form condensation polymerizations.

The term stepwise kinetics, or step-growth kinetics, refers to polymerizations in which the polymer's molecular weight increases in a slow, stepwise manner as reaction time increases.

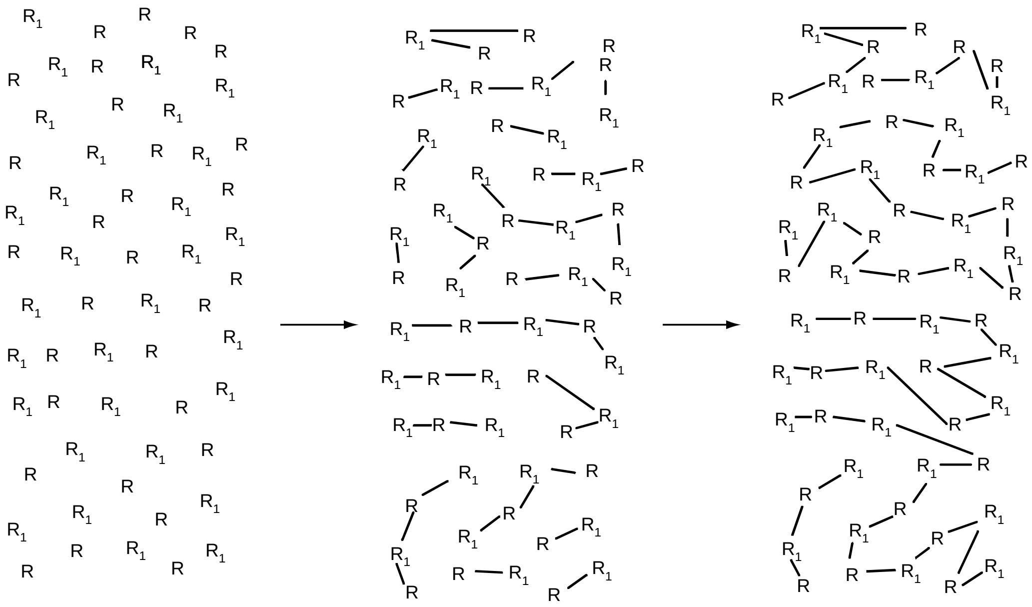


FIGURE 4.1 Depiction of stepwise chain growth for monomers R and R_1 as the polymerization begins (left) progressing toward the right.

Figure 4.1 depicts a stepwise polymerization process. Initially there is only monomer R and R_1 present (left). After some time, all the monomer has reacted, yet no high molecular weight chains are found with the greatest $\overline{DP}$ being 2.5 (center). As polymerization continues, longer chains grow with a high $\overline{DP}$ of 10 (right) for this depiction. Eventually, all of the chains will connect, resulting in polymer. Figure 4.2 contains a representative plot of $\overline{DP}$ as a function of time for this process.

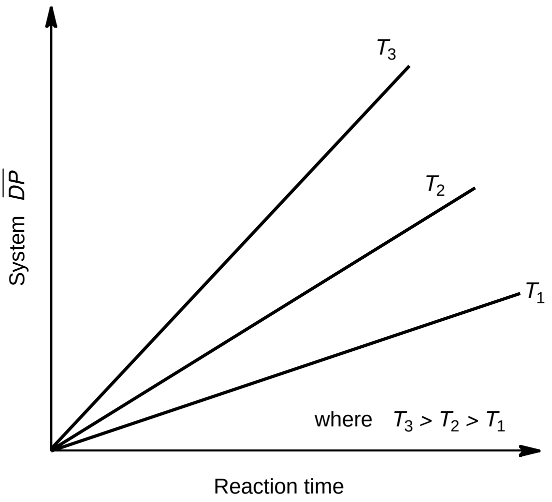
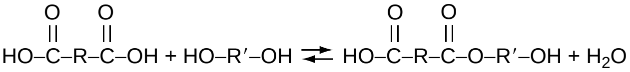


FIGURE 4.2 System molecular weight for stepwise kinetics as a function of reaction time and reaction temperature *T*.

The formation of polyesters from a dialcohol (diol) and a dicarboxylic acid (diacid) is used to illustrate the stepwise kinetic process. Polymer formation begins with one diol molecule reacting with one diacid, forming one repeat unit of the eventual polyester (structure 4.3):



$$\mathrm{HO{-}\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}OH + HO{-}R'{-}OH \rightleftarrows HO{-}\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'{-}OH + H_2O} \tag{4.3}$$

This ester-containing unit can now react with either an alcohol or acid group producing chains ending with either two active alcohol functional groups or two active acid groups (Equation 4.4):

$$\begin{aligned} &+\mathrm{HO-R'-OH} \rightleftarrows \mathrm{HO-R'-O-C(O)-R-C(O)-O-R'-OH} + \mathrm{H_2O} \\ &\mathrm{HO-C(O)-R-C(O)-O-R'-OH} \end{aligned} \tag{4.4}$$

$$\begin{aligned} &+\mathrm{HO-C(O)-R-C(O)-OH} \rightleftarrows \mathrm{HO-C(O)-R-C(O)-O-R'-O-C(O)-} \\ &\mathrm{RC(O)-OH} + \mathrm{H_2O} \end{aligned}$$

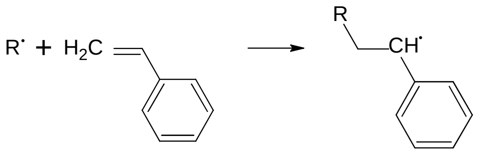
The chain with two alcohol ends can now condense with a molecule containing an acid end, and the chain with two acid ends can now condense with a molecule containing an alcohol group resulting in molecules that contain one acid and one acid active group. This reaction continues through the reaction matrix whenever molecules with the correct functionality, necessary energy of activation, and correct geometry collide. The net effect is the formation of dimers, trimers, etc., until polymer is formed. The monomer concentration is low to nonexistent during most of the polymerization:

$$\begin{gathered} \mathrm{HO-R'-O-C(O)-R-C(O)-O-R'-OH} + \mathrm{HO-C(O)-R-C(O)-OH} \rightleftarrows \\ \mathrm{HO-R'-O-C(O)-R-C(O)-O-R'-O-C(O)-R-C(O)-OH} + \mathrm{H_2O} \end{gathered} \tag{4.5}$$

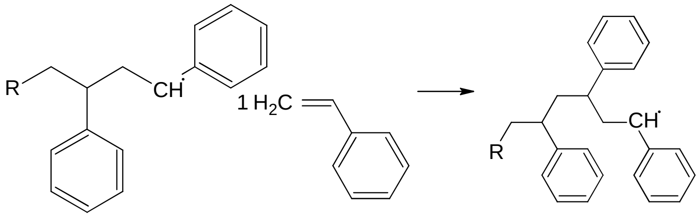
$$\begin{gathered} \mathrm{HO-C(O)-R-C(O)-O-R'-O-C(O)-RC(O)-OH} + \mathrm{HO-R'-OH} \rightleftarrows \\ \mathrm{HO-C(O)-R-C(O)-O-R'-O-C(O)-RC(O)-O-R'-OH} + \mathrm{H_2O} \end{gathered} \tag{4.6}$$

Thus, the reactants are consumed with few long chains formed until the reaction progresses toward total reaction of the chains with themselves. Thus, polymer formation occurs one step at a time, hence the name “stepwise” kinetics.

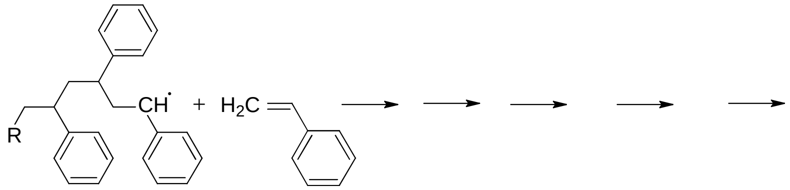
Chain-growth reactions require initiation to begin chain growth. We will look at a free radical example. Here, the initiation of a styrene molecule, R, will illustrate the chain-growth process. The initiator reacts with a styrene monomer creating a free radical active chain end. This free radical chain end then reacts with another styrene monomer, which in turn reacts with another styrene monomer, etc., until termination stops chain growth with the formation of a PS polymer chain (Figure 4.3). PS chains are formed from the beginning of the polymerization process, with growth occurring through formation of polymer chains. As the first chain is formed (Figure 4.3; center) only polymer and monomer are present. As additional polymer chains are formed (Figure 4.3; right) the polymer mix still consists of only polymer chains and unreacted monomers. This is shown in the following sequences:



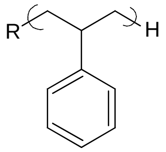
(4.7)



(4.8)



(4.9)



(4.10)

The average $\overline{DP}$ for the entire system, neglecting unreacted monomers, does not markedly change as additional polymer is formed (Figure 4.4). Also, unlike the stepwise process,

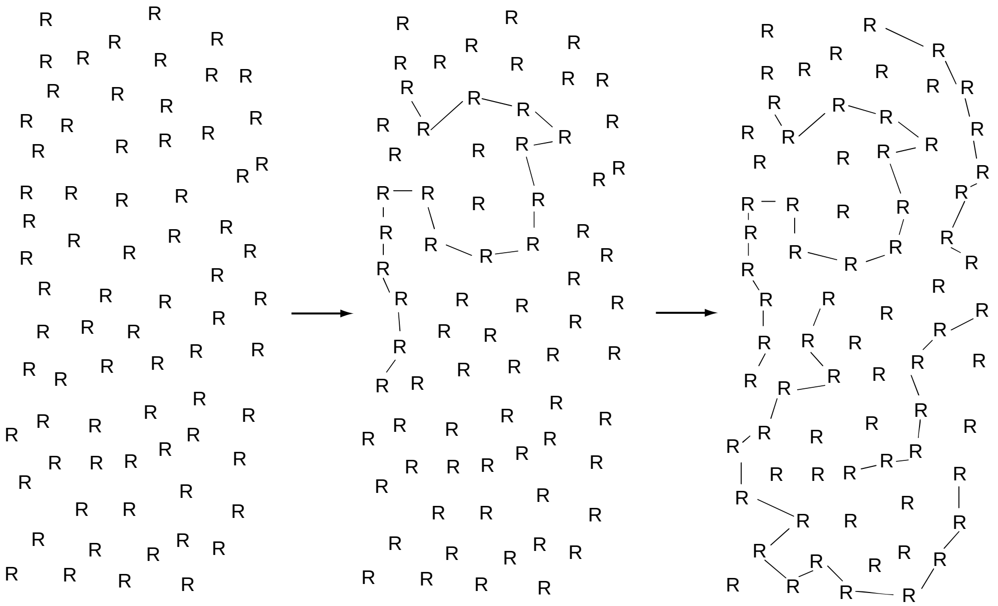


FIGURE 4.3 Molecular weight for chain-growth kinetics as a function of reaction time beginning with only monomer (R; left) with reaction progressing toward the right.

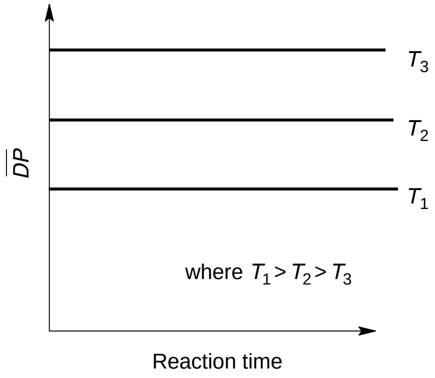


FIGURE 4.4 Idealized average molecular weight of formed polymer as a function of reaction time and temperature T for chain-type polymerization.

average chain length decreases with increasing reaction temperature. Chapters 5 and 6 elaborate on this topic.

Both the stepwise and chainwise polymerizations produce polymers that are polydisperse with respect to chain lengths.

Most addition polymers are formed from polymerizations exhibiting chain-growth kinetics. This includes the typical polymerizations, via free radical or some ionic mode, of the vast majority of vinyl monomers such as vinyl chloride, ethylene, styrene, propylene, methyl methacrylate, and vinyl acetate. By comparison, most condensation polymers are formed from systems exhibiting stepwise kinetics. Industrially this includes the formation of polyesters and polyamides (nylons). Thus, there exists a large overlap between the terms stepwise kinetics and condensation polymers, and chainwise kinetics and addition (or vinyl) polymers. A comparison of the two types of systems is given in Table 4.1.

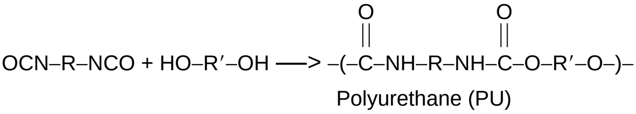
Even so, there is no total overlap between the various characteristics of vinyl-chain kinetics and condensation-step kinetics. Following are examples illustrating the lack of adherence to this overlap:

1. The formation of PUs and polyureas typically occur through stepwise kinetics with the polymer backbones clearly containing noncarbon atoms. Yet, no by-product is

TABLE 4.1
Comparison between Stepwise and Chainwise Polymerizations

Chain	Step
Growth occurs by addition of one unit at a time to the active growing chain end	Any two unlike molecular units can react
Monomer concentrations decrease steadily throughout the polymerization	Monomer disappears early in the reaction
Polymer chains are formed from the beginning of the polymerization and throughout the process	Polymer chain length increases steadily during the polymerization
Average chain length for reacted species remains approximately constant throughout the polymerization	Average molecular weight for the reaction (for the reacted species) increases throughout the polymerization
As reaction time is increased, polymer yield increases, but molecular weight remains about the same	High “extents” of reaction are required to obtain greater chain lengths
Reaction mixture contains almost only unreacted monomer, polymer, and very little growing polymer chains	Reaction system contains various stages, or chain lengths, of product present in a calculable distribution

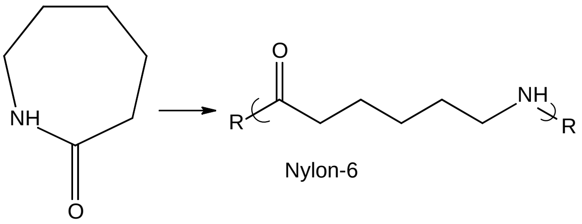
released through the condensation process because condensation occurs through an internal rearrangement and shift of the hydrogen—neither step resulting in expulsion of a by-product:



$$\text{OCN–R–NCO} + \text{HO–R}'\text{–OH} \longrightarrow \text{–(–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–NH–R–NH–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–O–R}'\text{–O–)–} \tag{4.11}$$

Polyurethane (PU)

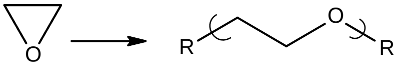
2. Internal esters (lactones) and internal amides (lactams) are readily polymerized through a chainwise kinetic process forming polyesters and polyamides, clearly condensation polymers with respect to having noncarbons in the backbone, but without expulsion of a by-product:



Nylon-6

(4.12)

A similar ring-opening polymerization (ROP) with ethylene oxide forming poly(ethylene oxide) forms a noncarbon backbone via a chainwise kinetic process:



Poly(ethylene oxide)

(4.13)

3. Interfacially formed condensation polymers such as polyesters, polycarbonates, nylons, and PUs are typically formed on a microscopic level in a chain-growth manner largely because of the highly reactive nature of the reactants employed for such interfacial polycondensations.

4.2 INTRODUCTION

While condensation polymers account for only a modest fraction of all synthetic polymers, most natural polymers are of the condensation type. The first all-synthetic polymer, Bakelite, was produced by the stepwise polycondensation of phenol and formaldehyde.

As shown by Carothers in the 1930s, the chemistry of condensation polymerizations is essentially the same as classic condensation reactions, leading to the formation of monomeric esters, amides, etc. The principle difference is that the reactions used for polymer formation are bifunctional instead of monofunctional.

Table 4.2 contains a listing of a number of industrially important synthetic condensation polymers.

4.3 STEPWISE KINETICS

The kinetics for stepwise polycondensation reactions and the kinetics for monofunctional aminations and esterifications are similar. Experimentally, both kinetic approaches are

TABLE 4.2
Properties and Uses of Some Important Synthetic Condensation-Type Polymers

Type (Common Name)	Typical Properties	Typical Uses
Polyamides (nylons)	Good balance of properties; high strength, good elasticity and abrasion resistance, good toughness, favorable solvent resistance, outdoor weathering, moisture resistance	Fibers—about half of all nylon fiber goes into tire, cord, rope, belting, fiber cloth, thread, hose, undergarments, dresses; plastics—use as an engineering material, substitute for metal bearings, bearings, cams, gears, rollers, jackets on electrical wire
Polyurethanes	Elastomers—good abrasion resistance, hardness, resistance to grease, elasticity; fibers—high elasticity, excellent rebound; coatings—good resistance to solvents and to abrasion, good flexibility, impact resistance; foams—good strength per weight, good rebound, high impact strength	Four major forms used: fibers—swimsuits, foundation garments; elastomers—industrial wheels, heel lifts; coatings—floors where impact and abrasion resistance are required, bowling pins; foams—pillows, cushions
Polyureas	High T_g, fair resistance to greases, oils, solvents	Not widely used
Polyesters	High T_g and T_m, good mechanical properties, resistance to solvents and chemicals, good rebound, low moisture absorption, high modulus; film—high tensile strength (about that of steel), stiff, high resistance to failure on repeated flexing, high impact strength, fair tear strength	Fibers—garments, permanent press and "wash & wear" garments, felts, tire cord; film—magnetic recording tape, high-grade film
Polyethers	Good thermoplastic behavior, water solubility, moderate strength and stiffness	Sizing for cotton and synthetic fibers; stabilizers for adhesives, binders, and film-formers in pharmaceuticals; thickeners; production of films
Polycarbonates	Crystalline with good mechanical properties, high impact strength, good thermal and oxidative stability, transparent, self-extinguishing, low moisture absorption	Machinery and business
Phenol–formaldehyde resins	Good heat resistance, dimensional stability, resistance to cold flow, solvent, dielectric properties	Used in molding applications, appliances, TVs, automotive parts, filler, impregnating paper, varnishes, decorative laminates, electrical parts, countertops, toilet seats, adhesive for plywood, sandpaper, brake linings, abrasive wheels
Polyanhydrides	Intermediate physical properties, medium to poor T_g and T_m	No large industrial applications
Polysulfides	Outstanding oil and solvent resistance, good gas impermeability, resistance to aging, ozone, bad odors, low tensile strength, poor heat resistance	Gasoline hoses, tanks, gaskets, diaphragms
Polysiloxanes	Available in a wide range of physical states from liquids to greases, to waxes, to resins, to elastomers; excellent high and moderate low temperature physical properties; resistant to weathering and lubricating oils	Fluids—cooling and dielectric fluids, in waxes and polishes, as antifoam and mold release, for paper and textile treatment; elastomers—gaskets, seals, cable, wire insulation, hot liquids and gas movement, surgical and prosthetic devices, sealing compounds; resins—varnishes, paints, encapsulating and impregnating agents
Polyphosphate and polyphosphonate esters	Good fire resistance, fair adhesion, moderate moisture stability, fair temperature stability	Additives promoting flame retardance; adhesive for glass (since it has a similar refractive index), pharmaceuticals, surfactant

essentially identical. Usual activation energies (120–240 kJ/mol) require only about one collision in 10^{12}–10^{15} to be effective in producing polymer at 100°C, whereas for the vinyl reactions, the activation energies are much smaller (8–20 kJ/mol), with most collisions of proper orientation being effective in lengthening the chain. This is in agreement with the slowness of the stepwise process in comparison to chain polymerizations.

While more complicated situations can occur, we will consider only the kinetics of simple polyesterification. The kinetics of most other common polycondensations follows an analogous pathway.

For uncatalyzed reactions where the diacid and diol are present in equimolar amounts, one diacid is experimentally found to act as a catalyst. The experimental expression dependencies are described in the usual manner as follows:

$$\text{Rate of polycondensation} = -\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]^2[D] \tag{4.14}$$

where $[A]$ is the concentration of diacid and $[D]$ is the diol concentration. Since $[A] = [D]$, we can write

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = k[A]^3 \tag{4.15}$$

Rearrangement gives

$$-\frac{\mathrm{d}[A]}{[A]^3} = k\mathrm{d}t \tag{4.16}$$

Integration of Equation 4.16 over the limits of $A = A_o$ to $A = A_t$ and $t = 0$ to $t = t$ gives

$$2kt = \frac{1}{[A_t]^2} - \frac{1}{[A_0]^2} = \frac{1}{[A_t]^2} + \text{constant} \tag{4.17}$$

It is usual to express Equation 4.17 in terms of the extent of reaction p, where p is defined as the fraction of functional groups that have reacted at time t. Thus, $1 - p$ is the fraction of groups unreacted. A_t is in turn $A_o(1-p)$:

$$A_t = A_o(1-p) \tag{4.18}$$

Substituting the expression for A_t from Equation 4.18 into Equation 4.17 and rearrangement gives

$$2A_o^2kt = \frac{1}{(1-p)^2} + \text{constant} \tag{4.19}$$

which is the equation of a straight line, i.e.,

$$mx = y + b$$

where $m = 2A_o^2k$, $x = k$, $y = \dfrac{1}{(1-p)^2}$, and b is the constant. A plot of $1/(1-p)^2$ as a function of time should be linear, with a slope $2A_o^2k$ from which k is determined. Determination of k at different temperatures allows the calculation of activation energy. Thus, one definition of the specific rate constant is $k = Ae^{-E_a/kt}$. The log of both sides gives $\log k = \log A - E_a/kt$, which again is the equation of a straight line, where $y = \log k$, $b = \log A$, $m = -E_a/k$ and $x = 1/t$ where E_a is the activation energy, A is a constant, k is the specific rate constant, and t is the temperature.

The number-average degree of polymerization can be expressed as

$$\overline{DP}_n = \frac{\text{number of original molecules}}{\text{number of molecules at time } t} = \frac{N_o}{N} = \frac{A_o}{A_t} \tag{4.20}$$

Thus,

$$\overline{DP}_n = \frac{A_o}{A_t} = \frac{A_o}{A_o\,(1-p)} = \frac{1}{1-p} \tag{4.21}$$

The relationship given in Equation 4.21 is called the Carothers equation because it was first found by Carothers while working with the synthesis of polyamides (nylons). For an essentially quantitative synthesis of polyamides where p is 0.9999, the $\overline{DP}$ is approximately 10,000, the value calculated using Equation 4.21:

$$\overline{DP}_n = \frac{1}{1-p} = \frac{1}{1-0.0000} = \frac{1}{0.0001} = 10{,}000 \tag{4.22}$$

Thus, the Carothers equation allows calculation of maximum $\overline{DP}$ as a function of extent of polymerization, and the purity of reactants. This value of 10,000 Da is sufficient to produce polyesters that will give strong fibers. The high value of p decreases, as does $\overline{DP}$, if impurities are present or if some competing reaction, such as cyclization, occurs. Since the values of k at any temperature can be determined from the slope $(2kA_o^2)$ when $1/(1-p)^2$ is plotted against t, $\overline{DP}_n$ at any time t can be determined from the expression

$$(\overline{DP}_n)^2 = 2kt[A_o]^2 + \text{constant} \tag{4.23}$$

Much longer times are required to effect formation of high polymer polyesters in uncatalyzed esterifications than for acid or base-catalyzed systems. For catalyzed systems, since the added acid or base is a catalyst, its apparent concentration does not change with time; thus, it is not included in the kinetic rate expression. In such cases the reaction follows the rate expression

$$\text{Rate of polycondensation} = -\frac{d[A]}{dt} = k[A][B] \tag{4.24}$$

For $[A] = [B]$ we have

$$-\frac{d[A]}{dt} = k[A]^2 \tag{4.25}$$

and rearrangement gives

$$-\frac{d[A]}{[A]^2} = kt \tag{4.26}$$

which on integration and subsequent substitution gives

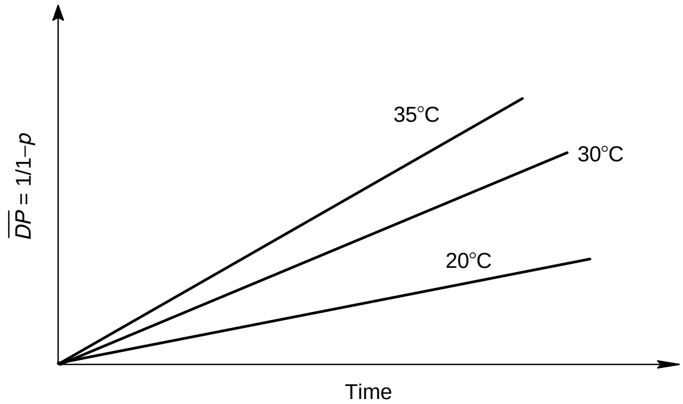


FIGURE 4.5 Plot of average chain length $\overline{DP}$, as a function of reaction time for the acid-catalyzed condensation of ethylene glycol with terephthalic acid producing poly(ethylene terephthalate) (PET).

$$kt = \frac{1}{A_t} - \frac{1}{A_o} = \frac{1}{A_o(1-p)} - \frac{1}{A_o} \tag{4.27}$$

Rearrangement gives

$$A_okt = \frac{1}{1-p} - 1 = \overline{DP}_n - 1 \tag{4.28}$$

which predicts a linear relationship of $1/1 - p$ with reaction time. This is shown in Figure 4.5.

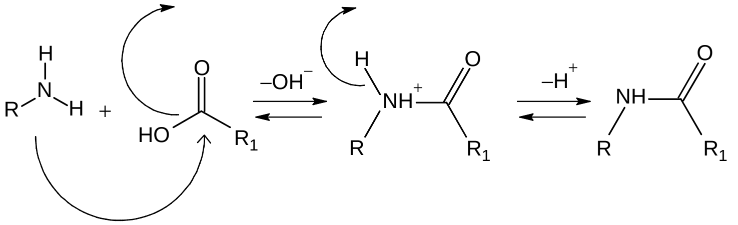
Useful polymers are not obtained unless the value for the fractional conversion p is at least 0.990, i.e., a $\overline{DP}$ greater than 100.

It is important to note that the rate constant k for reactions of similar monofunctional compounds is essentially the same as for the difunctional compounds used in the formation of polycondensation polymers. Likewise, as in the case of reactions of small molecules, the rate constant k increases with temperature in accordance with the Arrhenius equation:

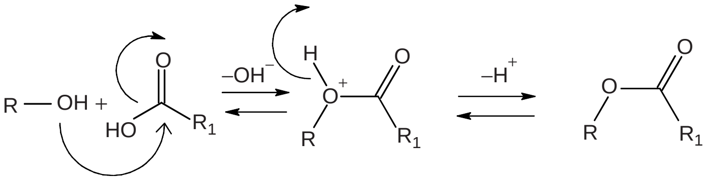
$$k = Ae^{-E_a/kt} \tag{4.29}$$

4.4 POLYCONDENSATION MECHANISMS

Proposed mechanisms for polycondensations are essentially the same as those proposed in the organic chemistry of smaller molecules. Here, we will briefly consider several examples to illustrate this similarity between reaction mechanisms for small molecules and those forming polymers. For instance, the synthesis of polyamides (nylons) is envisioned as a simple S_N2 type Lewis acid–base reaction, with the Lewis base nucleophilic amine attacking the electron-poor, electrophilic carbonyl site followed by loss of a proton.

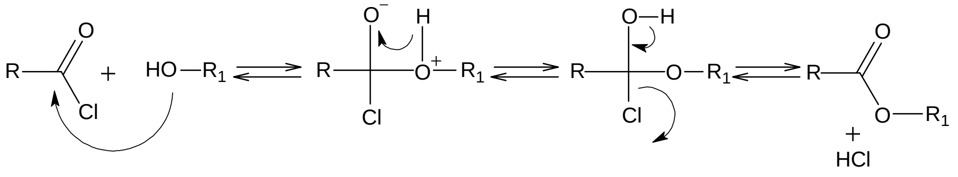


(4.30)



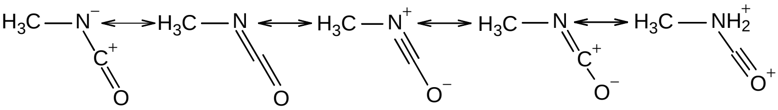
(4.31)

A similar mechanism is proposed for most polyesterifications:



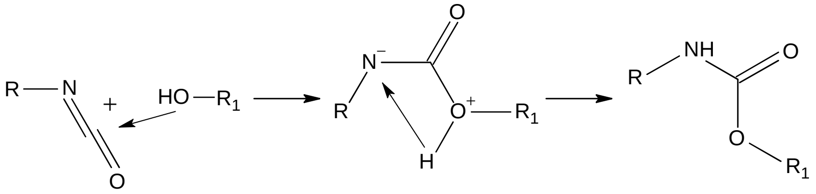
(4.32)

Below are a number of resonance forms for the isocyanate moiety. Because it is surrounded on both sides by atoms, N and O, which have greater electronegativities than the carbon atom, the carbon is electron-poor and is the site for attack by amines (polyureas) and alcohols (PUs):



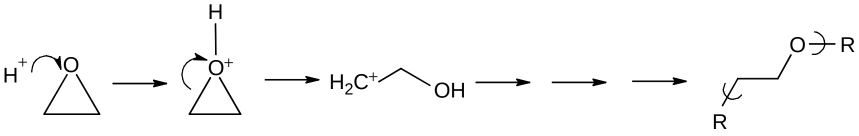
(4.33)

PU formation occurs with attack of the nucleophilic alcohol at the electron-poor isocyanate carbon with a proton shift followed by rearrangement to the urethane structure:

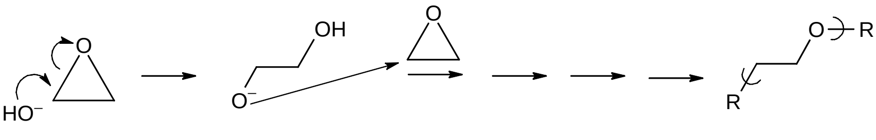


(4.34)

Polyether formation from ring opening forming poly(ethylene oxide) occurs through acid or base catalysis as shown below:



(4.35)



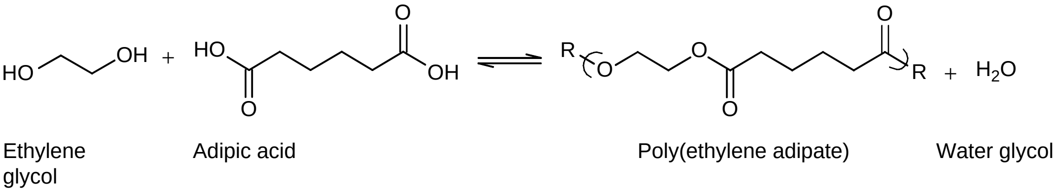
(4.36)

Ethylene oxide is a polar molecule with an excess of electron density on the oxygen making it the site for acid attack, whereas the ethylene moiety is electron-poor and the site for nucleophillic attack by the base.

Again, what we have learned from smaller molecule chemistry applies to polymer reactions typically with only modifications that consider the larger size of the polymer.

4.5 POLYESTERS

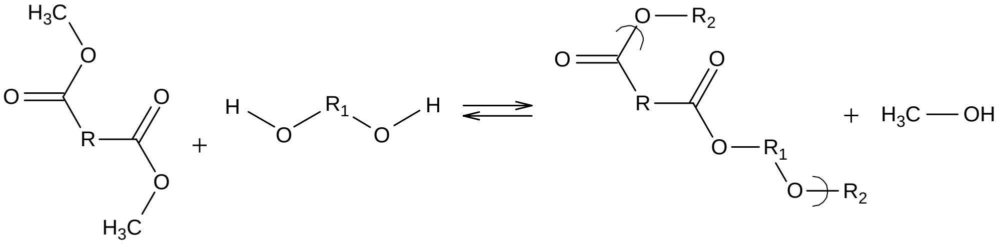
Carothers and his research group at DuPont began to investigate the formation of polymers from the reaction of aliphatic diacids with diols, generally adipic acid and ethylene glycol (derived from reaction of ethylene oxide with water; major ingredient in most antifreeze), in search of materials that would give them fibers. They were only able to form syrupy mixtures. This is because unlike reactions with diamines (Section 4.7), the equilibrium reaction greatly disfavors ester formation. Further, the ability to have almost equal amounts of functional groups is easily achieved with the amines through formation of salts with the amines as shown in structure 4.48 but diols do not form such salts. The critical need to have the reactants present in equal molar amounts for equilibrium-determined reactions is clearly seen in Equation 4.21. Carothers' group understood the principle of "driving" an equilibrium reaction, so it sought to remove water, thus forcing the reaction toward ester formation. For this they developed a so-called "molecular still" that simply heated the mixture and applied a vacuum coupled with a "cold-finger," which allowed evacuated water to condense and be removed from the reaction system. Since the fractional conversion (p) was only 0.95 the average chain length of these polyesters was less than 20:



(4.37)

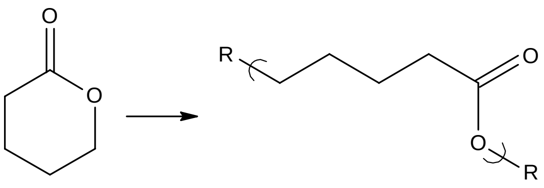
The DuPont research team turned from the synthesis of polyesters to tackle, more successfully, the synthesis of the first synthetic fiber material, nylon, which approached, and in some cases exceeded, the physical properties of natural analogs (Section 4.7). The initial experience with polyesters was put to good use in the nylon venture.

Today, we know that Carothers would have had greater success in producing high molecular weight polyesters had his group employed transesterification (4.38, 4.47):



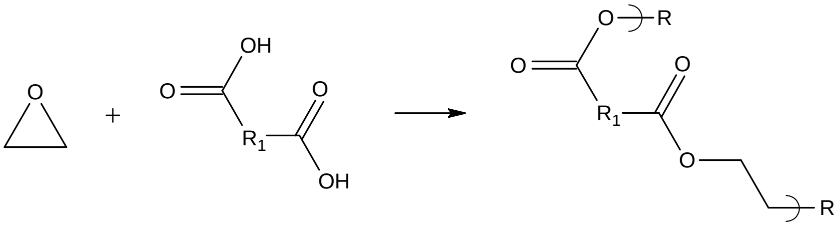
(4.38)

ring opening of an internal ester (lactone; 4.39):



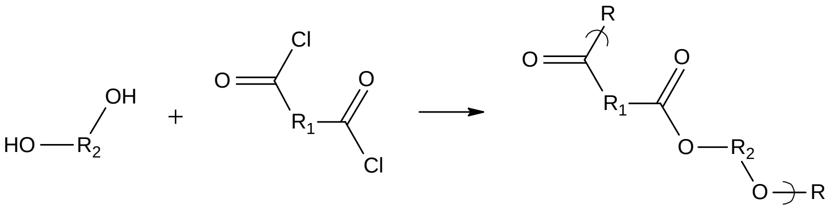
(4.39)

ring opening of internal ethers (4.40, 4.48):



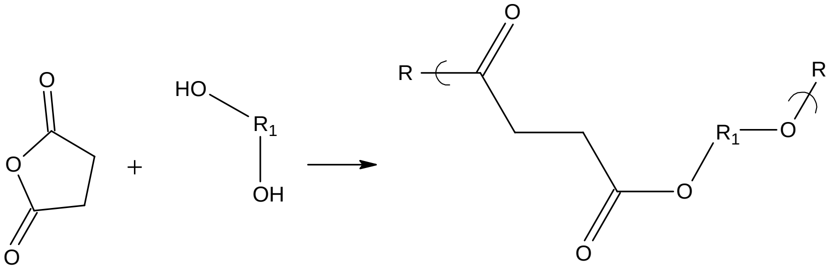
(4.40)

reaction of diols with acyl dichlorides (Schotten–Baumann reaction; 4.32, 4.41):



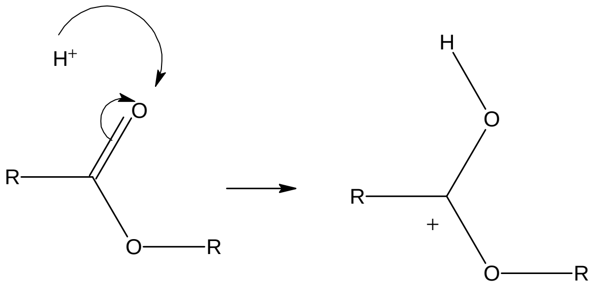
(4.41)

or diols with anhydrides (4.42, 4.45, and 4.46):



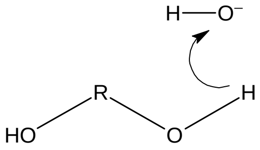
(4.42)

These techniques then compose, along with the simple reaction of diacids with diols (Equations 4.5 and 4.6), the major techniques employed in the synthesis of polyesters. Each of these reactions involves the nuclophilic addition to the carbonyl group as shown in Section 4.5 and illustrated in Equation 4.32. Focusing on the carbonyl-containing reactant, polyester formation employing direct esterification (reaction between an acid and alcohol) and transesterification is relatively slow with each step reversible. Reaction rates are increased through the use of acid catalysts that coordinate the carbonyl oxygen enhancing the electrophilic nature of the carbonyl carbon:



(4.43)

Basic catalysts are often employed in transesterification reactions probably to increase the nucleophilicity of the alcohol through formation of secondary bonding to the alcohol-proton, resulting in the alcohol being more nucleophilic (4.44):



(4.44)

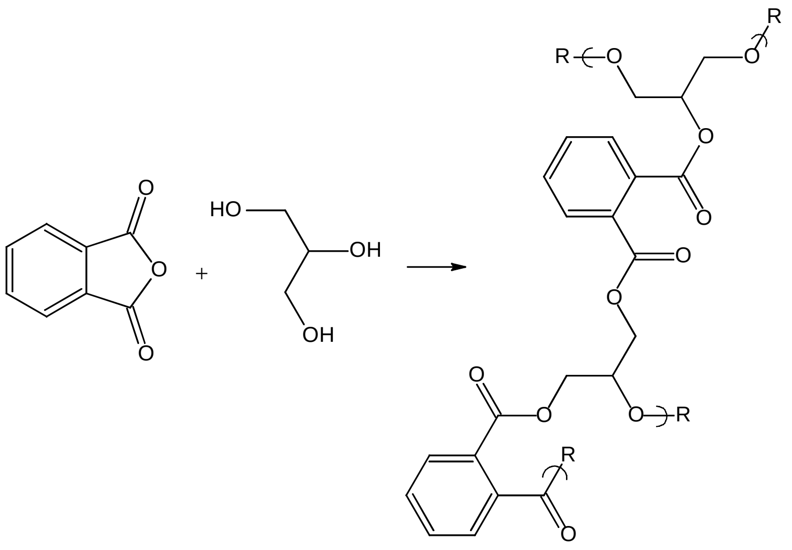
Reactions with anhydrides and acid chlorides are more rapid and can occur in an essentially nonreversible fashion. But, anhydrides and acid chlorides are considered "high-energy" reactants since they often involve additional energy-requiring steps in their production, and are thus less suitable for large-scale production of materials. The activity energies for direct esterification and transesterification are on the order of 30 kcal/mol (120 kJ/mol) while the activation energies for anhydride and acid chloride reaction with alcohols are on the order of 15–20 kcal/mol (60–80 kJ/mol).

The initial polyester formation actually occurred early and is attributed to Gay Lussac and Pelouze in 1833 and Berzelius in 1847. These polyesters are called glyptals and alkyds, and they are useful as coatings materials and not for fiber production. While these reactions had low fractional conversions, they formed high molecular weight materials because they had functionality (i.e., number of reactive groups on a single reactant) greater than 2, resulting in cross-linking.

When the average functionality is greater than 2, cross-linking occurs. Glyptal polyesters were produced in 1901 by heating glycerol and phthalic anhydride. Since the secondary hydroxyl is less active than the terminal primary hydroxyls in glycerol, the first product formed at conversions of less than 70% is a largely linear polymer. A cross-linked product is formed by further heating because the functionality of glycerol is 3 (Equation 4.45).

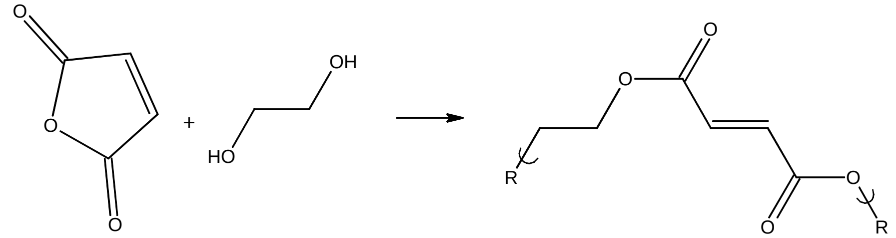
Alkyds were synthesized by Kienle in the 1920s from trifunctional alcohols and dicarboxylic acids. Unsaturated oils, called drying oils, were transesterified with the phthalic anhydride in the reaction so that an unsaturated polymer was obtained which could later be reacted producing a cross-linked product.

The term alkyd is sometimes used to describe all polyesters produced from polybasic acids and a polyhydric alcohol. The terms "saturated" and "unsaturated" polyesters have been used to distinguish between those alkyd polyesters that are saturated from those that contain unsaturation.



(4.45)

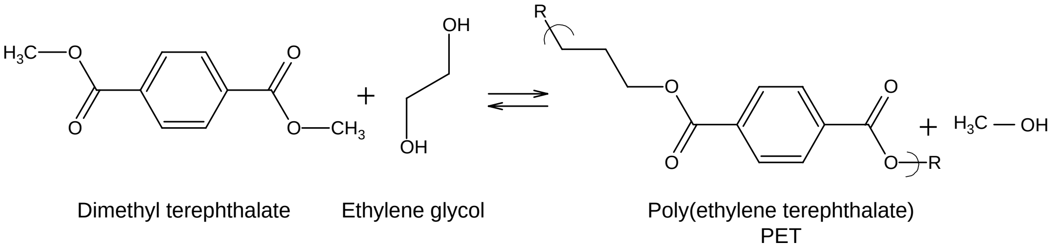
Unsaturated polyesters have been produced from reaction of ethylene glycol with phthalic anhydride, or maleic anhydride (structure 4.46). These polyesters may be dissolved in organic solvents and used as cross-linking resins for the production of fibrous glass–reinforced composites:



(4.46)

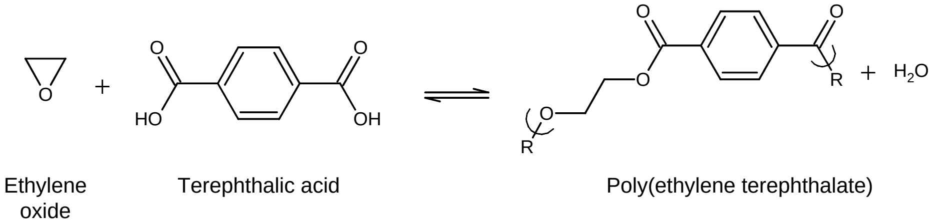
Aromatic polyesters had been successfully synthesized from the reaction of ethylene glycol and various aromatic diacids but commercialization awaited a ready inexpensive source of aromatic diacides. An inexpensive process was discovered for the separation of the various xylene isomers by crystallization. The availability of inexpensive xylene isomers allowed the formation of terephthalic acid through the air oxidation of the *p*-xylene isomer. DuPont produced polyester fibers from melt spinning in 1953, but it was not until the 1970s that these fibers became commercially available.

Expanding on the work of Carothers and Hill on polyesters, Whinfield and Dickson in England overcame the problems of Carothers and coworkers by employing an ester interchange reaction between ethylene glycol and the methyl ester of terephthalic acid forming the polyester PET, with the first plant coming on line in 1953. This classic reaction producing Dacron, Kodel, and Terylene fibers is shown in structure 4.47:



(4.47)

While PET is normally made as described in structure 4.47, it can also be made from the ring-opening reaction with ethylene glycol as shown in structure 4.48:

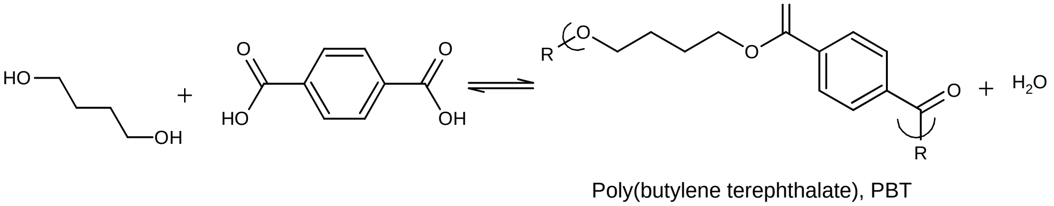


(4.48)

Polyester fibers (PET; structures 4.47 and 4.48) are the world's leading synthetic fibers produced at an annual rate of over 1.5 million tons in the United States. Fibers are produced when the product is pushed through a small hole. As the polyester emerges from the hole, tension is applied assisting the polymer chains to align, giving the fiber additional strength in the direction of pulling. Crystallization of polyester resin can be achieved by heating to about 190°C followed by slow cooling. Rapid cooling, called quenching, produces a more amorphous material from which transparent film is made. Film strength is increased through application of heat and pulling of the film. Biaxially oriented PET film is one of the strongest films available. Thicker film, because of its low carbon dioxide permeability, is used in the manufacture of containers for carbonated drinks through injection molding. It is also used as magnetic film in x-ray and other photographic applications. Thinner film is used in applications such as food packaging including the boil-in-a-bag foods.

PET is difficult to mold because of its high melting point, T_m 240°C. PET also crystallizes relatively slowly so that extra care must be exercised to ensure that the PET-molded products are fully crystallized, otherwise the partially crystallized portions will be preferred sites for cracking, crazing, shrinkage, etc. Thus, nucleating agents and crystallization accelerators have been used to improve the crystallization rate. Post annealing has been used where appropriate.

Poly(butylene terephthalate) (PBT), because of the addition of two methylene units in the diol-derived portion, has a lower melting point than PET with a T_g of about 170°C (structure 4.49). Moldability of aryl polyesters has been improved through the use of PBT instead of PET or by use of blends of PET and PBT. These aryl polyesters are used for bicycle wheels, springs, and blow-molded containers.



Poly(butylene terephthalate), PBT

(4.49)

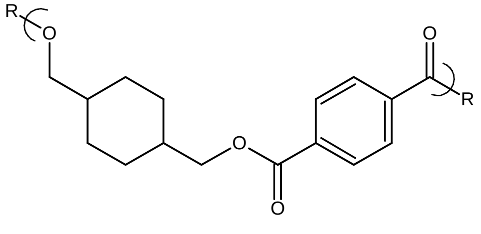
TABLE 4.3
General Physical Properties of PET and PBT

	PET	PBT
Heat deflection temperature (1820 kPa; °C)	100	65
Maximum resistance to continuous heat (°C)	100	60
Crystalline melting point (°C)		
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	6.5	7.0
Compressive strength (kPa)	8.6×10^4	7.5×10^4
Flexural strength (kPa)	1.1×10^5	9.6×10^4
Impact strength (Izod: cm-N/cm of notch)	26	53
Tensile strength (kPa)	6.2×10^4	5.5×10^4
Ultimate elongation (%)	100	100
Density (g/mL)	1.35	1.35

In comparison to PET, PBT melts at a lower temperature and crystallizes more rapidly, and is often employed as a molding compound. PBT offers a balance of properties between nylons and acetals with low moisture absorption, good fatigue resistance, good solvent resistance, extremely good self-lubrication, and good maintenance of physical properties even at relatively high use temperatures. Fiber-reinforced PBT molding compound is sold under the trade name Celanex. A PBT molding compound was first sold under the trade name Valox. Today, there are many PBT molding compounds available.

Table 4.3 contains selected physical properties of PET and PBT.

Poly(dihydroxymethylcyclohexyl terephthalate) (structure 4.50) was introduced by Eastman Kodak as Kodel in 1958. In comparison to PET and PBT, the insertion of the cyclohexyl moiety gives a more hydrophobic material as well as a more moldable product, which can be injection-molded. The sole raw material is again dimethyl terephthalate. Reduction of the dimethyl terephthalate gives the dialcohol cyclohexanedimethanol. (Notice the recurring theme of reusing or using in a modified form the same readily available and inexpensive materials.) This material, along with blends and mixtures, is often extruded into film and sheeting for packaging. Kodel-type materials are used to package hardware and other heavy items as well as blow-molded to produce packaging for shampoos, liquid detergents, etc.



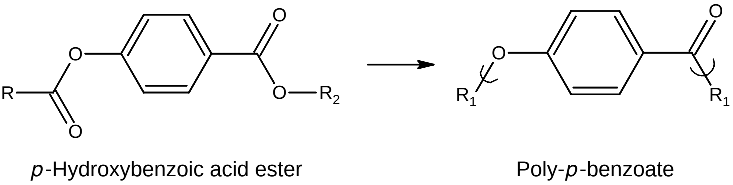
(4.50)

Poly(dihydroxymethylcyclohexyl terephthalate)

The hard–soft block copolymer approach employed to produce segmental PUs (Section 7.6) has also been used with polyesters, with the hard block formed from 1,4-butadienediol and terephthalic acid while the soft block is provided by oligomeric (approximate molecular weight of 2000 Da) poly(tetramethylene glycol) and is sold under the trade name Hytrel.

Along with nylons, polyester fibers approach and exceed common natural fibers such as cotton and wool in heat stability, wash-and-wear properties, and wrinkle resistance. Blended textiles from polyester, cotton, and wool also can be made to be permanent-press and wrinkle-resistant. The fibers are typically formed from melt or solvent spinning. Chemical and physical modification is often employed to produce differing fiber appearances from the same basic fiber material. Self-crimping textiles are made by combining materials with differing shrinkage properties. Differently shaped dyes produce materials with varying contours and properties including hollow fibers.

Several “wholly” aromatic polyesters are available. As expected, they are more difficult to process, stiffer, and less soluble, but are employed because of their good high-thermal performance. Ekonol is the homopolymer formed from *p*-hydroxybenzoic acid ester (structure 4.51). Ekonol has a T_g in excess of 500°C. It is highly crystalline and offers good strength:

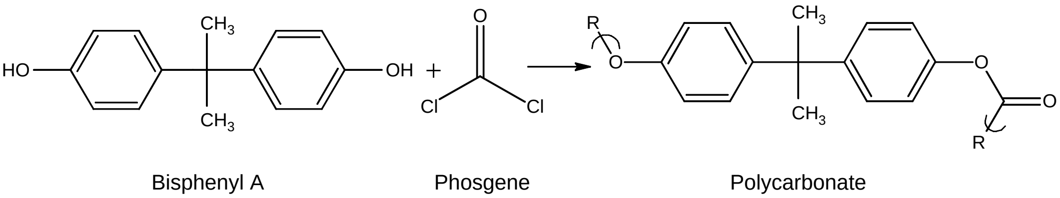


(4.51)

It is not unexpected that such aromatic polyesters have properties similar to polycarbonates because of their structural similarities.

4.6 POLYCARBONATES

Polycarbonates were originally produced from the interfacial polymerization reaction of phosgene with bisphenol A [2,2′-bis(4-hydroxyphenyl)propane] (structure 4.52). The bisphenol A is dissolved in an NaOH aqueous solution, resulting in the bisphenol losing the two “phenol” protons, thus creating a more effective Lewis base or nucleophile. Phosgene is added typically via a chlorinated solvent and tertiary amine. The product is an unusually tough and transparent plastic available under the trade names Lexan (General Electric) and Merlon (Mobay). Polycarbonates can also be made from the ester interchange between diphenyl carbonate and bisphenol A. The melting point of polycarbonates is decreased from 225°C to 195°C when the methyl pendant groups are replaced by propyl groups:



(4.52)

Polycarbonates and polycarbonate–polyester copolymers are used for glazing, sealed beam headlights, door seals, popcorn cookers, solar heat collectors, and appliance housings.

Essentially all CDs, and related audio and video storing devices, have similar components. Here, we will focus on the composition of purchased CDs already containing the desired information and CDs that can be recorded on, CD/Rs. The major material of all of these storage devices is a polycarbonate base. Thus, these devices are polycarbonate, laid over with thin layers of other materials. Of the less than 20 g CD weight, over 95% is polycarbonate.

The aromatic rings contribute to the polycarbonate’s high glass transition temperature and stiffness (Table 4.4). The aliphatic groups temper this tendency giving polycarbonate a decent solubility. The two methyl groups also contribute to the stiffness because they take up

TABLE 4.4
General Physical Properties of a Polycarbonate

Heat deflection temperature (1820 kPa; °C)	130
Maximum resistance to continuous heat (°C)	115
Crystalline melting point (°C)	225
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	6.8
Compressive strength (kPa)	8.6×10^4
Flexural strength (kPa)	9.3×10^4
Impact strength (Izod: cm-N/cm of notch)	530
Tensile strength (kPa)	7.2×10^4
Ultimate elongation (%)	110
Density (g/mL)	1.2

space, somewhat hindering free rotation around the aliphatic central carbon moiety. Factors contributing to polycarbonate chain association are interaction between the aromatic rings of different parts of the same or different polycarbonate chain segments and the permanent dipole present within the carbonyl group. The lack of "hydrogen-bonding" hydrogen on polycarbonate means that this type of association is not present. The associations between polycarbonate segments contribute to a general lack of mobility of individual chains. This results in polycarbonate having a relatively high viscosity, which ultimately leads to a low melt flow during processing. The moderate inflexibility, lack of ready mobility, and nonlinear structure contribute to polycarbonate having a relatively long time constant for crystallization. Cooling is allowed to be relatively rapid so that most polycarbonate products possess a large degree of amorphous nature, and it accounts for polycarbonate having a high impact strength that is important in its use to blunt high impacts and important to CDs to provide a semirigid disc that can be dropped and not readily shattered. Thus, control of the rate of flow and cooling is an important factor in producing CD-quality polycarbonate material. A high degree of amorphous nature also contributes to the needed optical transparency, with amorphous polycarbonate having a transparency near that of window glass.

While polycarbonate has the desirable qualities as the basic material for information storage, it also has some debits. First, polycarbonate is relatively expensive in comparison with many polymers. Its superior combination of properties and ability for a large cost markup allows it to be an economically feasible material for specific commercial uses. Second, the polar backbone is susceptible to long-term hydrolysis so that water must be ruthlessly purged. The drying process, generally 4 h, is often achieved by placement of polycarbonate chips in an oven at 120°C with a dew point of −18°C.

The polycarbonate utilized for information storage has strict requirements including high purity, greater than 87% spectral light transmission based on a 4 mm thick sample, yellowness index less than 2, and light scattering less than 0.3 cd/(m^2-lx). The two main sources of polycarbonate are virgin and recycled. Virgin polycarbonate has a yellowness index of 1.8 but the first reground polycarbonate has a yellow index of about 3.5. Thus, CDs employ only virgin polycarbonate.

Requirements for CD-quality material are polycarbonate with low levels of chemical impurities, low particle levels, thermal stability, excellent mold release, excellent clarity, as well as constant flow and constant mechanical behavior (for reproducibility). There exists a time/cost balance. High molecular weight polycarbonate offers a little increase in physical property but the flow rate is slow, making rapid production of CDs difficult. The molecular weight where good mechanical strength and reasonable flow occurs, and that allows for short cycles, is in the range of 16,000–28,000 Da.

Injection molding requires the barrel temperature to be about 350°C with a barrel pressure in excess of 138 MPa. The mold is maintained at 110°C to ensure uniform flow and high definition, and to discourage an uneven index of refraction, birefringence. The CD is about four one-hundredths of an inch (0.5 mm) thick. For prerecorded CDs, the PC is compression-molded on a stamper imprinted with the recorder information. This takes about 4 sec. Once the clear piece of polycarbonate is formed, a thin, reflective aluminum layer is sputtered onto the disc. Then, a thin acrylic layer is sprayed over the aluminum to protect it. The label is then printed onto the acrylic surface and the CD is complete. This process is described later in greater detail.

The construction of the recordable CD or CD/R, is more complex. Standard CDs contain four or five (a label layer) layers. These five layers are:

- Polycarbonate base
- Dye surface
- Reflective layer
- Lacquer layer
- Label

We must remember that the information is closest to the label side of the CD, not the clear plastic side the data is read from. It is fairly easy to scratch the top surface of the CD, thus rendering it unusable. Some CDs have a special hard top coating that helps resist surface damage. Dust, minor scratches, and fingerprints are generally not harmful because the laser assemblies are designed to focus beyond the disc surface.

The "play only" CD contains a series of pits and lands generated during the mastering process based specifically on the data provided. The polycarbonate layer for the CD/R does not contain these pits and lands but rather contains a shallow groove or pregroove used for timing and tracking. A CD/R writes, or records, information by using its lasers to physically "burn" pits into the organic dye layer. When heated beyond a certain temperature, the area that was "burned" becomes opaque and reflects a different amount of light in comparison to areas that have not been "burned." These "burned" and "unburned" areas correspond to the pits and lands of the prerecorded CD, allowing it to be "read" by a regular CD player.

CD/Rs are write once/read many (WORM) storage discs. They cannot be erased once they have been written on.

The dye coating is the most important, expensive, and complex part of the CD manufacturing process. The dye layer serves to inhibit or permit laser radiation from piercing the polycarbonate. There are three competing organic dye polymers used to manufacture CD/Rs. The original dye polymer used was the cyanine (and metal-stabilized cyanine) materials identified by a greenish tint with a gold reflective layer or blue when a silver reflective layer is present. The employed cyanine dye is itself blue. The suggested age for storage on cyanine dye discs is about 20 years and for metal-stabilized cyanine about 100 years.

The second dye system is based on an almost clear yellow-green phthalocyanine dye. The estimated lifetime of a disc based on the phthalocyanine dye is 100 years. The third dye system is based on azo dyes. The azo dye used in the process has a deep blue color partially caused by its unique silver alloy reflective layer. Again, a projected lifetime of 100 years is cited.

The two most widely employed reflective layers are 24 K gold and a silver alloy. The layers are thin enough, about 50–100 nm thick, to allow us to see through them.

The first step in the manufacturing of a blank CD is the creation of a glass master with a laser beam recorder (LBR). For the prerecorded CDs, pits and lands are etched into the photoresist or nonphotoresist on the glass. For the CD/R, the LBR records a shallow groove as a continuous spiral called the pregroove. This pregroove is not a perfect spiral, but it is "wobbled." On the recorded disc, the timing information necessary to control the disc's rate of spin is included as data. But for the CD/R, the CD recorder needs to have a way to guide the recording laser and speed of the blank disc. The wobbled pregroove provides the tracking and timing information for the recording laser. The wobble is a slight sinusoidal wave that is about 0.03 mm from the center of the track path. This wobble corresponds to about one-thousandth of the length of one complete waveform, and is so small that it cannot be seen by the naked eye, although it is "seen" by the recording laser. This slight diversion from a completely spiral pathway provides the timing information and guides the recorder. This information is called the absolute time in pregroove (ATIP). It ensures that data is recorded at a constant rate. The resulting data trail obliterates the wobble pregroove, leaving recorded data in its place.

Once the glass master has been written, it is tested, silvered, and ready to be electroplated. It is electrically conductive and is placed in a reservoir with an electrolyte solution containing a nickel salt. Current is applied to the glass master, eventually resulting in a metal layer on the glass after about 2 h. The nickel copy of the glass master is called the metal "father" and is used as a stamper to produce CD/Rs. If the replication run is large, the metal "father" is returned to the electroplating process for creation of metal "mothers," which are used to make metal "sons" identical to the fathers. These "sons" are then employed in the manufacture of "blank" CD/Rs.

Injection molding is employed to stamp out copies of the master discs from polycarbonate. The molded polycarbonate discs are cooled and hardened quickly, within about 4–6 sec, and evenly. The dye layer is then applied. The applied dyes are often proprietary and continually modified in an attempt to get a "better" dye. The dye must be compatible with the system and adhere to the polycarbonate base. It is applied by spin coating; i.e., the disc is spun and the dye is sprayed onto the surface. The dye is then dried and cured.

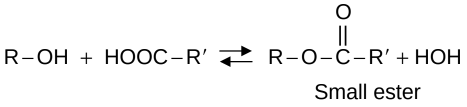
A metal layer is now added since the disc surface must reflect laser light. Aluminum is the most cost-effective and widely used for prerecorded discs but most CD/Rs use gold or silver because of their greater reflectivity. The gold or silver is applied using sputtering or vacuum deposition. A thin acrylic plastic layer is then applied by spin coating and cured in UV light to aid in the protection of the disc. An optional label layer can now be added. CD/Rs with this additional layer are stronger and appear to record better. The CD/Rs are now packaged, generally in lots of 10, 25, 50, and 100. The packaging is also plastic. My latest group of CD/Rs has a black PS base and a clear polypropylene cone. The bulk purchase price is about 5–10 cents per disc, on sale. In a glass case, the individual CD/Rs often cost about a dollar. Thus, for all the high technology required to produce a CD/R, it is inexpensive.

A laser is used to encode information through creation of physical features, sometimes referred to as "pits and lands" of different reflectivity at the polycarbonate–metal interface. As noted above, recordable CDs contain an organic dye between the polycarbonate and metal film. A laser creates areas of differing reflectiveness in the dye layer through photochemical reactions.

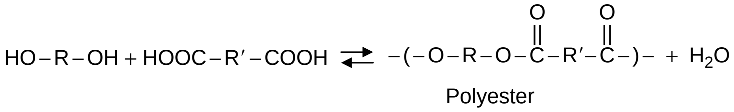
A beam from a semiconductor diode laser "interrogates" the undersides of both recordable and recorded CDs seeking out areas of reflected, corresponding to the binary "one," and unreflected, corresponding to the binary "zero," light. The ability to "read" information is dependent on the wavelength of the laser. Today, most of the CD players use a near-infrared laser because of the stability of such lasers. Efforts are underway to develop stable and inexpensive lasers of shorter wavelengths that will allow the holding of more information within the same space.

4.7 SYNTHETIC POLYAMIDES

Wallace Hume Carothers was brought to DuPont because his fellow researchers at Harvard and the University of Illinois called him the best synthetic chemist they knew. He started a program aimed at understanding the composition of natural polymers such as silk, cellulose, and rubber. Many of his efforts related to condensation polymers was based on his belief that if a monofunctional reactant reacted in a certain manner forming a small molecule (structure 4.53), similar reactions except employing reactants with two reactive groups would form polymers (structure 4.54):



$$R{-}OH + HOOC{-}R' \rightleftarrows \underset{\text{Small ester}}{R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'} + HOH \tag{4.53}$$



$$HO{-}R{-}OH + HOOC{-}R'{-}COOH \rightleftarrows \underset{\text{Polyester}}{-({-}O{-}R{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-})-} + H_2O \tag{4.54}$$

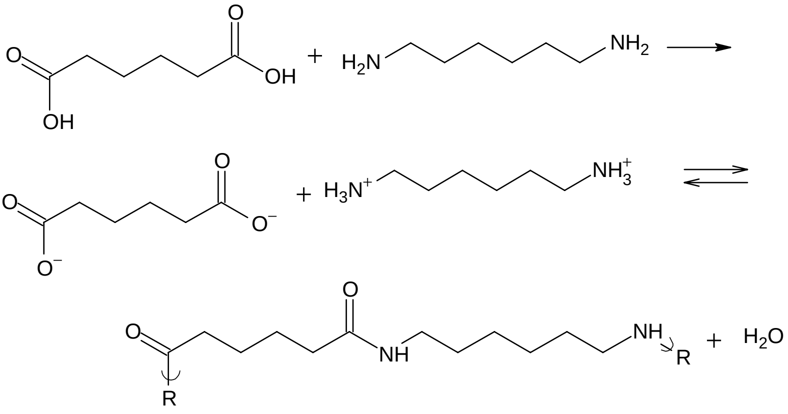
While Carothers' group had made both polyesters and polyamides, they initially emphasized work on the polyesters since they were more soluble and easier to work with. One of Carothers' coworkers, Julian Hill, noticed that he could form fibers if he took a soft polyester material on a glass stirring rod and pulled some of it away from the clump. Because the polyesters had too low softening points for use as textiles, the group returned to work with the polyamides. They found that fibers could also be formed by the polyamides similar to those formed by the polyesters. These polyamides allowed the formation of fibers that approached, and in some cases surpassed, the strength of natural fibers. This new miracle fiber was introduced at the 1939 New York World's Fair in an exhibit that announced the synthesis of this wonder fiber from "coal, air, and water"—an exaggeration but nevertheless eye-catching. When the polyamides, nylons, were first offered for sale in New York City, on May 15, 1940, nearly one million pairs were sold in the first few hours. Nylon sales took a large drop when it was noted that nylon was needed to produce the parachute material so critical to World War II.

The first polyesters produced by Carothers had relatively low molecular weights because of low fractional conversions. Carothers was successful in producing higher molecular weight polymers by shifting the equilibrium by removing the water produced. Structure 4.54 is an equilibrium process with the removal of water driving it toward polymer formation. However, these aliphatic polyesters, which he called "super polymers," lacked stiffening groups in the chain and thus had melting points that were too low for laundering and ironing.

Carothers' next step was to move from polyesters to nylons and to increase the fractional conversion (p) by making salts using the equivalent reaction of 1,6-hexanediamine (hexamethylenediamine) and adipic acid. These salts were recrystallizable from ethanol giving essentially a true 1:1 ratio of reactants. Thus, a high molecular weight polyamide, generally known as simply a nylon, in this case nylon-6,6, was produced from the thermal decomposition of this equimolar salt as shown in structure 4.55. This product has a melting point of 265°C.

Since the molecular weight of this nylon-6,6, produced by Carothers, was higher than he desired, 1% acetic acid (a monofunctional acid that acted to terminate chain growth) was added, resulting in a product with a lower molecular weight and a melting point of about 200°C.

Molded nylon-6,6 is used for lawn mower blades, bicycle wheels, tractor hood extensions, skis for snowmobiles, skate wheels, motorcycle crank cases, bearings, and electrical connections. Fiber nylon-6,6 is used in clothing, fabrics, and rugs:

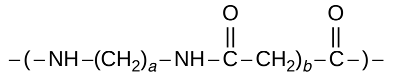


(4.55)

Nylon-6,6

In the early 1950s George deMestral, when he got home from his walk in the Swiss countryside, noticed that his jacket had lots of cockleburs on it. For some reason he examined the cockleburs and noticed that they had many tiny "hooks." His cotton jacket had loops that "held" the cockleburs. He began putting his observations into practice, making combinations of materials with rigid hooks with materials that had flexible loops or eyes. The initial hook and eye for commercial use was made in France. Today, Velcro, the name given to the hook-and-eye combination, is often based on nylon as both the hook and eye material. Remember that nylon can be made to behave both as a fiber and as a plastic. Polyester is blended with the nylon to make it stronger. Polyesters have also been employed to make hook-and-eye material. The hook-and-eye material is used to fasten shoes, close space suits, and in many other applications.

The general structure for aliphatic nylons for naming purposes is

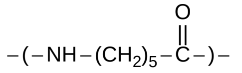


$$-(-NH-(CH_2)_a-NH-\overset{O}{\overset{\|}{C}}-CH_2)_b-\overset{O}{\overset{\|}{C}}-)- \qquad (4.56)$$

where *a* is the number of carbons derived from the amine-associated portion, and *b* is the number of carbons, including the carbonyl carbon atoms, associated with the diacid. Thus, nylon-6,6 has 6 carbons derived from hexamethylenediamine (*a* is 6) and 6 carbons derived from adipic acid.

Nylon-6,10 is derived from hexamethylenediamine and sebacic acid (dodeconic acid) and is more resistant to moisture and more ductile than nylon-6,6 because of the presence of the additional flexible nonpolar methylenes.

Nylon-6, structurally quite similar to nylon-6,6, was initially produced in Germany by the ROP of caprolactam, partly as a way to avoid the patents established by DuPont a decade earlier. The copolymer of nylon-6 and nylon-6,6 has a smoother surface than either of the homopolymers:



$$-(-NH-(CH_2)_5-\overset{O}{\overset{\|}{C}}-)- \qquad (4.57)$$

Nylon-6

Nylon-6,6 is the dominant (sales-wise) nylon in the United States while nylon-6 is the dominant nylon in Europe.

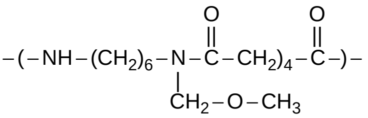
TABLE 4.5
General Physical Properties of Nylon 6,6 and Nylon 6

	Nylon 6,6	Nylon 6
Heat deflection temperature (1820 kPa; °C)	75	80
Maximum resistance to continuous heat (°C)	120	125
Crystalline melting point (°C)	265	225
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	8.0	8.0
Compressive strength (kPa)	1×10^5	9.7×10^4
Flexural strength (kPa)	1×10^5	9.7×10^4
Impact strength (Izod: cm-N/cm of notch)	80	160
Tensile strength (kPa)	8.3×10^4	6.2×10^4
Ultimate elongation (%)	30	—
Density (g/mL)	1.2	1.15

Table 4.5 contains general physical properties of nylon 6,6 and nylon 6. As expected, they are similar.

The properties of polyamides are improved by the formation of polyether blocks such as nylon block copolymer (NBC) and by blending with thermoplastics such as ethylene propylene diene monomer (EPDM), PET, PBT, and thermoplastic elastomer (TPE) (rubber-toughened nylons). NBC (Nyrim) is more expensive than reaction injection molding (RIM) PU, but it can be heated to 200°C without melting. NBC moldings are produced from the RIM of poly(propylene glycol) (and other elastomeric materials) and caprolactam. Nylon and the elastomeric materials are incompatible but they are chemically combined in the RIM process, giving a semicrystalline material with nylon and elastomeric blocks. Nyrim is referred to as a rubber-toughened recyclable nylon thermoplastic. Nyrim materials are used as dozer pads, skew blades, gears, half tracks, skew propellers, and as the tracks for swamp-going vehicles. The tendency of these moldings to swell in water is reduced by reinforcing them with fibrous glass. They differ from toughened nylons, which are blends and not chemically connected.

The ability to form strong hydrogen bonding is reduced, and the flexibility increased, by placing bulky methoxymethyl pendants onto nylons:



$$-(-NH-(CH_2)_6-\underset{\substack{|\\ CH_2-O-CH_3}}{N}-\overset{\substack{O\\ \|}}{C}-(CH_2)_4-\overset{\substack{O\\ \|}}{C}-)- \tag{4.58}$$

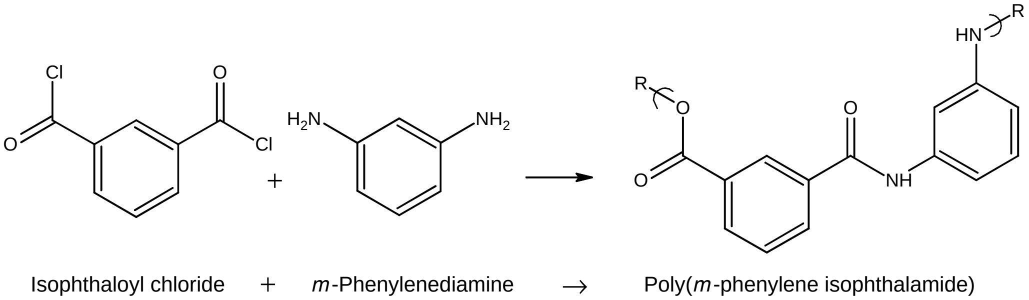
While aliphatic-containing polyamides are given the name nylons, those in which at least 85% of the amide groups are attached to an aromatic are called aramids. Aramids are stronger and tougher than nylons but they are also more difficult to solubilize and fabricate. Because the presence of the aromatic groups causes the aramids to be stiff, they often form liquid crystals (LCs) that are present in a nematic LC state in concentrated solution.

Aramids are generally prepared by the solution or interfacial polycondensation of meta- and para-substituted diacid chlorides and/or diamines. In some systems, synthesis is achieved under rapidly stirred conditions where the polymer is quasi-soluble in the system. The polymer mixture is forced through a small opening into a nonsolvent, forming a fiber without the need to dissolve the polymer before fiber formation. General properties of an amide such as Nomex are given in Table 4.6. Notice the generally higher "strength" values and the greater stiffness (less elongation) in comparison to nylon 6,6.

TABLE 4.6
General Physical Properties of a Typical Aramid

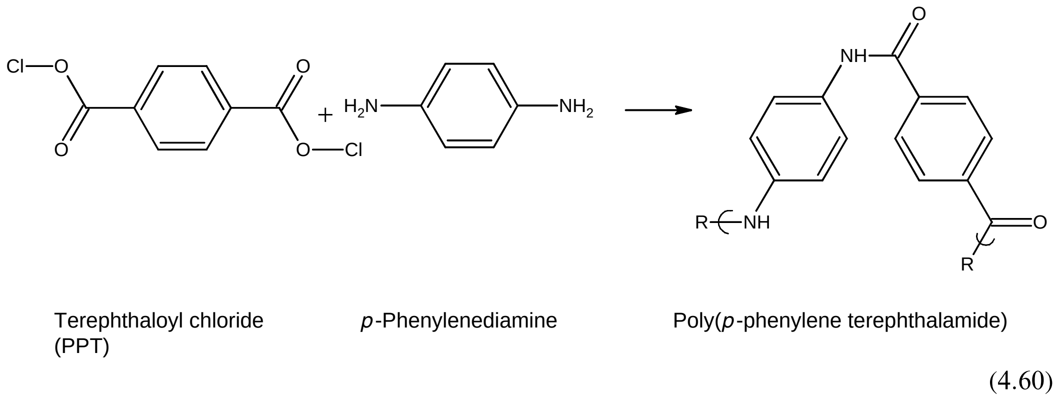
Heat deflection temperature (1820 kPa; °C)	260
Maximum resistance to continuous heat (°C)	150
Crystalline melting point (°C)	>370
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	2.6
Compressive strength (kPa)	2×10^5
Flexural strength (kPa)	1.7×10^5
Impact strength (Izod: cm-N/cm of notch)	75
Tensile strength (kPa)	1.2×10^5
Ultimate elongation (%)	5
Density (g/mL)	1.2

Poly(*m*-phenylene isophthalamide) (structure 4.59), sold under the trade name Nomex, exhibits good thermal stability decomposing above 370°C. It is used in flame-resistant clothing. It is also used in the form of thin pads to protect sintered silica-fiber mats from stress and vibrations during the flight of the space shuttle:



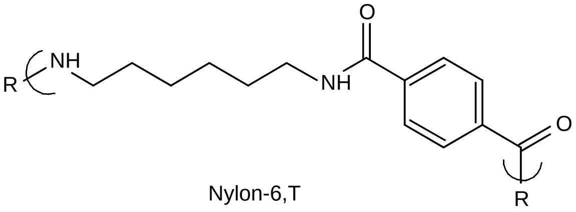
(4.59)

The corresponding aramid produced using the para-reactant in place of the meta-reactant gives poly(*p*-phenylene terephthalamide) (PPT) (structure 4.60), produced under the trade name Kevlor. It also exhibits good thermal stability, decomposing above about 500°C. By weight it has a higher strength and modulus than steel and is used in the manufacture of "bulletproof" clothing. Because of its outstanding strength, it was used as the skin covering of the Gossamer Albatross which was flown, using only human-power, across the English Channel. Aramids are also used as fiber reinforcement in composites and as tire cord.



(4.60)

Several so-called semiaromatic nylons have been produced. Nylon-6,T is produced from condensation of terephthalic acid and 1,6-hexanediamine (structure 4.61). Both reactants are readily available and inexpensive, and the resulting materials offer greater strength than simply wholly aliphatic nylons such as nylon-6,6. Nylon-6,T has a very high T_m of 370°C and a T_g of 180°C. The high T_m results in the need for a high temperature to be employed in processing so that a third reactant is often introduced to lower the T_m and the processing temperature. "Third reactants" often used are adipic acid, caprolactam, isophthalic acid, and 1,5-hexyldiamine. These materials are sold under the trade names Zytel HTN, Ultramid T, and Amodel R.



(4.61)

Nylons offered new challenges to the chemical industry. Because of the presence of polar groups the attractive forces between chains were high in comparison to vinyl polymers. Nylons are generally semicrystalline, meaning they have a good amount of order. Thus, while they have a T_g, the main physical transition is the T_m so that they undergo a sharper transition from solid to melt in comparison with many of the vinyl polymers discussed in the next three chapters. Thus, the processing temperature window is narrower. If melt flow is required for processing, the temperature must be sufficient to allow for ready flow but low enough so as not to break primary bonds within the processed material. Even so, processing techniques have been developed that allow nylons to be readily processed using most of the standard techniques.

Since chains of nylons having an even number of carbon atoms between the amide and acid groups pack better, some of their melting points are higher than comparable nylons with odd numbers of carbon atoms (Table 4.7). Further, the melting points decrease and the water resistance increases as the number of methylene groups between the amide and acid groups increases.

TABLE 4.7
Melting Point of Selected Polyamides

Aliphatic Nylons

Nylon	Melting Point (°C)	Nylon	Melting Point (°C)
3	320	11	190
4	265	12	185
5	270	46	275
6	225	56	225
7	227	66	265
8	195	410	240
9	200	510	190
10	185	610	230

Aromatic (Terephthalamides) Nylons

Diamine	Melting Point (°C)	Diamine	Melting Point (°C)
1,2-Ethylene	460	1,4-Tetramethylene	440
1,3-Trimethylene	400	1,5-Pentamethylene	350
		1,6-Hexamethylene	370

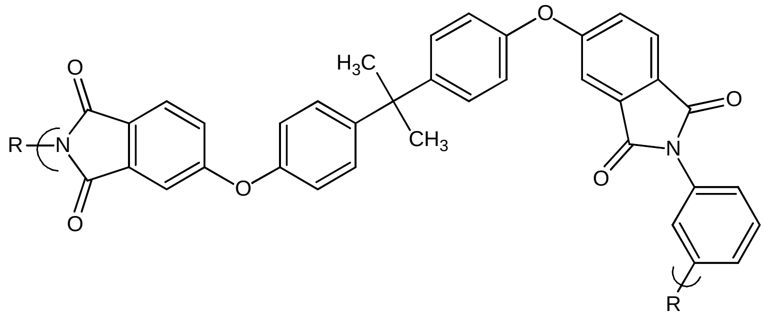
The presence of the polar groups results in materials with relatively high T_g and T_m values so that unlike most vinyl polymers that must be above their T_g to allow needed flexibility, nylons and many condensation polymers function best where strength, and not flexibility, is the desired behavior. Because of the presence of these polar groups, which also allow for hydrogen bonding, nylons and most condensation polymers are stronger, more rigid and brittle, and tougher in comparison to most vinyl polymers. Nylons are also "lubrication-free" meaning they do not need a lubricant for easy mobility so that they can be used as mechanical bearings and gears without the need for periodic lubrication.

In general, more crystalline nylons are used as fibers while less crystalline nylon materials are used as plastics. The amount of crystallinity is controlled through a variety of means including introduction of bulky groups and asymmetric units, rapid cooling of nonaligned melts, and introduction of plasticizing materials. The theme of using asymmetric units was used by Grace & Co. in developing Trogamid T, an amorphous transparent nylon, from the condensation of terephthalic acid with a mixture of 2,2,4- and 2,4,4-trimethylhexamethylene diamines.

4.8 POLYIMIDES

The initial announcement for the commercial preparation of polyetherimides (PEIs) was made by General Electric in 1982 under the trade name Ultem. The final reaction involves the imidization of a diacid anhydride through reaction with a diamine, here *m*-phenylenediamine (structure 4.62). The "ether" portion of the polymer backbone results from the presence of ether linkages within the diacid anhydride.

These products are high melting, offer good stiffness, transparency, impact and mechanical strength, high flame resistance, low smoke generation, and broad chemical resistance. Some of these properties are expected. The high flame resistance is at least in part derived from the presence of already partially or largely oxidized atoms in the product. The low smoke generation is partially derived from the largely cyclic structure, with other cyclic structures predictable from the product structure if exposed to sufficient heat. These cyclic structures often give products that are not evolved with good char formation when the material is exposed to ordinary flame conditions:



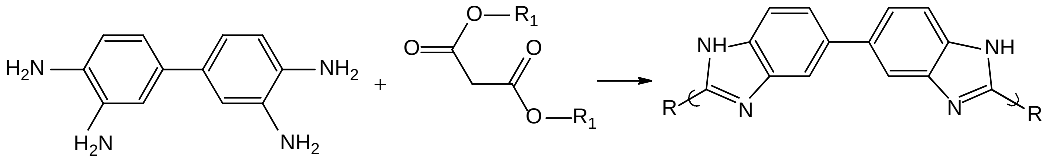
(4.62)

Polyetherimide

The general good mechanical properties are a result of the presence of strong double bonds within polycyclic structures composing the polymer backbone as well as the presence of strong polar bonding units that allow good interactions between chains. Further, the structure is largely rigid, with good dimensional stability along the polymer backbone. Any flexibility is gained largely from the presence of the ether linkages for the polyetherimides and the presence of methylene units for the polyimides. These products offer good stable melt viscosities even after recycling several times. They can be processed using a variety of techniques including formation of sections as thin as 5 mil.

4.9 POLYBENZIMIDAZOLES AND RELATED POLYMERS

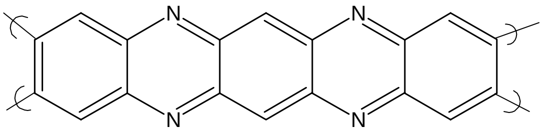
Many heterocyclic polymers have been produced in an attempt to develop high-temperature-resistant polymers for aerospace applications. Among these are the polybenzimidazoles (PBIs), which are prepared from aromatic tetramines and esters of dicarboxylic acids (structure 4.63). In standardized procedures, the reactants are heated to below 300°C forming soluble prepolymer, which is converted to the final insoluble polymer by further heating:



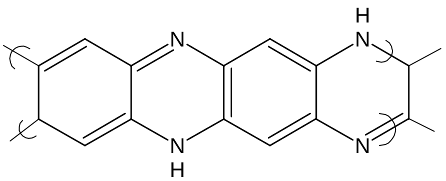
Tetraaminobiphenyl Dicarboxylic acid ester Polybenzimidazole

(4.63)

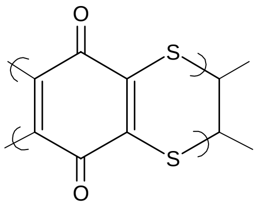
Polymers such as PBI have a weak link in them since a single covalent bond connects the phenyl rings in biphenyl. This weakness is overcome by the synthesis of ladder polymers, such as polyquinoxaline structures 4.64 and 4.65, and polydithione (structure 4.66), which have two covalent bonds throughout the chain. Thus, the integrity of the polymer is maintained even if one bond is broken:



Polyquinoxaline (4.64)



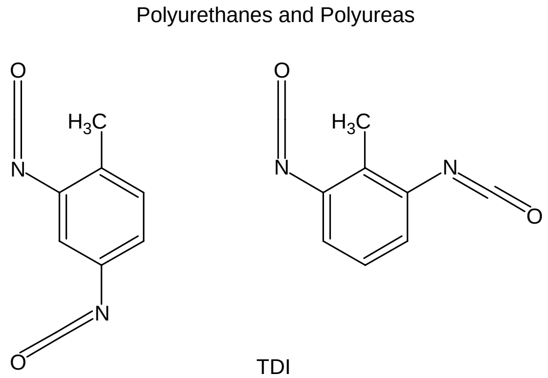
Polyquinoxaline (4.65)



Polydithione (4.66)

4.10 POLYURETHANES AND POLYUREAS

PUs, or polycarbamates, were first made by Bayer, reacting diols and diisocyanates. PUs are generally sold as flexible foams, rigid foams, and elastomers. Elastomer PU materials are used as adhesives, coatings, and sealants. The basic reactants for these materials are diisocyanates and HO-containing reactants including macroglycols called polyols. As expected, more flexible materials are made as the distance between the diol is larger and occupied by methylene and alkylene oxide moieties. Typical diisocyanates are tolyene diisocyanate (TDI; mixture of two isomers), methylene diphenyl isocyanate (MDI), and polymeric methylene diphenyl isocyanate (PMDI) mixtures formed from phosgenating polyamines derived from the reaction of aniline with formaldehyde (Figure 4.6). The aromatic unit provides stiffness to the polymer chain.



TDI

(4.67)

MDI and PMDI are both formed from the same reaction as shown in Figure 4.6.

The hydroxyl-containing reactants are polyesters, polyethers, polycaprolactones, and diols. The manufacture of the polyether and polycaprolactone macroglycols is given in Figure 4.7.

Flexible foams are generally made from TDI and longer chained polyether triols. Trifunctional reactants are needed to produce a three-dimensional product. These foams are generally water-blown meaning that water is added that reacts with isocyanate end groups, producing carbon dioxide gas giving open-celled foam products. Isocyanates react with water, producing unstable carbamic acids that decompose forming diamines and carbon dioxide. Low-density flexible foams are used in bedding applications and furniture while higher-density foams are used in automotive seating and semiflexible foams are

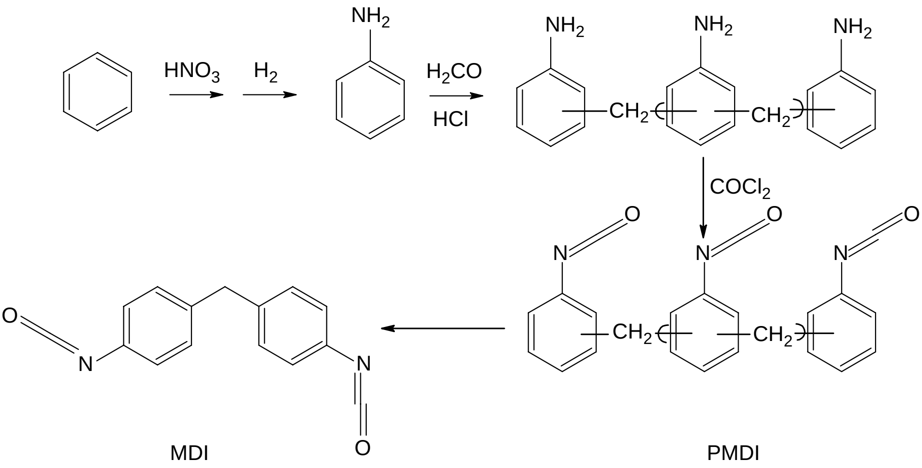


FIGURE 4.6 Synthesis of PMDI and MDI.

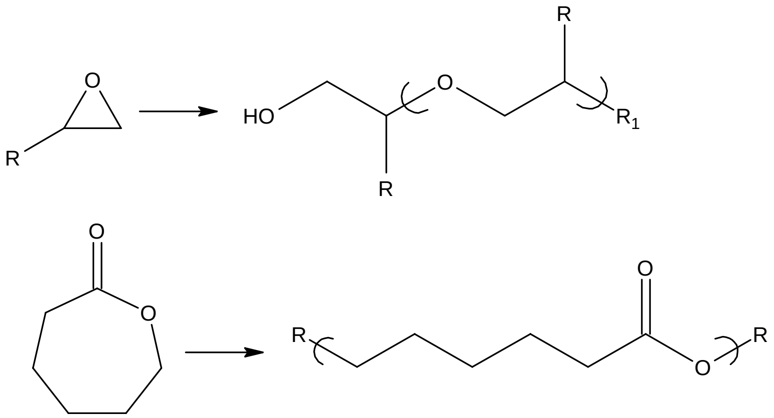


FIGURE 4.7 Synthesis of polyether and polycaprolactone macroglycols.

employed in automotive interior padding. Some of the flexible foams are used as carpet underlay material.

Most rigid foam is made from PMDI and difunctional polyether polyols. The PMDI provides the needed additional functionality, offering an average functionality of 2.7 resulting in the formation of three-dimensional products. At times, the overall functionality is increased by introduction of polyols with a functionality greater than 2. The resulting foams are close-celled with outstanding insulation properties. These foams are used as commercial insulations in the construction and transportation industries. They can be used as a spray-on product for insulating pipes and tanks as well as in construction in places where insulation is needed.

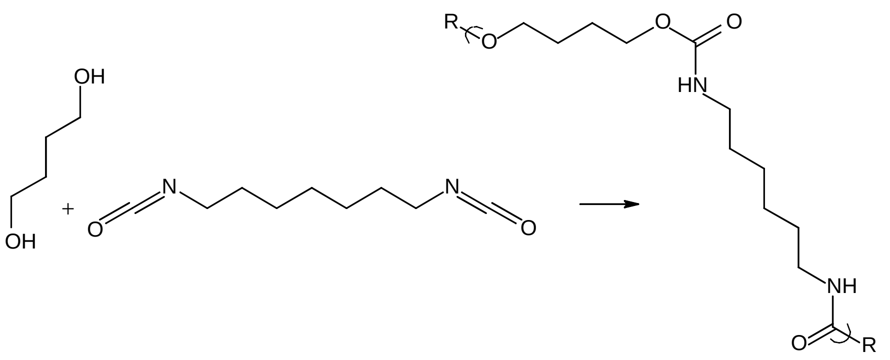
Notice that open-celled products are employed where ready flexibility, or softness, is needed while close-cell products are used when insulation is needed. Close-celled materials retain heat or cold while open-celled products allow rapid heat exchange to occur.

Cross-linked PU coatings, elastomers, and foams can be produced using an excess of the diisocyanate, which reacts with the urethane hydrogen producing an allophanate, or by incorporating polyols such as glycerol in the reaction mixture. Larger polyols called macroglycols are used to form segmented products including Spandex, which is used for clothing and undergarments. These products are one basis for segmented elastomers where aromatic PUs that form hydrogen bonding act as the "hard" segment, and the polyols such as poly(ethylene glycol) form the "soft" segment. These segmented PUs can be thermoplastics or thermosets depending on whether or not cross-linking is introduced.

RIM is increasing in importance and emphasizes the production of thermoset PUs. Here, liquid monomers are mixed together under high pressure prior to injecting into the mold. Polymerization occurs within the mold. Most automotive dash panels are RIM-produced. Notice the tough surface and semiflexible underbelly of the dash. The amount of "foam" formation is controlled to give the finished product.

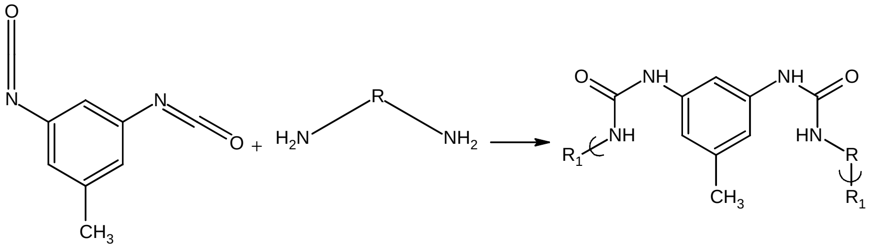
PUs are also widely used as coating materials sold as finished polymers, two-part systems, and prepolymer systems. Water-based PU systems are now available allowing easy home use. Aromatic diisocyanate-derived coatings generally offer poor external light stability while aliphatic-derived systems offer good light stability.

The nonaromatic PU shown in structure 4.68 is sold under the trade name Perlon U. As in the case with nylons and polyesters, higher melting products are formed when the number of carbon atoms is even since this allows a closer packing of the chains.



(4.68)

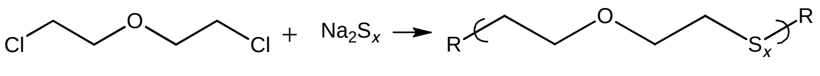
Polyureas (structure 4.69) are made similar to PUs, except that diamines are employed in place of alcohols.



(4.69)

4.11 POLYSULFIDES

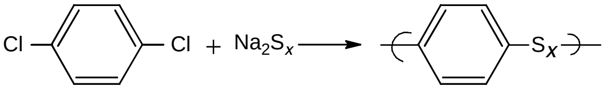
Thiokol (structure 4.70), which was the first synthetic elastomer, was synthesized by Patrick in the 1920s, by the condensation of alkylene dichlorides and sodium polysulfides. These solvent-resistant elastomers have limited uses because of their foul odor. They can be reduced to liquid polymers that can be reoxidized to solid elastomers, which is used in caulking material and some rocket propellant formulations:



(4.70)

Because natural sulfur has eight sulfur atoms contained within each molecule, the number of sulfur atoms generally varies between 1 and 8.

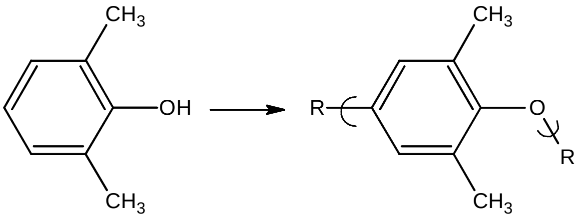
Poly(phenylene sulfide) (PPS; Ryton) is a solvent-resistant plastic that is useful in high-temperature service (structure 4.71). PPS is used for pumps, sleeve bearing, cookware, quartz halogen lamp parts, and electrical appliance housings.



(4.71)

4.12 POLYETHERS AND EPOXYS

Hay, in 1956, discovered an oxidative coupling catalyst that allowed the production of polymeric aromatic ethers. The hope was to make polymers from readily available starting materials, mainly phenol. The main aromatic polyether today is derived not from phenol but rather from the catalytic coupling of 2,6-dimethylphenol. The resulting poly(phenylene ether) (PPE) or PPO was given the name Noryl by General Electric. PPO is made by a room temperature oxidation brought about by bubbling oxygen through a solution of the phenol in the presence of copper (I) chloride and pyridine. Initially, there was no ready, inexpensive source of 2,6-dimethylphenol but because of the timely discovery of the positive properties of PPO, an inexpensive source of 2,6-dimethylphenol was found and both the monomer and polymer were commercialized in 1964.



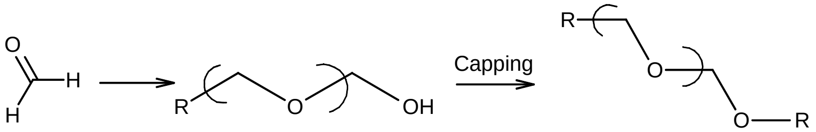
(4.72)

PPO has a very high T_g of 215°C and T_m of about 270°C, exhibits good hydrolytic stability, but has a very high melt viscosity and a tendency to oxidize and gel at processing temperatures (Table 4.8). In spite of these negative processing features, PPO shows good compatibility with PS and has therefore found a place in the marketplace. While the methyl groups discouraged good interactions between PPO chains, the aromatic character positively interacts with the phenyl group on the PS, and the methyl groups interact positively with the aliphatic PS backbone. The Noryl trade name covers a variety of related PPOs. PPO resins are the most important materials for forming blends and alloys with PS and styrene derivatives. These blends and alloys with PS raise the heat distortion temperature to over 100°C, allowing production of materials that can be boiled. Combinations with PS are more easily processed and the PPO imparts the needed flame resistance. The combinations also offer good hydrolytic stabilities and electrical properties, and they are relatively lightweight. They can also be modified by addition to glass and other mineral fillers, and are especially adaptable to metallizing. PPO-extruded sheet is used for solar energy collectors, lifeguards on broadcasting towers, airline beverage cases, and window frames.

TABLE 4.8
General Physical Properties of Poly(Phenylene Oxide) (PPO)

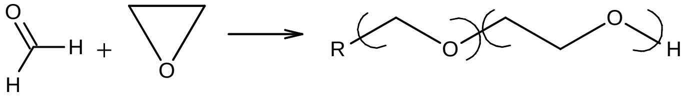
Heat deflection temperature (1820 kPa; °C)	100
Maximum resistance to continuous heat (°C)	80
Crystalline melting point (°C)	215
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	5.0
Compressive strength (kPa)	9.6×10^4
Flexural strength (kPa)	8.9×10^4
Impact strength (Izod: cm-N/cm of notch)	270
Tensile strength (kPa)	5.5×10^4
Ultimate elongation (%)	50
Density (g/mL)	1.1

Aliphatic polyethers are also referred to as polyacetals. Polyoxymethylene, POM, precipitates spontaneously from uninhibited aqueous solutions of formaldehyde and was isolated by Butlerov in 1859. Staudinger, in the 1920s and 1930s, experimented with the polymerization of formaldehyde but failed to produce chains of sufficient length to be useful. While pure formaldehyde readily polymerized, it also spontaneously depolymerized, unzippers. In 1947 DuPont began a program to make useful polymers from formaldehyde since formaldehyde is inexpensive and readily available. After 12 years DuPont announced the commercialization of the polymer from formaldehyde, POM, under the trade name Delrin. The "secret" was capping the end groups by acetylation of the hydroxyl end groups, thus preventing the ready unzipping of the polymer chain (structure 4.73). POM has a T_g of -75°C and a T_m of 180°C. General physical properties are given in Table 4.9:



(4.73)

Celanese came out a year later with a similar product under the trade name Celcon. Celanese circumvented DuPont's patent on the basis of employing a copolymer variation that allowed enhanced stabilization against thermal depolymerization (structure 4.74). The copolymer has a T_m of 170°C:



(4.74)

Polyacetals and other engineering plastics cost about half that of cast metals, and are therefore used as replacements for cast metal–intense applications. They have been approved by the Food and Drug Administration for contact with foods. Some of the uses of molded polyacetals are as valves, faucets, bearings, appliance parts, springs, automotive window brackets, hose clamps, hinges, video cassettes, tea kettles, chains, flush toilet float arms, gears, shower heads, pipe fittings, pasta machines, desktop staplers, and air gun parts.

POMs are also employed in plumbing and irrigation because they resist scale accumulation, and have good thread strength, torque retention, and creep resistance. POMs are also

TABLE 4.9
General Physical Properties of POM and Epoxy Resins

	POM	Epoxy Resins
Heat deflection temperature (1820 kPa; °C)	125	140
Maximum resistance to continuous heat (°C)	100	120
Crystalline melting point (°C)	180	—
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	10.0	2.5
Compressive strength (kPa)	1.1×10^5	1.2×10^5
Flexural strength (kPa)	9.7×10^4	1.2×10^5
Impact strength (Izod: cm-N/cm of notch)	80	50
Tensile strength (kPa)	6.9×10^4	5.1×10^4
Ultimate elongation (%)	30	5
Density (g/mL)	1.4	1.2

employed to assist in the flow of water in fire hoses, water displays, and for some large ships it is “squirted” from the front of the ship to cut down on friction because they help align the water, allowing increased fuel efficiency.

POMs are resistant to many solvents including aqueous salt and alkaline solution, as well as weak acids.

Epoxy resins are really polyethers but are named epoxies because of the presence of epoxide groups in the starting material. They were initially synthesized from epichlorohydrin and bisphenol A in the 1940s. General properties are listed in Table 4.9.

The reaction is generally carried out in the presence of a base such as sodium hydroxide. Bisphenol A is a phenol and, as such, a weak acid. The generated RO$^-$ reacts with the electron-poor chlorine-containing carbon on epichlorohydrin, creating a cyclic ether end group. The phenoxy moiety can also react with the cyclic ether, eventually forming the polyether structure. This sequence is described in Figure 4.8.

High molecular weight thermoplastics called phenoxy resins are formed by the hydrolysis of the epoxy resins so that no epoxy groups are present. These transparent resins can be further reacted, forming cross-linked material through reaction of the hydroxyl pendant groups with diisocyanates or cyclic anhydrides.

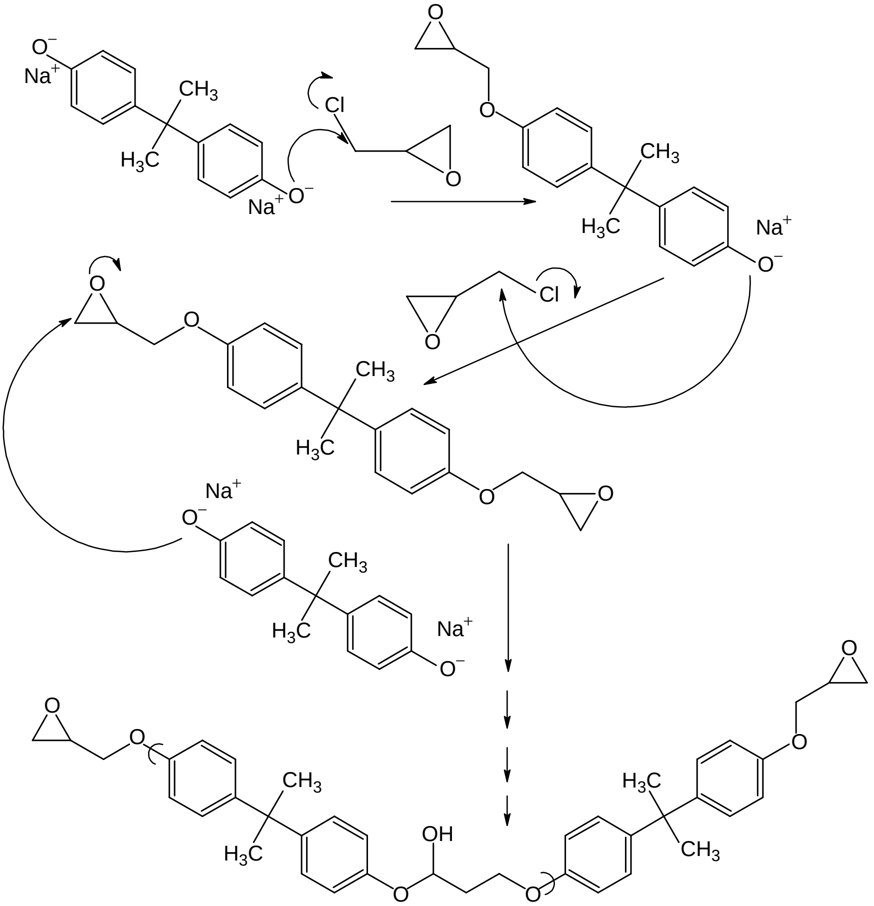


FIGURE 4.8 Mechanistic outline for the formation of epoxy resins.

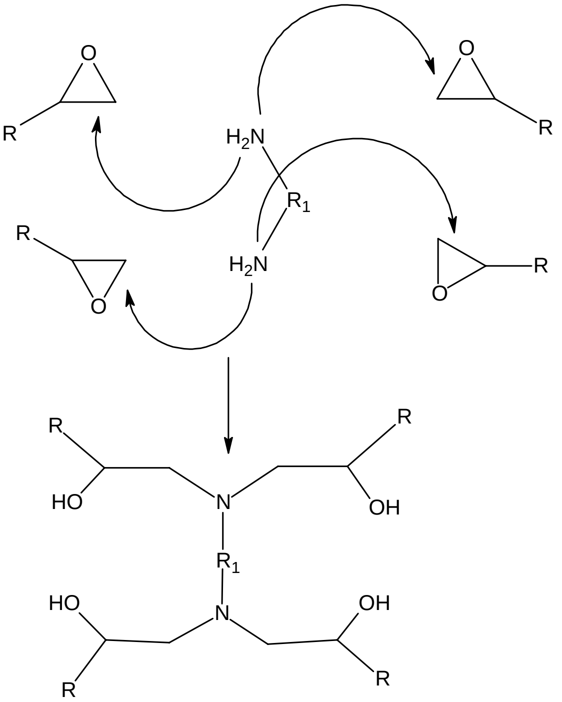


FIGURE 4.9 Curing of two-part epoxy resin adhesives.

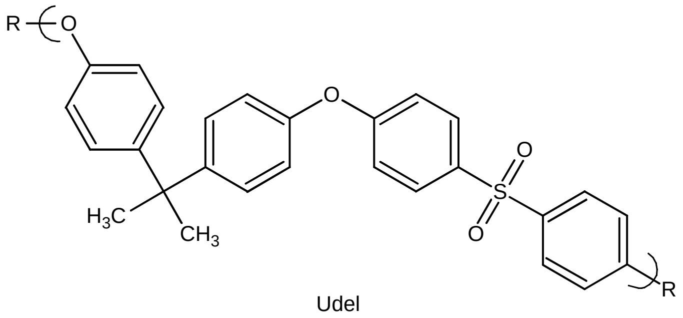
The $\overline{DP}$ is dependent on the ratio of reactants. Generally an excess of the epichlorohydrin is used to produce cyclic ether end groups. Epoxies are formed from the reaction of diamines with low molecular weight epoxy resins that retain their cyclic ether end groups. Figure 4.9 shows the formation of this process. These materials are often sold as two-part, or two-pot, epoxy adhesives. Most "use-at-home" epoxy packages contain a part A of epoxy resin and a part B of hardener (typically a diamine). These two are mixed as directed and applied. They dry fast, so they can be handled in 5–10 min. Full strength occurs after 5–7 days.

These cross-linked, cured epoxies have outstanding resistance to chemicals, durability, and toughness, making them good coating materials. They are easily poured, prior to hardening, without bubble formation and are used for encapsulating electrical wires and electrical components for televisions and computers. As adhesives epoxies have good metal adhesion, and are therefore used to join automotive hoods and doors. They are also used in aerospace composites, batteries, as well as sporting and hardware goods.

There are also one-part adhesives based on low molecular weight epoxy units that contain the unopened cyclic ether end groups. These materials can be cured when heated to about 200°C for 30–60 min.

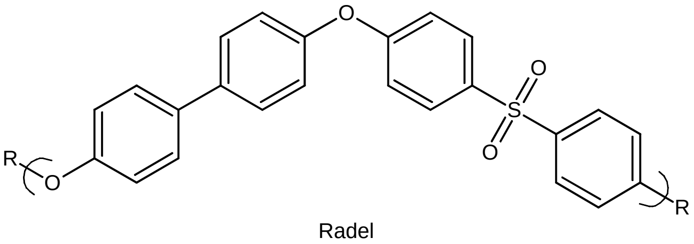
4.13 POLYSULFONES

Polysulfones exhibit excellent thermal oxidative resistance, and resistance to hydrolysis and other industrial solvents, and creep. The initial commercial polysulfones were synthesized by the nucleophilic replacement of the chloride on bis(*p*-chlorophenyl) sulfone by the anhydrous sodium salt of bisphenol A. It became commercially available in 1966 under the trade name Udel. It exhibits a reasonably high T_g of 190°C.



(4.75)

Union Carbide, in 1976, made available a second generation polysulfone under the trade name Radel. Radel was formed from the reaction of a bisphenol and bis(*p*-chlorophenyl) sulfone (structure 4.76). This polysulfone exhibits greater chemical and solvent resistance, greater T_g of 220°C, greater oxidative stability, and good toughness in comparison to Udel.



(4.76)

Polysulfones can also be made from the Friedel–Crafts condensation of sulfonyl chlorides. Polysulfones are used for ignition components, hair dryers, cookware, and structural foams. Because of their good hydrolytic stability, good mechanical properties, and high-thermal endurance they are good candidate materials for hot water and food-handling equipment, alkaline battery cases, surgical and laboratory equipment, life support parts, autoclavable trays, tissue culture bottles, and surgical hollow shapes, and film for hot transparencies. Their low flammability and smoke production, again because of their tendency for polycyclic formation on thermolysis and presence of moieties that are already partially oxidized, makes them useful as materials for the aircraft and automotive industries. General properties of PPS are given in Table 4.10.

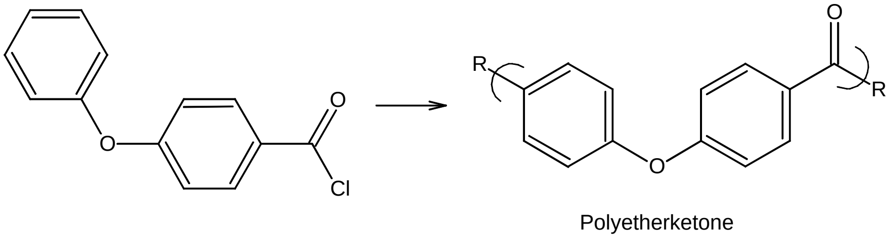
TABLE 4.10
General Physical Properties of PPS

Heat deflection temperature (1820 kPa; °C)	135
Maximum resistance to continuous heat (°C)	110
Crystalline melting point (°C)	190
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	5.0
Compressive strength (kPa)	1.1×10^5
Flexural strength (kPa)	9.6×10^5
Impact strength (Izod: cm-N/cm of notch)	21
Tensile strength (kPa)	7.4×10^4
Ultimate elongation (%)	1.1
Density (g/mL)	1.3

4.14 POLY(ETHER KETONE) AND POLYKETONES

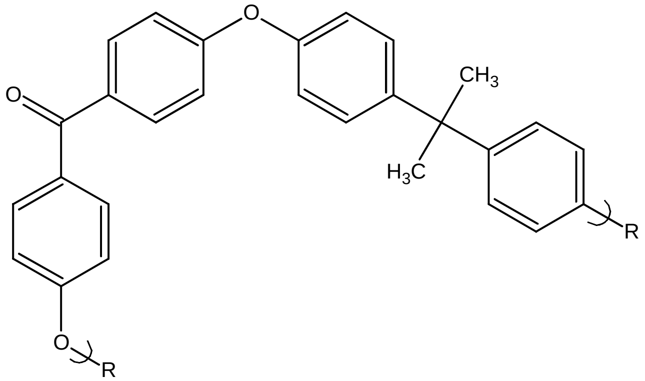
Aromatic polyketones are semicrystalline materials that contain both ketone groups generally flanked by aromatic units. Many also have within them ether moieties that allow for some flexibility and better processing. They have good thermal stabilities, as well as offering good mechanical properties, flame resistance, impact resistance, and resistance to the environment.

Polyetherketone (PEK) was introduced by Raychem in the 1970s (Equation 4.77). It is made by the Friedel–Crafts reaction requiring good solvents or an excess of aluminum chloride to keep the polymer in solution, allowing polymer growth to occur. Most polymerizations require that the reactants remain mobile, through solution or by melting, so that the individual units involved in the reaction can get together. Rapid precipitation of growing polymer chains often results in the formation of only oligomeric to small chains.



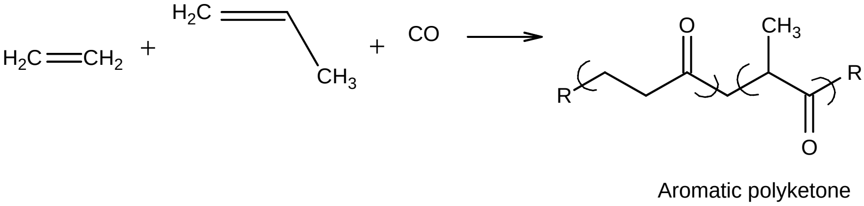
(4.77)

Imperial Chemical Industries has introduced a new crystalline poly(ether ether ketone) (PEEK) (structure 4.78). Applications are for compressor plates, valve seats, thrust washers, bearing cages, and pump impellers. In the aerospace industry it is employed as aircraft fairing, fuel valves, and ducting. It is also used in the electrical industry as wire coating and semiconductor wafer carriers.



(4.78)

Aliphatic polyketones are made from the reaction of olefin monomers and carbon monoxide using a variety of catalysts. Shell commercialized a terpolymer of carbon monoxide, ethylene, and a small amount of propylene in 1996 under the trade name Carilon (structure 4.79). They have a useful range between the T_g (15°C) and T_m (200°C) that corresponds to the general useful range of temperatures for most industrial applications. The presence of polar groups causes the materials to be tough, with the starting materials readily available.

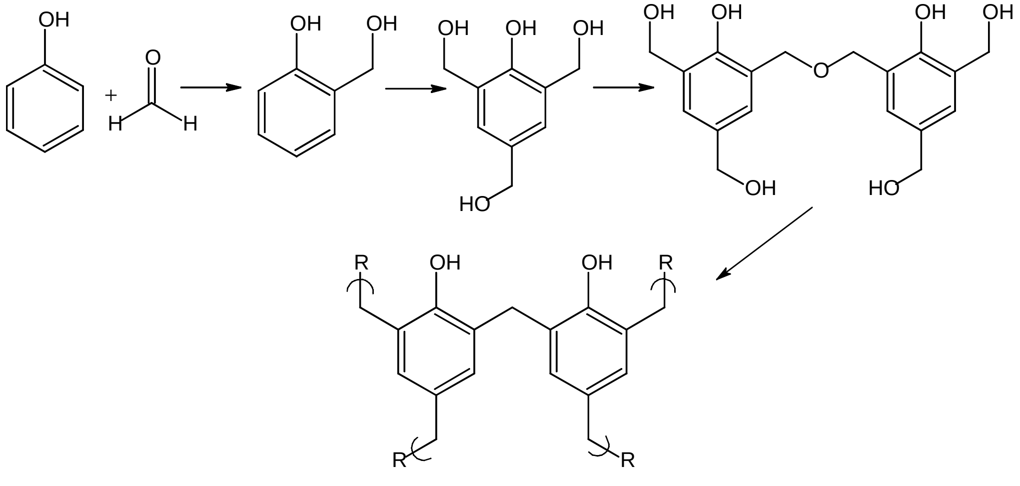


Aromatic polyketone

(4.79)

4.15 PHENOLIC AND AMINO PLASTICS

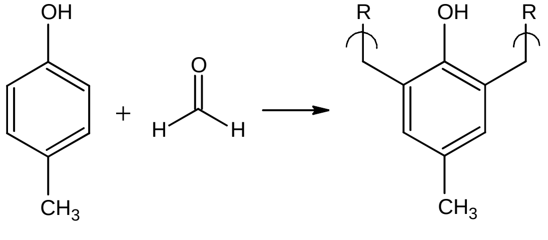
Baekeland found that a relatively stable resole prepolymer could be obtained by the controlled condensation of phenol and formaldehyde under alkaline conditions. These linear polymers of phenol–formaldehyde (PF) may be converted to infusible cross-linked polymers called resites by heating or by the addition of mineral acids. As shown in structure 4.80, the initial products obtained when formaldehyde is condensed with phenol are hydroxybenzyl alcohols. The linear resole polymer is called an A-stage resin, and the cross-linked resite is called a C-stage resin.



C-stage (resite resin)

(4.80)

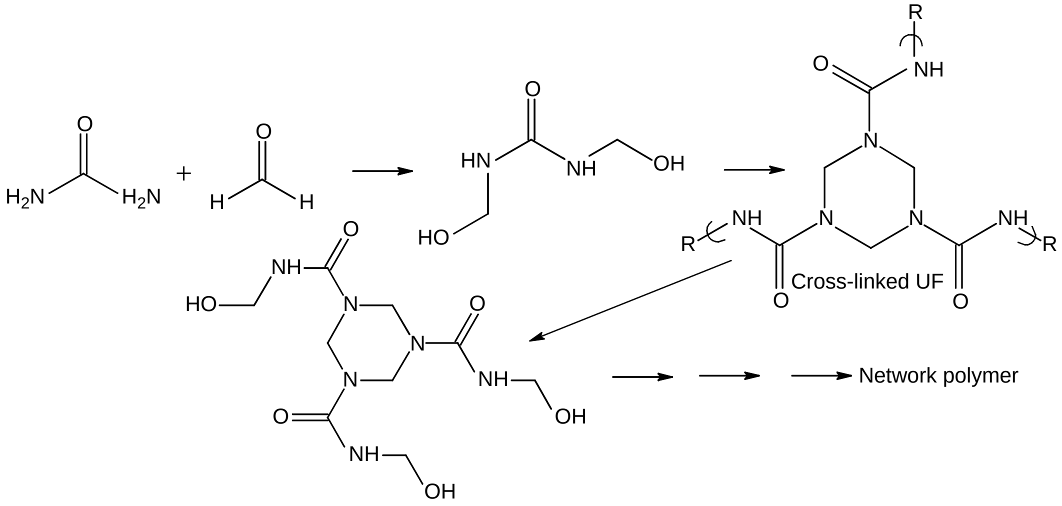
Baekeland recognized that the trifunctional phenol would produce network polymers and therefore used difunctional ortho- or para-substituted phenols to produce linear paint resins. Linear thermoplastic products are formed by alkaline or acid condensation of formaldehyde with phenol derivatives such as *p*-cresol (structure 4.81).



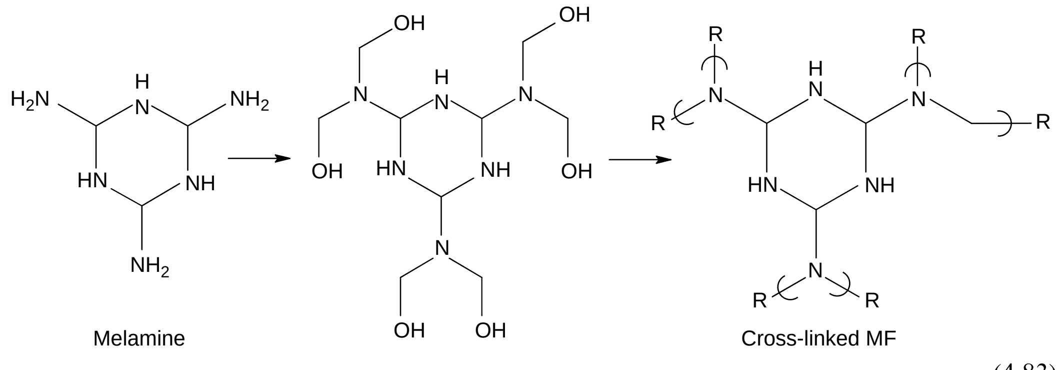
(4.81)

Since the acid condensation of 1 mol of phenol with 1.5 mol of formaldehyde produced thermoset C-stage products, Baekeland reduced the relative amount of formaldehyde and made useful novolac resins in a two-step process. Thus, stable A-stage novolac resin is produced by heating 1 mol of phenol with 0.8 mol of formaldehyde in the presence of acid. After removal of water by vacuum distillation, the A-stage resin produced is cooled and then pulverized. The additional formaldehyde required to convert this linear polymer into a thermoset resin is supplied by hexamethylenetetramine. The latter, which is admixed with the pulverized A-stage resin, is produced by the condensation of formaldehyde and ammonia. Other ingredients such as filler, pigments, and lubricants are mixed in with the resin and hexamethylenetetramine. The A-stage resin is further polymerized. The term phenol-molding compound is applied to the granulated B-stage novolac resin.

While the condensation of urea and formaldehyde was described in 1884, urea–formaldehyde (UF) resins were not patented until 1918. Comparable products, based on the condensation of formaldehyde and melamine (2,4,6-triamino-1,3,5-triazine), were not patented until 1939. The term MF (structure 4.83) is used to describe these products.



(4.82)



(4.83)

Urea and melamine are tetra- and hexa-functional molecules. However, the formation of a network polymer is prevented by adding alcohols such as *n*-butanol and by condensing with formaldehyde at low temperatures under basic conditions. While phenol resins have better moisture and weather resistance than urea resins, the latter are preferred for light-colored

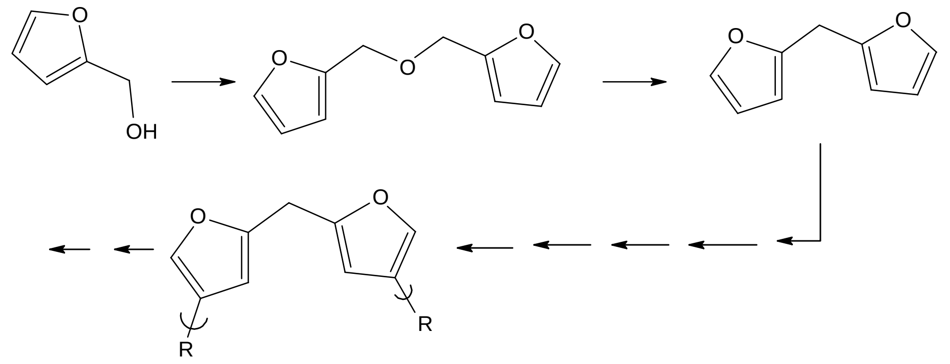


FIGURE 4.10 Synthesis of furan resins from furfuryl alcohol.

objects. For example, the interior layers of laminated countertops are bonded together by phenolic resins, but either urea or melamine resins are used for the decorative surface. Melamine plastics are more resistant to heat and moisture than UF and thus, are used for decorative surfaces and for dinnerware.

4.16 FURAN RESINS

Furan resins are produced by the polymerization of furfural or furfuryl alcohol in the presence of acids (Figure 4.10). Furan resins are deep brown in color and have a relatively low heat deflection temperature (80°C) and good mechanical properties. They are used as joining materials for brick and tile. They have excellent resistance to nonoxidizing acids, bases, and salts but are degraded by the presence of oxidizing acids such as nitric acid. They are resistant to nonpolar and most polar solvents at room temperature. Many of these are further reacted giving cross-linked thermoset materials. Since the furan starting materials are generally derived from vegetable matter they are classified as a green chemistry polymer.

4.17 SYNTHETIC ROUTES

The previous sections describe the synthesis of a number of important condensation polymers. Here, we will briefly consider the three main synthetic techniques utilized in the synthesis of these polymers.

The "melt technique" is also called other names to describe the same or similar processes including high melt, bulk melt, and simply bulk or neat. The melt process is an equilibrium-controlled process in which polymer is formed by driving the reaction toward completion, usually by removal of the by-product. For polyesterifications involving the formation of hydrogen chloride or water, the driving force is the removal of the hydrogen chloride or water. Reactants are introduced along with any added catalyst to the reaction vessel. Heat is applied to melt the reactants, allowing them to condense together. The heat is maintained or increased above this melt temperature. Pressure is reduced to remove the condensate. Typical melt polymerizations take several hours to several days before the desired polymer is produced. Yields are necessarily high.

"Solution condensations" are also equilibrium processes, with the reaction often driven by removal of the by-product through distillation, salt formation, or precipitation. Many solution condensations are carried out near room temperature. Solvent entrapment is a problem, but since a reaction may occur under considerably reduced temperatures, compared to the melt process, thermally induced side reactions are minimized. Side reactions with the

TABLE 4.11
Comparison of Requirements for Different Polycondensation Techniques

Requirement	Melt	Solution	Interfacial
Temperature	High	Limited only by the MP and BP of the solvent used—generally about room temperature	
Stability to heat	Necessary	Unnecessary	Unnecessary
Kinetics	Equilibrium, stepwise	Equilibrium, stepwise	Generally nonequilibrium, chainwise
Reaction time	1 h to several days	Several minutes to 1 h	Several seconds to 1 h
Yield	Necessarily high	Less necessarily high	Low to high
Stoichiometric Equivalence	Necessarily high	Less necessarily high	Less necessary
Purity of reactants	Necessary	Less necessary	Less necessary
Equipment	Specialized, often sealed	Simple, open	Simple to complex, can be open
Pressure	High, low	Atmospheric	Atmospheric

solvent may be a problem. Because the reactants must be energetic, many condensations are not suitable for the solution technique.

The "interfacial technique", while old, gained popularity with the work of Morgan and Carraher in the 1960s and 1970s. Many of the reactions can be carried out under essentially nonequilibrium conditions. The technique is herterophasic, with two fast-reacting reactants dissolved in a pair of immiscible liquids, one of which is usually water. The aqueous phase typically contains the Lewis base such as diol, diamine, or dithiol. The organic phase contains the Lewis acid, generally an acid halide, dissolved in a suitable organic solvent such as hexane. Reaction occurs near the interface, hence the name. With all the potential that the interfacial system offers, it has not attracted wide industrial use because of the high cost of the necessarily reactive monomers as well as of solvent removal. One commercial use for the interfacial technique is the production of polycarbonates. Another involves the synthesis of aramids. Morgan and others noted that some polymers formed with rapid stirring remained in solution for a while before they precipitated. The problem with aramids was the need to form fibers from their solutions. Thus, the aromatic nylons had to be redissolved after formation. Today, aramids are synthesized using rapidly stirred systems where the polymer solution is sent through a small hole into a nonsolvent. This allows fibers to be produced without needing to redissolve the polymer.

Table 4.11 contains a comparison of these three major polycondensation processes.

4.18 LIQUID CRYSTALS

Every day of our lives we "run across" LCs. They are commonly found in computer monitors, digital clocks, television screens, and other "read-out" devices.

Reintzer, in 1888, first reported "liquid crystal" behavior. In working with cholesteryl esters, he observed that the esters formed opaque liquids, which turned clear on heating. We now know that as a general rule many materials are clear if they are anisotropic, random, or if they are composed of ordered molecules or segments of molecules, whereas they are opaque if there exists a mixture of ordered and disordered regions. Lehmann interpreted this behavior as evidence of a "third" phase that exists "between" the solid and isotropic liquid states. He named this new phase the liquid crystal phase. Friedel called this phase the mesophase after the Greek *mesos* meaning intermediate. The initial molecules investigated as LCs were large monomeric molecules.

Flory, in 1956, predicted that solutions of rodlike polymers could also exhibit LC behavior. The initial synthetic polymers found to exhibit LC behavior were concentrated solutions of poly(gamma-benzyl glutamate) and poly(gamma-methyl glutamate). These polymers exist in a helical form that can be oriented in one direction into "ordered groupings," giving materials with anisotropic properties.

LCs are materials that undergo physical reorganization in which at least one of the rearranged structures involve molecular alignment along a preferred direction, causing the material to exhibit nonisotropic behavior and associated birefringent properties, i.e., molecular asymmetry.

Liquid crystalline materials can be divided into two large groupings: thermotropic and lyotropic. Thermotropic LCs are formed when "pure" molecules such as cholesteryl form ordered structures upon heating. When LCs occur through mixing with solvents they are called lyotropic LCs.

Thermotropic LCs can be further divided into (a) enantiotropic materials, in which the LC phases are formed on both heating and cooling cycles, and (b) mesotropic materials, in which the LCs are stable only on supercooling from the isotropic melt. Mesotropic LCs have been further divided into three groupings as follows:

- Smectic, meaning "soap"
- Nematic, meaning "thread"
- Cholesteric, derived from molecules with a chiral center

LC polymers are typically composed of materials that are rigid and rodlike with a high length/breadth ratio or materials that have a disc shape. The smaller groupings that give the material LC behavior are called "mesogens." These mesogens are simply portions of the overall polymer that are responsible for forming the anisotropic LC and that, in fact, form the LC segments. Such mesogens can be composed of only segments from the backbone of the polymer, segments from the side chain, or segments from both the backbone and side chain.

Mesogens form the ordered structures necessary to give the overall material anisotropic behavior. A number of different mesogen groupings have been identified. Chains arranged so that the mesogen portions are aligned in one preferred direction, with the ordering occurring in a three-dimensional layered fashion, compose one group of arrangements called smectic arrangements. Here, the lateral forces between the mesogen portions are relatively higher than the lateral forces between the nonmesogen portions, allowing a combination of segments that permit "flowing" (the passage of nonmesogen portions) and segments that retain contact (mesogen portions) as the material flows imparting a "memory"-type behavior of the material. A number of different "packings" of the mesogens have been identified (Figure 4.11). The most ordered of the mesogenic groupings is called "smectic B," which is a hexagonal, close-packed structure present in a three-dimensional arrangement. A much less-ordered grouping is called the "smectic A" phase, in which there is a somewhat random distribution of the mesogens between the layers.

Nematic LCs offer much less order in comparison to smectic arrangements. Here, the directional ordering of the mesogen portions along one axis is retained, but the centers of gravity of the mesogen portions are no longer "coupled." Thus, the forces between the chains are less, resulting in a generally greater fluidity for nematic LCs in comparison with smectic structures. Nematic LCs also offer nonlinear optical behavior.

The chiral nematic assembly is formed by materials that have chiral centers and that form a nematic phase. Here, a "chiral-imposed twist" is imparted to the linear chains composing each layer, resulting in a three-dimensional helical arrangement.

The molecular asymmetry typically occurs not because of intermolecular interaction, but because two molecules cannot occupy the same space at the same time. Molecular chains can

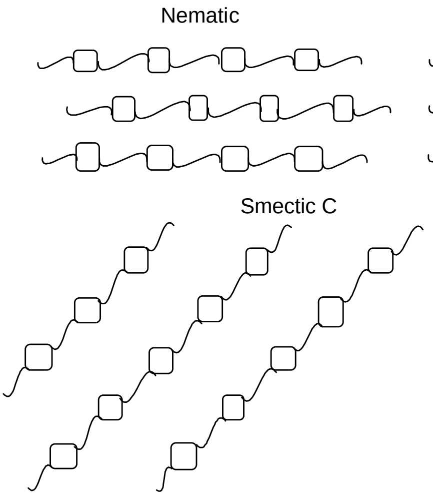
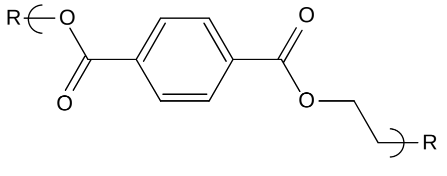


FIGURE 4.11 Different mesophasic structures where the mesogenic unit is designated by a rounded square.

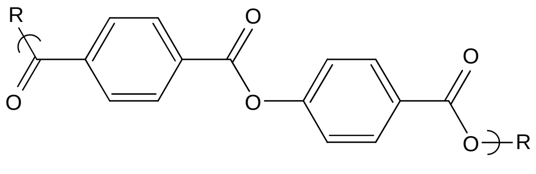
exist in a random arrangement until a given concentration is exceeded, causing the molecules to rearrange in a more ordered fashion to accommodate the larger number of molecules within the same volume. Often, this occurs such that there is an ordered phase and a more random phase. As the concentration of polymer increases, the ordered phase becomes larger at the expense of the disordered phase. This increase in polymer concentration can occur via several routes such as addition of more polymer, addition of a solution containing a higher concentration of polymer, and evaporation of the solvent.

For crystalline polymer systems, transition from the crystalline structure to a mesophase structure occurs, whereas for amorphous polymer systems, the mesophase occurs after the T_g has occurred. Some polymer LC systems form several mesophases. Mesophases can be detected using DSC, x-ray diffraction, and polarizing microscopy.

Introduction of flexible "spacer" units such as methylene, methylene oxide, and dimethylsiloxane groups lowers the melting point and increases the temperature range within which the mesophase is stable. Often these spacer units are introduced by copolymerization. Thus, preformed *p*-acetoxybenzoic acid is reacted with PET, introducing a mesogenic unit in a polymer that has flexible spacer units (from the ethylene glycol) in it.



Poly(ethylene terephthalate), PET (4.84)



Mesogenic unit (4.85)

In addition to the mesogen units contained within the polymer backbone, they can occur as side chains. These mesogen units can be introduced either through reaction with monomers that contain the mesogen unit or through introduction with already formed polymers.

LC materials have also been employed as films, plastics, and resins. Poly(1,4-benzoate) has been marketed under the name Ekonol. It decomposes before it melts, hence it does not form LC melts. Copolymerization with 4,4′-biphenol and terephthalic acid gives Ekkcel, which melts before it decomposes. Certain forms can be compression-molded and others injection-molded. Reaction of poly(1,4-benzoate) with PET gives a material that can be injection-molded. These LCs are chemical-resistant, with high tensile strength. LC films with mesogenic side chains can be used in information storage devices.

In general, because of the high order present in LCs, especially within their ordered state, they have low void densities; exhibit good stability to most chemicals including acids, bleaches, common liquids; low gas permeability; relatively high densities; are strong and stiff with tensile moduli on the order of 10–25 GP and tensile strengths in the range of 120–260 MPa.

Today, there exist a number of routes for processing that have been modified for LC materials. In general, they offer low shrinkage and warpage during molding, good repeatability from part to part, and low heat of fusion allowing rapid melting and cooling during processing.

Their low melt viscosity permits molding of thin sections and complex shapes. However, their tendency to form ordered structures causes LC materials to be particularly susceptible to molecular orientation effects during processing.

An illustration of the use of LC materials is given in Figure 4.12. A typical LC display (LCD) may contain thin layers of LC molecules sandwiched between glass sheets. The glass sheets have been rubbed in different directions and then layered with transparent electrode strips. The outside of each glass sheet is coated with a polarizer material parallel to the rubbing direction. One of the sheets is further coated with a material to make it a reflecting mirror. The liquid crystalline molecules preferentially align along the direction that the two glass surfaces have been rubbed. Because the two glass surfaces are put at 90° to one another, the LC orientation changes as one goes from one glass surface to the other, creating a gradual twist of 90°.

Ordinary light consists of electromagnetic waves vibrating in various planes perpendicular to the direction of travel. As light hits the first polarizer material, only light that vibrates in a single plane is allowed to pass through. This plane-polarized light then passes through the layers of LCs that effectively twist the plane of the light 90°, allowing the "twisted" light to pass through the second polarized surface, striking the mirrored surface, and "bouncing back" to be seen as a white background.

The LCD image is formed as a voltage and is applied to an appropriate pattern of tiny electrodes that causes reorientation in the LCs. Orientated LCs are no longer at 90° to one

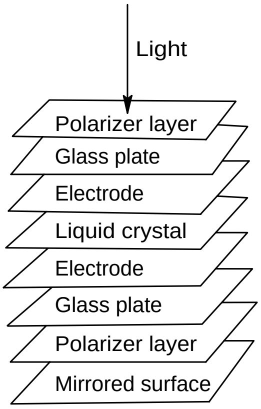


FIGURE 4.12 Composition of a typical LCD.

another and are thus unable to transmit light through to the mirrored surface; therefore, they appear as dark areas. This combination of dark and light surfaces then creates the LCD image.

Assemblies similar to the above have been employed to create images in clocks and watches and other similar LCD image–containing products.

4.19 MICROFIBERS

The term microfibers does not refer to new chemically distinct fibers, but rather to fibers that have smaller diameters. DuPont first introduced microfibers in 1989. Microfibers have diameters that are less than typical fibers: they are half the diameter of fine silk fiber, quarter the diameter of fine wool, and a hundred times finer than human hair. Denier, the weight in grams of 9000 m of a fiber, is the term used to define the diameter or fineness of a fiber. While the definition for the thickness of microfibers is varied, a typical definition is that microfibers are 0.9 denier or less. For comparison, the nylon stocking is knit from 10–15 denier fiber.

Microfibers allow a fabric to be woven that is lightweight and strong. They can be tightly woven so that wind, rain, and cold do not easily penetrate. Rainwear manufacturers use microfibers for this reason. They also have the ability to allow perspiration to pass through them. Thus, so-called microfiber athletic-wear is becoming more commonplace. Microfibers are also very flexible because the small fibers can easily slide back and forth on one another. The first fabric made from microfiber was Ultrasuede™ in which short polyester microfibers were imbedded into a PU base. Today microfibers are made mainly from polyesters, nylon, acrylic, and rayon fibers.

The use of the term microfibers is now extended to glass and Teflon-related materials. Here we will restrict ourselves to only fabric applications.

In 1970, Miyoshi Okamoto, a scientist from Toray Industries, created the first microfiber. A few months later his colleague Toyohiko Hikota developed a process that allowed the production of fabric that was later trademarked as Ultrasuede™. Ultrasuede was produced from such thin PET polyester fibers that a pound of them laid end-to-end would reach from the earth to the moon and back. Ultrasuede is soft and supple, resistant to stains and discoloration, and machine-washable and dry-cleanable.

Because of progress made in spinning and fiber processing, smaller fibers can be routinely made with varying configurations, coatings, etc. Microfiber production is mainly achieved using three techniques. The first will be illustrated using the processing technique employed to manufacture Ultrasuede.

The process in forming Ultrasuede is complex. First, ultra-microfibers are spun that are so light and fine that a single 50-mile-long strand would weigh less than 1 g. These ultra-microfibers are then extruded through spinnerets creating a configuration that is similar to that present in tendons and hair bundles. These strands are then transformed by ironing, curling, cutting, and needle-punching into a feltlike material, which is then impregnated with a special adhesive binder. The material is then formed into the desired contours and the protective coating is dissolved with a solvent, and the material undergoes further processing creating the nonwoven fabric.

Microfibers are also made by simple extrusion through a spinneret with a smaller hole than normally employed for fiber production. The third method involves spinning a bi-component fiber and using a solution to split the fiber into smaller pieces. Initially, bi-component fibers in the range of 2–4 denier are spun and then split into microfibers. If a 32-segment pie of nylon–polyester fiber is used, the final fineness is on the order of 0.1 denier. Brushing and other techniques can be used to enhance the effects. Hollow fibers are also being used to achieve fiber splitting. For instance, for polyester–polypropylene fiber combinations, "natural" splitting occurs after passage through the spinneret. After mechanical drawing, the yarn has a fineness of about 0.2 denier, which is well within that described for microfibers. Recently, tipped fibers are being studied. A bi-component fiber is made except that the second polymer is placed on the tip of the fiber. After spinning, the fibers are twisted and then wet heat is applied, resulting in the tips of the fibers breaking apart into microfibers with a fineness of about 0.2 denier. Because the two different polymers have different heats of elongation, the physical changes cause the two polymer components to break apart.

The shape of the microfiber influences the end properties. For instance, Tomen has developed Technofine™, a polyester microfiber with a W-shaped cross section. The increased surface allows a more rapid transport of water away from the skin and also increases the evaporation rate, making garments sowed from it quicker-drying and more adsorbent.

Most textiles have limited elongation but many of the microfiber textiles have elongations of 100%.

Currently, no industry regulations exist that describe the amount of microfiber that must be present to call it a microfiber material. Even so, typically industrial use calls for a material to be at least 35%–40% microfiber to be called a microfiber product. Microfibers are most commonly used in dress and blouse garments. They are also used to make hosiery, ties, scarves, intimate apparel, curtains, draperies, sheets, towels, rainware, swimwear, blankets, tents, sleeping bags, track and jogging wear, as well as many other items. The greater surface area results in a fabric with deeper, richer, and brighter colors possible.

The care of microfiber products is similar to that of the normal fiber materials made from the same polymer. One caution is heat sensitivity. Because the fibers are so fine, heat penetrates easily causing them to scorch or glaze more quickly than "normal" fibers if too much heat is applied or heat is applied over too long a period. Typically, microfibers are wrinkle-resistant, but if ironing is done, it should be accomplished using lower temperatures and only as directed.

4.20 GENERAL STEPWISE POLYMERIZATION

From an equation such as 4.86 it is possible to derive expressions describing the MWD of stepwise polymerizations at any extent of polymerization. This relationship is more easily derived from a statistical standpoint. The following statistical treatment assumes the reaction to be independent of chain length.

We can write a general equation for the formation of a linear polymer formed from the reaction of bifunctional reactants A and B as follows:

$$nA + nB \rightarrow A(BA)_{n-1}B \tag{4.86}$$

The probability of finding a repeating unit AB in the polymer is p, and the probability of finding "$n-1$" of these repeat units in the polymer chain is p^{n-1}. Likewise, the probability of finding an unreacted molecule of A or B is $1-p$. Thus, the probability (p_n) of finding a chain with n repeat units $(BA)_n$ is

$$p_n = (1-p)p^{n-1} \tag{4.87}$$

N_n is the probability of choosing (at random) a molecule with $(AB)_n$ repeat units, where N is the total number of molecules and is given as follows:

$$N_n = N(1-p)p^{n-1} \tag{4.88}$$

Since

$$\frac{N_o}{N} = \frac{1}{1-p} \quad \text{or} \quad N = N_o(1-p) \tag{4.89}$$

Where N_o is the total number of structural units present, and is described by

$$N_n = N_o(1-p)^2 p^{n-1} \tag{4.90}$$

The corresponding weight-average MWD W_n can be calculated from the relationship

$$\overline{W}_n = \frac{nN_n}{N_o} \tag{4.91}$$

as follows:

$$\overline{W}_n = \frac{nN_o(1-p)^2 p^{n-1}}{N_o} = n(1-p)^2 p^{n-1} \tag{4.92}$$

The relationship shown in Equations 4.91 and 4.92 shows that high values of p (0.99) are essential in producing high N_n and W_n values. The number-average molecular weight M_n calculated from Equations 4.89 and 4.90 is as follows:

$$\overline{M}_n = \frac{mN_o}{N} = \frac{m}{1-p} \tag{4.93}$$

Where $m =$ the molecular weight of the mer and

$$\overline{M}_w = \frac{m(1+p)}{(1-p)} = M_n(1+p) \tag{4.94}$$

Thus, the index of polydispersity M_w/M_n becomes $1 + p$, as shown below:

$$\frac{\overline{M}_w}{\overline{M}_n} = \frac{m(1+p)/(1-p)}{m/(1-p)} = 1 + p \tag{4.95}$$

Thus, when $p = 1$, the index of polydispersibility for the most probable distribution for stepwise polymerizations is 2.

Because the value of p is essentially 1 in some stepwise polymerizations employing very pure monomers, the products obtained under normal conditions will have very high molecular weights and are found to be difficult to process. The value of p can be reduced by using a slight excess of one of the reactants or by quenching (stopping) the reaction before completion. Thus, if a reaction is quenched when the fractional conversion p is 0.995, the average degree of polymerization becomes 200.

When more than 1 mol of B is used with 1 mol of A, the ratio of A/B, or r, may be substituted in the modified Carothers' equation as follows:

$$\text{Average } \overline{DP} = \frac{\text{total } nA \text{ at } p}{\text{total } nA \text{ at } rp} = \frac{n[\,(1 + 1/r)]}{2n[1 - p + (1 - rp/r)]/2} = \frac{[1 + (1/r)]}{[1 - p + (1 - rp)/r]} \tag{4.96}$$

Multiplying the top and bottom by r gives

$$\text{Average } \overline{DP} = \frac{r + 1}{r(1 - p) + (1 - rp)} = \frac{(1 + r)}{(1 + r) - 2rp} \tag{4.97}$$

For the formation of nylon-6,6, if $r = 0.97$ and p is about 1, the average $\overline{DP}$ is equal to

$$\text{Average } \overline{DP} = 1 + r(1 + r) - 2rp = \frac{1 + 0.97}{1 + 0.97 - 2(0.97)} = \frac{1.97}{0.03} = 66 \tag{4.98}$$

The average $\overline{DP}$ of 66 is above the threshold limit of 50 required for nylon-6,6 fibers.

Since quenching the reaction or adding a stoichiometric excess of one reactant is seldom economical, the commercial practice is to add a specific amount of a monofunctional reactant in the synthesis of polyesters, nylons, and other similar polymers. In these cases, a functionality factor f is used that is equal to the average number of functional groups present per reactive molecule. While the value of f in the preceding examples has been 2.0, it may be reduced to lower values and used in the following modified Carothers' equation:

$$\text{Average } \overline{DP} = \frac{A_o}{A_o[1 - (pf/2)]} = \frac{2}{2 - pf} \tag{4.99}$$

Thus, if 0.01 mol of monofunctional acetic acid is used with 0.99 mol of two difunctional reactants, the average functionality or functional factor f is calculated as follows:

$$f = \frac{\text{mole of each reactant} \times \text{functionality}}{\text{total number of moles}} = \frac{0.99\text{ mol} \times 2 + 0.99\text{ mol} \times 2 + 0.01\text{ mol} \times 1}{1.99\text{ mol}} = 1.99 \tag{4.100}$$

Substitution of $f = 1.99$ and $p = 1.00$ in Equation 4.99 gives an average $\overline{DP}$ of 200 representing an upper limit for chain size often employed commercially for nylon-6,6. The same calculation but employing $p = 0.95$ gives an average $\overline{DP}$ of only 20, below the lower desired value for nylon-6,6.

Since the average molecular weight increases with conversion, useful high molecular weight linear polymers may be obtained by the step-reaction polymerization when the fractional conversion p is high (>0.99). The concentration of reactants decreases rapidly in the early stages of polymerization, and differing chain lengths will be present in the final product. The requirement for a linear polymer is a functionality of 2. Network polymers are typically formed when the functionality is greater than 2.

4.21 SUMMARY

1. Many naturally occurring and some synthetic polymers are produced by condensation reactions, many of which are described kinetically by the term stepwise polymerization. A high fractional conversion is required to form linear polymers such as polyesters, nylons,

polysulfides, PUs, polycarbonates, polysulfones, polyimides, polybenzimidazoles, and polyethers. But a high fractional conversion is not required for the production of network, cross-linked products such as epoxy, phenol, urea, formaldehyde, and melamine resins. One major exception to the production of condensation polymers through the stepwise kinetic process is the use of the interfacial reaction system employing reactive reactants that follows a chainwise kinetic process. The interfacial system is employed to produce polycarbonates and some aramids. The remainder of the condensation polymers are generally produced using the melt and solution techniques.

2. The rate expressions and values, mechanisms, and the activation energies for the condensation reactions forming polymers are similar to those of small molecule reactions. Reaction rate increases with temperature in accordance with the Arrhenius equation. Average $\overline{DP}$ also increases as the reaction temperature increases to the ceiling temperature where polymer degradation occurs. Long chains are only formed at the conclusion of classical polycondensation processes.
3. The average $\overline{DP}$ for formation of linear condensation polymers can be calculated using Carothers' equation, average $\overline{DP} = 1/(1 - p)$.
4. Cross-linked products are formed when the functionality of either reactant is greater than 2. Linear products are formed when the functionality of both reactants is 2.
5. Condensation polymers tend to exist below their T_g at room temperature. They typically form fairly ordered structures with lots of strong interactions between the various chains giving strong materials with some, but not much, elongation when stretched. They are normally used as fibers and plastics. They have high stress/strain ratios.
6. Condensation polymers include many of the materials referred to as synthetic or man-made fibers including polyesters (especially PET) and a variety of nylons (mainly nylon 6,6 and nylon 6).
7. A number of plastics are condensation polymers and include polyesters and nylons that are not as highly oriented as the same materials but in fiber form. Other plastics have been developed that have outstanding heat stability, strength, and other properties that allow their wide use. These plastics include polycarbonates, polyimides, polybenzimidazoles, polysulfides, polyethers, polysulfones, and polyketones.
8. PUs derived from the reaction of diisocyanates and a variety of hydroxyl-containing materials form the basis for foamed products and a variety of elastomeric materials.
9. Highly cross-linked condensation materials form the basis for a number of important adhesives and bulk materials, especially phenolic and amino plastics. Most of these products have formaldehyde as one of their starting reactants. These materials are thermosets that decompose prior to melting, and are therefore more difficult to recycle than most condensation polymers that are thermoplastics and do melt prior to decomposition.
10. Microfibers are simply fibers that are much thinner than typical fibers. They may be derived from any fiber-producing material that is suitably treated to give thin fibers.

GLOSSARY

alkyds Term originally used to describe oil-modified polyester, but now used for many polyester plastics and coatings.

allophanates Reaction product of a urethane and an isocyanate.

amino resins Urea and melamine–formaldehyde (MF) resins.

aramids Aromatic polyamides.

A-stage Linear prepolymer of phenol and formaldehyde.

Bakelite Polymer produced by condensation of phenol and formaldehyde first by Leo Baekeland.

bifunctional Molecule with two active functional groups.

bisphenol A 2,2′-bis(4-hydroxphenol)propane.

B-stage Advanced A-stage resin.

carbamate A urethane.

carbamic acids Unstable compounds that decompose spontaneously giving amines and carbon dioxide.

Carothers, W.H. Inventor of nylon who also standardized much of the polymer nomenclature we use today.

Carothers equation $1/(1 - p)$

condensation reaction Reaction in which two molecules react producing a third molecule and a by-product such as water.

cyclization Ring formation.

Dacron Trade name for PET fiber.

drying Cross-linking of an unsaturated polymer generally in the presence of oxygen.

drying oil An unsaturated oil like tung oil.

engineering plastic Plastics whose physical properties are good enough to permit their use as structural materials; generally they can be cut, sawn, and drilled.

epoxy resin Polymer produced by the condensation of epichlorohydrine and a dihydric alcohol or by the epoxidation of an unsaturated molecule.

ester interchange Reaction between an ester of a volatile alcohol and a less volatile alcohol in which the lower boiling alcohol is removed by distillation.

filament Extrudate when a polymer melt or solution is forced through a hole in a spinneret.

functionality Number of active functional groups present in a molecule.

functionality factor Average number of functional groups present per reactive molecule in a mixture of reactants.

furan resin Resin produced form furfuryl alcohol or furfural.

gel point Point at which cross-linking begins to produce polymer insolubility.

glyptals Polyesters, usually cross-linked by heating.

interfacial polymerization One in which the polymerization reaction occurs at the interface of two immiscible liquids.

Kodel Trade name for a PET fiber.

ladder polymer Double-chained temperature-resistant polymer.

laminate Layers or sheets of paper, wood, or other material adhered by resins and pressed together like plywood.

long oil alkyd Alkyd obtained in the presence of 65%–80% of an unsaturated oil.

medium oil alkyd Alkyd obtained in the presence of 50%–65% of an unsaturated oil.

melamine–formaldehyde (MF) resin Resin produced by the condensation of melamine and formaldehyde.

microfibers Small diameter fibers.

molding compound Name given to describe a mixture of a resin and essential additives.

nonoil alkyd An oil-free alkyd containing no unsaturated oils.

novolac Polymers prepared by the condensation of phenol and formaldehyde under acidic conditions.

nylon Synthetic polyamide.

oil length Term used to indicate the relative percentage of unsaturated oils used in the production of alkyds.

phenoxy resin Polymer with hydroxyl pendant groups resembling an epoxy resin without epoxy groups.

poly(ethylene terephthalate) (PET) Linear polyester used to produce fibers and for blow-molding preparation of soft drink bottles; produced from terephthalic acid and ethylene glycol.

prepolymer Low molecular weight material (oligomer) capable of further polymerization.

resite Cross-linked resole.

resole Linear polymer prepared by condensation of phenol and formaldehyde under alkaline conditions.

Schotten–Baumann reaction Traditionally the reaction between an acid chloride and a Lewis base.

short oil alkyd An alkyd obtained in the presence of 30%–50% of an unsaturated oil.

step-reaction polymerization polymerization in which polyfunctional reactants react to produce larger units in a continuous stepwise manner.

Thiokol Trade name for a polysulfide elastomer.

unsaturated polyester Term used to describe alkyds with unsaturated chains, particularly those produced by the condensation of maleic anhydride and ethylene glycol.

urea–formaldehyde resin Resin produced by condensation of urea and formaldehyde.

wasted loops Formation of cyclic compounds instead of polymer chains.

EXERCISES

1. Which of the following will give a polymer when condensed with adipic acid: (a) ethanol; (b) ethylene glycol; (c) glycerol; (d) aniline; or (e) ethylenediamine?
2. Could Carothers have produced strong polyester fibers by ester interchange or Schotten–Baumann reactions using aliphatic reactants?
3. Which would be useful as a fiber: (a) poly(ethylene terephthalate) or (b) poly(hexylene terephthalate)?
4. If the fractional conversion in an ester interchange reaction is 0.99999, what would be the average degree of polymerization of the polyester produced?
5. Use the logarithmic form of the Arrhenius equation to show that the value of the rate constant k increases as the temperature increases.
6. What is the first product produced when a molecule of sebacyl chloride reacts with a molecule of ethylene glycol?
7. What is the next product formed in question 6?
8. How would you improve the strength of the filament produced in the nylon rope trick without changing the reactants?
9. Name the product produced by the condensation of adipic acid and 1,4-tetramethylenediamine.
10. In which reaction would you expect the more "wasted loop": the reaction of oxalyl chloride with (a) ethylenediamine or (b) 1,6-hexanediamine?
11. Which system would be more apt to produce "wasted loops": (a) a dilute solution or (b) a concentrated solution?
12. If the values of A_o and k are 10 mol/L and 10^{-3} L mol/s, respectively, how long would it take to obtain an average $\overline{DP}$ of 37?
13. Which will give the low index of polydispersity: (a) $p = 0.000$ or (b) $p = 0.90$?
14. If you used a 2% molar excess of bisphenol A with TDI, what would be the maximum average degree of polymerization obtainable assuming $p = 1$?
15. Why would you predict the product obtained in question 14 be a useful fiber assuming an average $\overline{DP}$ of 100?
16. Name the product from the reaction of a phenol with formaldehyde.
17. What is Carothers' equation? What is its significance?
18. What is the product of polymerized formaldehyde? Is it stable?
19. What is the product of a diol and diisocyanate? What are general uses of this product?
20. Which would be the better or stronger fiber: one made from an ester of (a) terephthalic acid or (b) phthalic acid?
21. What would be the deficiency of a nylon film that was stretched in one direction only?
22. Which would be more flexible: (a) poly(butylene terephthalate) or (b) poly(hexylene terephthalate)?
23. Which would be more apt to deteriorate in the presence of moisture: (a) Lexan molding powder or (b) Lexan sheet?
24. What reactants are typically employed to make a polycarbonate?
25. How would you prepare a nylon with greater moisture resistance than nylon-6,6?
26. How would you prepare a nylon that would be less "clammy" when used as clothing?
27. Which would be higher melting: (a) a polyamine or (b) a polyester with similar members of methylene groups in the repeat unit?
28. Why is a methoxymethylated nylon more flexible than nylon?
29. Why is Bakelite not used in forming molded objects?
30. Is it not wasteful to decompose a diisocyanate by hydrolysis to produce foams?
31. How would you prepare a hydroxyl-terminated polyester?
32. For the acid-catalyzed condensation of ethylene glycol with terephthalic acid, what is the relationship between $\overline{DP}$ and the extent of reaction?
33. For stepwise kinetics what happens to chain length as time increases?
34. Why do PUs and epoxy resins have good adhesive properties?
35. Why are furan resins relatively inexpensive?
36. To produce cross-linked polyesters what is normally present?
37. Could you produce a soluble novolac resin from resorcinol?

38. Can you explain why there are so many terms, such as novolac, resole, etc., used in phenolic resin technology?
39. Why is Bakelite not used for dinnerware?
40. Which of the following could be a nonpetrochemical plastic: (a) Bakelite; (b) urea plastics; or (c) melamine plastics?
41. Which would produce a better fiber: the reaction product of phthalic acid and (a) 1,4-butanediol or (b) 2-hydroxylbutanol?
42. What are some properties of microfibers?
43. What are the main uses of PUs?
44. What are the advantages of open-celled foams and how do they differ from closed-cell foams?
45. What is the most important property that LCs have?
46. Name three uses of LCs.

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5 Ionic Chain-Reaction and Complex Coordination Polymerization (Addition Polymerization)

In contrast to the relatively slow step-reaction polymerizations discussed in Chapter 4, chain polymerizations are usually rapid, and the initiation species continues to propagate until termination. Thus, in the extreme case, a single initiation species could produce one high-molecular chain, leaving all of the other monomer molecules unchanged. In any case, the concentration of monomer, which is often a substituted vinyl compound, decreases continuously throughout the reaction. In contrast to stepwise polymerization, the first species produced in chain polymerizations is a high-molecular polymer.

A kinetic chain reaction usually consists of at least three steps: (1) initiation, (2) propagation, and (3) termination. The initiator may be an anion, a cation, a free radical, or a coordination catalyst. Although coordination catalysts are the most important commercially, the ionic initiators will be discussed first in an attempt to simplify the discussion of chain-reaction polymerization.

In almost all of the polymerizations described in this chapter, there is a sensitive and critical balance between the catalyst activity and polymerization. For instance, if the catalyst is highly active it may bind at unwanted sites, including the solvent. If the catalyst complex is not sufficiently active, ready initiation does not occur. The choice of the solvent is also important. Some solvents will react with the catalysts binding it rather than allowing the catalyst to initiate the desired polymerization. Others may "hold" the catalyst complex together rather than allowing the catalyst to initiate polymerization. Still others may not allow the catalyst complex to form. As in much of science, the precise ingredients and conditions were developed through a combination of intuition, science, art, and research. This process continues.

While many vinyl monomers undergo free radical polymerization (Chapter 6), a smaller number undergo ionic polymerization. Cationic polymerizations require monomers that have electron-releasing groups such as an alkoxy, phenyl, or vinyl group. Anionic polymerization occurs with monomers containing electron-withdrawing groups such as carboxyl, nitrile, or halide. This selectivity is due to the strict requirements for stabilization of anionic and cationic species.

Compared with free radical polymerizations, the kinetics of ionic polymerizations are not well defined. Reactions can use heterogeneous initiators and they are usually quite sensitive to the presence of impurities. Thus, kinetic studies are difficult and the results sensitive to the particular reaction conditions. Further, the rates of polymer formation are more rapid.

TABLE 5.1
Major Technique Used in the Production of Important Vinyl Polymers

Free radical	Low-density polyethylene (LDPE)
	Poly(vinyl chloride)
	Poly(vinyl acetate)
	Polyacrylonitrile and acrylic fibers
	Poly(methyl methacrylate)
	Polyacrylamide
	Polychloroprene
	Poly(vinyl pyridine)
	Styrene–acrylonitrile copolymers (SAN)
	Polytetrafluoroethylene
	Poly(vinylene fluoride)
	Acrylonitrile–butadiene–styrene (ABS) copolymers
	Ethylene–methacrylic acid copolymers
	Styrene–butadiene rubber copolymers (SBR)
	Nitrile butadiene rubber (NBR)
	Polystyrene (PS)
Cationic	Polyisobutylene (PIB)
	Butyl rubber
	Polyacetal
Anionic	Thermoplastic olefin elastomers (copolymers of butadiene, isoprene, and styrene)
	Polyacetal
Complex	High-density polyethylene (HDPE)
	Polypropylene
	Polybutadiene
	Polyisoprene
	Ethylene–propylene elastomers

Cationic and anionic polymerizations are similar. Both involve the formation and propagation of ionic species. While high energy, low stability, ions would be expected to react with most double bonds, ionic species that are stable enough to propagate are difficult to form and are easily destroyed. The "energenic window" that allows the formation of such charged species that promote polymer formation is narrow. While polar solvents might be desirable to solvate the ions, and hence help stabilize them, they often cannot be used. Some polar solvents, such as water and alcohol, react with and destroy most ionic initiators. Other polar solvents, such as ketones, prevent initiation because of the formation of stable complexes with the initiators. Ionic polymerizations are therefore conducted in low or moderately polar solvents, such as hexane and ethylene dichloride.

By bulk, almost all vinyl polymers are made by four processes (Table 5.1): free radical (about 50%), complex coordinate (about 20%), anionic (10%–15%), and cationic (8%–12%). Three of these techniques are covered in this chapter.

5.1 CHAIN-GROWTH POLYMERIZATION—GENERAL

Chapters 5 through 7 deal with polymers formed from chain-growth polymerization. Chain-growth polymerization is also called addition polymerization and is based on free radical, cationic, anionic, and coordination reactions where a single initiating species causes the growth of a polymer chain.

The kinetic chain reaction typically consists of three steps: (1) initiation, (2) propagation, and (3) termination. The initiators for free radical, anionic, and cationic polymerizations are organic radicals, carbanions, and carboniums. Chain growth is exothermic with the polymerization mainly controlled by the steric and resonance factors associated with the monomer. Generally, the less resonance stabilization, the more heat is given off during the reaction. Also, the greater the steric factors, the less heat is given off during the polymerization.

5.2 CATIONIC POLYMERIZATION

The art of cationic polymerization, like that of many other types of polymerization, is at least a century old. However, the mechanisms for these reactions have only recently become better understood.

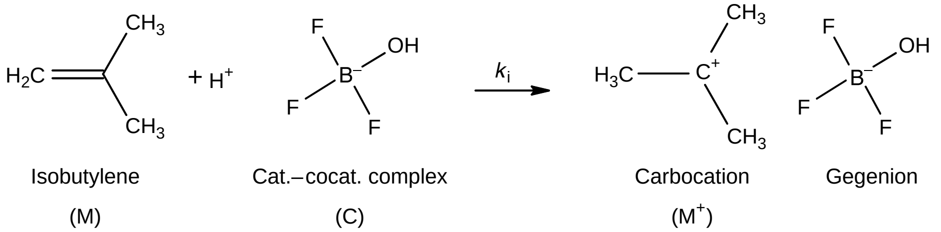
The first species produced in cationic polymerizations are carbocations, and these were unknown as such prior to World War II. It is now known that pure Lewis acids, such as boron trifluoride and aluminum chloride, are not effective as initiators. A trace of a proton-containing Lewis base, such as water, is also required. The Lewis base coordinates with the electrophilic Lewis acid, and the proton is the actual initiator. Since cations cannot exist alone, they are accompanied by a *counterion*, also called a *gegenion*.

$$\begin{array}{ccccc} BF_3 & + & H_2O & \rightleftarrows & H^+, BF_3OH^- \\ \text{Lewis acid} & & \text{Lewis base} & & \text{Catalyst–cocatalyst} \\ \text{catalyst} & & \text{cocatalyst} & & \text{complex} \end{array} \qquad (5.1)$$

Since the required activation energy for ionic polymerization is small, these reactions may occur at very low temperatures. The carbocations, including the macrocarbocations, repel one another; hence, chain termination does not occur by combination but is usually the result of reaction with impurities.

Both the initiation step and the propagation step are dependent on the stability of the carbocations. Isobutylene (the first monomer to be commercially polymerized by ionic initiators), vinyl ethers, and styrene have been polymerized by this technique. The order of activity for olefins is $Me_2C{=}CH_2 > MeCH{=}CH_2 > CH_2{=}CH_2$, and for para-substituted styrenes the order for the substituents is $Me{-}O > Me > H > Cl$. The mechanism is also dependent on the solvent as well as the electrophilicity of the monomer and the nucleophilicity of the gegenion. Rearrangements may occur in ionic polymerizations.

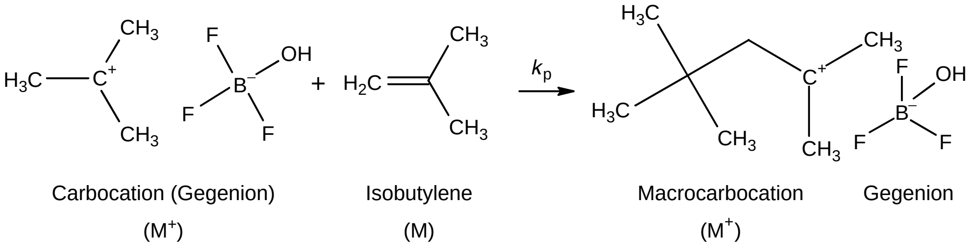
The rate of initiation (R_i) for typical cationic reactions is proportional to the concentration of the monomer [M] and the concentration of the catalyst–cocatalyst complex [C] as follows:



(5.2)

$$R_i = k_i[C][M] \qquad (5.3)$$

Propagation, or chain growth, takes place in a head-to-tail configuration as a result of resonance stabilization and steric factors by carbocation (M^+) addition to another monomer molecule. The head stabilizes the cation best so it is the growing site while the least sterically hindered site is the site for attack by the cation resulting in the typical head-to-tail arrangement. The rate constant for growth is essentially independent of chain length so is the same for all propagation steps and is influenced by the dielectric constant of the solvent. The rate is fastest in solvents with high dielectric constants, promoting separation of the carbocation–gegenion pairs. The chemical and kinetic equations for this are as follows:



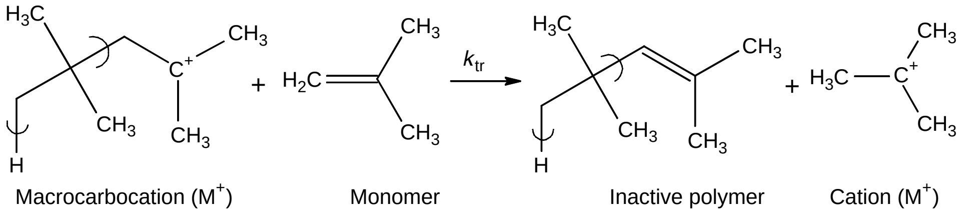
(5.4)

$$R_p = k_p[M][M^+] \tag{5.5}$$

The termination rate R_t, assumed to be a first-order process, is simply the dissociation of the macrocarbocation–gegenion complex here forming BF_3 and H_2O and the now neutral "dead" polymer chain. This is expressed as follows:

$$R_t = k_t[M^+] \tag{5.6}$$

Termination may also occur by chain transfer, where a proton is transferred to a monomer molecule, leaving a cation which can serve as an initiator. The DP is equal to the kinetic chain length (ν) when chain transfer occurs. The chemical and kinetic equations for termination via chain transfer are as follows:



(5.7)

$$R_{tr} = k_{tr}[M][M^+] \tag{5.8}$$

It is experimentally found that the rate of initiation equals the rate of termination and since the propagation step is so rapid, then the number of growing chains is constant. Since it is difficult to determine values for some members of the kinetic expressions, including $[M^+]$ the following approach is normally taken to eliminate the need for determining $[M^+]$. Since there is a steady state of growing chains, the rate of initiation is equal to the rate of termination, giving $R_i = R_t$, and solving for $[M^+]$ gives the following:

$$k_i[C][M] = k_t[M^+], \quad \text{therefore} \tag{5.9}$$

$$[M^+] = k_i[C][M]/k_t \tag{5.10}$$

This expression of $[M^+]$ is substituted into the propagation rate expression Equation 5.5 giving the following equation:

$$R_p = k_p[M][M^+] = k_p k_i[C][M]^2/k_t = k'[C][M]^2 \tag{5.11}$$

For termination by chain transfer we have

$$k_i[C][M] = k_t[M][M^+] \tag{5.12}$$

and

$$[M^+] = k_i[C][M]/k_t[M] = k_i[C]/k_t \tag{5.13}$$

giving

$$R_p = k_p[M][M^+] = k_p k_i[C][M]/k_t = k'[C][M] \tag{5.14}$$

The $\overline{\text{DP}}$ can also be described when internal dissociation is the dominant termination step as follows:

$$\overline{\text{DP}} = R_p/R_t = k_p[M][M^+]/k_t[M^+] = k''[M] \tag{5.15}$$

But if chain transfer is the dominant termination step then

$$\overline{\text{DP}} = R_p/R_{tr} = k_p[M][M^+]/k_{tr}[M][M^+] = k_p/k_{tr} = k'' \tag{5.16}$$

It is important to note that regardless of how termination occurs, the molecular weight is independent of the concentration of the initiator. However, the rate of ionic chain polymerization is dependent on the dielectric constant of the solvent, the resonance stability of the carbonium ion, the stability of the gegenion, and the electropositivity of the initiator.

The rates of all single-step reactions increase as the temperature increases. This may not be true for multistep reactions such as those involved with multistep polymerizations, here the cationic polymerization. For cationic polymerizations the activation energies are generally of the order $E_{tr} > E_i > E_p$. Remembering that the description of the specific rate constant is

$$k = Ae^{-E_a/RT} \tag{5.17}$$

the overall or ‘‘net’’ activation energy for chain growth from Equation 5.11 is

$$E_{(\text{overall})} = E_p + E_i - E_{tr} \tag{5.18}$$

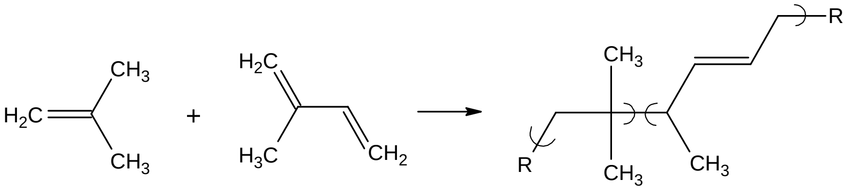
and for chain length from Equation 5.16 it is

$$E_{(\text{overall})} = E_p - E_{tr} \tag{5.19}$$

For many cationic polymerizations, the net activation is negative, using the relationships given in Equation 5.11, so that the overall rate of polymerization decreases, for these cases, as the temperature is increased. Further, using Equation 5.16 and since $E_{tr} > E_p$, the overall DP does decrease as the temperature is increased. This is pictured in Figure 4.4.

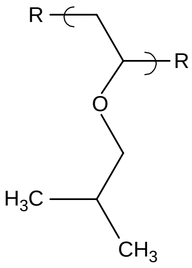
PIB is produced using cationic polymerization. It is used as an adhesive, caulking compound, chewing gum base, and an oil additive. Its use as an oil additive is related to its change in shape with increasing temperature. PIB is present as a coil at room temperature as lubricating oil is not a good solvent for it. However, as the temperature increases it begins to uncoil acting to counteract the decrease in viscosity of the oil as the temperature is increased.

Butyl rubber (IIR) is widely used for inner tubes and as a sealant. It is produced using the cationic polymerization with the copolymerization of isobutylene in the presence of a small amount (10%) of isoprene. Thus, the random copolymer chain contains a low concentration of widely spaced isolated double bonds, from the isoprene, that are later cross-linked when the butyl rubber is cured. A representation is shown in structure 5.20 where the number of units derived from isobutylene units greatly outnumbers the number of units derived from the isoprene monomer. The steric requirements of the isobutylene-derived units cause the chains to remain apart giving it a low stress to strain value and a low T_g.



(5.20)

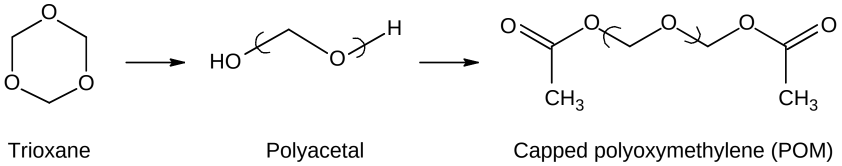
The cationic polymerization of vinyl isobutyl ether at −40°C produces stereoregular polymers (structure 5.21). The carbocations of vinyl alkyl ethers are stabilized by the delocalization of "p" valence electrons in the oxygen atom, and thus these monomers are readily polymerized by cationic initiators. Poly(vinyl isobutyl ether) has a low T_g because of the steric hindrance offered by the isobutyl group. It is used as an adhesive and an impregnating resin.



(5.21)

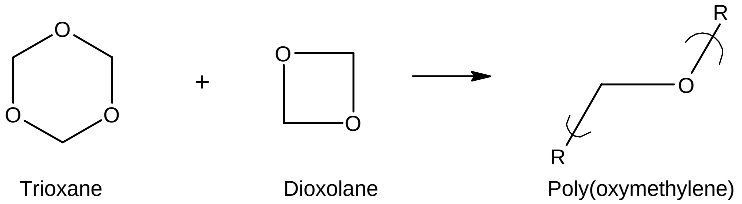
This production of stereoregular structures has been known for sometime and is especially strong for vinyl ethers. Several general observations have been noted. First, the amount of stereoregularity is dependent on the nature of the initiator. Second, stereoregularity increases with a decrease in temperature. Third, the amount and type (isotactic or syndiotactic) are dependent on the polarity of the solvent. For instance, the isotactic form is preferred in nonpolar solvents, but the syndiotactic form is preferred in polar solvents.

Commercial polymers of formaldehyde are also produced using cationic polymerization. The polymer is produced by ring opening of trioxane. Since the polyacetal, POM, is not thermally stable, the hydroxyl groups are esterified (capped) by acetic anhydride (structure 5.22). These polymers are also called poly(methylene oxides). The commercial polymer is a strong engineering plastic. Engineering plastics typically have higher modulus and higher heat resistance than general purpose plastics.



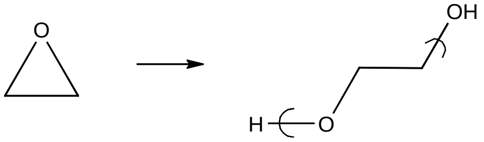
(5.22)

Another stable polyacetal (POM; Celcon) is produced by the cationic copolymerization of a mixture of trioxane and dioxolane (structure 5.23).



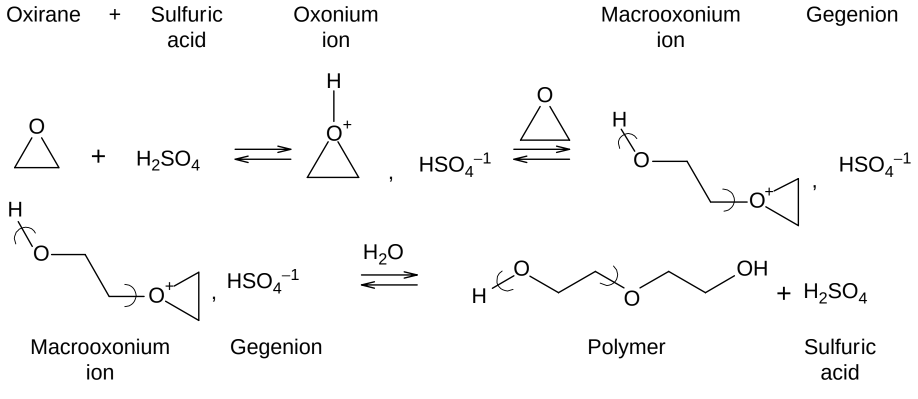
(5.23)

Many other cyclic ethers have been polymerized using cationic polymerization. Ethylene oxide (also called oxirane) polymerizes forming poly(ethylene oxide) (PEO) (structure 5.24) in the presence of acids such as sulfuric acid, producing a wide range of chain-sized polymers sold under various trade names including Carbowax and Polyox. PEO is also used in cosmetics and pharmaceuticals (as water-soluble pill coatings and capsules).



(5.24)

Polymer production proceeds as described in structure 5.25. An initiator, such as sulfuric acid, produces an oxonium ion and a gegenion. The oxonium ion then adds to the oxirane, ethylene oxide, producing a macrooxonium ion with growth eventually terminated by chain transfer with water.

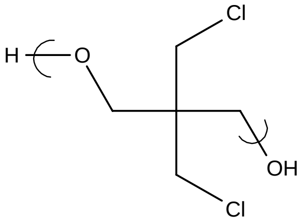


(5.25)

Propagation is an equilibrium reaction that limits polymerization. The highest chains are produced in mildly polar solvents, such as methylene chloride, at low temperatures (−20°C to −100°C).

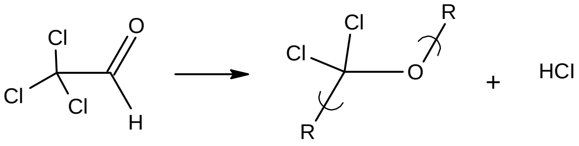
In addition to the production of polyacetals by the ROP of trioxane, Staundinger investigated ring opening of other ethers such as ethylene oxide (oxirane), above. Other homologous cyclic ethers, such as tetrahydrofuran (THF), have been polymerized by cationic ROP reactions. The tendency for ring opening decreases as the size of the ring increases and some oxirane is generally added as a promoter for the polymerization of THF. The six-member ring oxacyclohexane is so stable that it does not undergo cationic ROP even in the presence of a promoter.

The oxacyclobutane derivative, 3,3-bischloromethyloxacyclobutane, is polymerized (structure 5.26) using cationic ROP giving a water-insoluble, crystalline, corrosion-resistant polymer sold under the trade name of Penton.



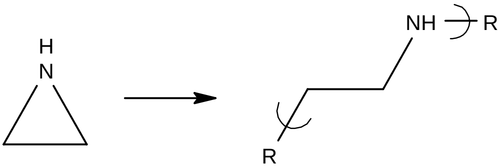
(5.26)

Polychloral (structure 5.27) does not exist above its ceiling temperature of 58°C. Above this temperature the polymer decomposes. The production of polychloral is carried out by cationic polymerization through the introduction of a hot mixture of trichloroacetaldehyde and initiator into a mold and allowing polymerization to occur *in situ* as the mixture cools below the ceiling temperature. Even though polychloral has a low ceiling temperature it is used as a flame-resistant material because of the presence of the chlorine atoms.



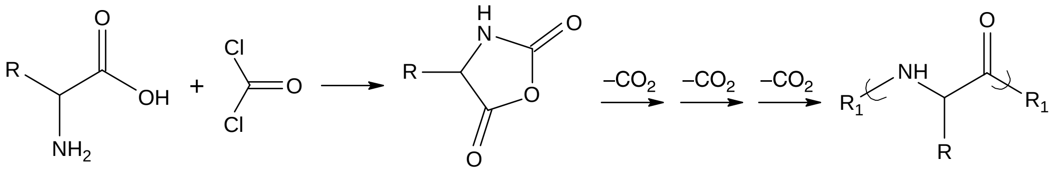
(5.27)

An acid-soluble polymer, Montrek, has been produced by the ROP of ethyleneimine, aziridine (structure 5.28). The monomer is a carcinogen so care is taken to remove unreacted monomer.



(5.28)

While lactams are often polymerized by anionic ROPs, *N*-carboxyl-alpha-amino acid anhydrides, called Leuchs' anhydrides, can be polymerized by either cationic or anionic techniques (structure 5.29). These polypeptide products, which are called nylon-2 products, were initially produced by Leuchs in 1908. The synthetic approach can be used to produce homopolypeptides that are used as model compounds for proteins. Carbon dioxide is eliminated in each step of the propagation reaction.



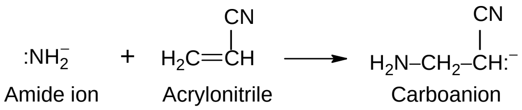
(5.29)

Polyterpenes, coumarone–indene resins, and so-called petroleum resins are produced commercially using cationic polymerization. These are used as additives for rubber, coatings, floor coverings, and adhesives.

5.3 ANIONIC POLYMERIZATION

Anionic polymerization was used to produce synthetic elastomers from butadiene at the beginning of the 20th century. Initially, alkali metals in liquid ammonia were used as initiators, but by the 1940s they were replaced by metal alkyls such as *n*-butyllithium. In contrast to vinyl monomers with electron-donating groups polymerized by cationic initiators, vinyl monomers with electron-withdrawing groups are more readily polymerized using anionic polymerization. Accordingly, the order of activity using an amide ion initiator is acetonitrile > methyl methacrylate > styrene > butadiene.

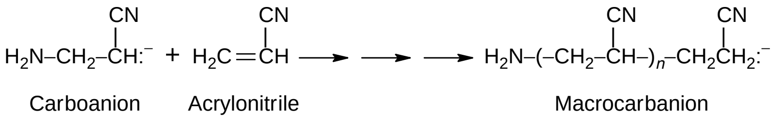
The chemical and kinetic relationships for the anionic polymerization of acrylonitrile follow the same three major steps found for cationic polymerizations: (1) initiation, (2) propagation, and (3) termination:



$$\mathrm{:NH_2^-} + \mathrm{H_2C{=}\overset{CN}{CH}} \longrightarrow \mathrm{H_2N\text{–}CH_2\text{–}\overset{CN}{CH}:^-} \tag{5.30}$$

$$R_\mathrm{i} = k_\mathrm{i}[\mathrm{C}][\mathrm{M}] \tag{5.31}$$

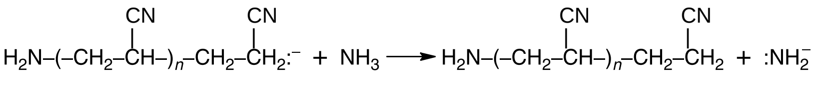
where $\mathrm{C} = :\mathrm{NH_2^-}$



$$\mathrm{H_2N\text{–}CH_2\text{–}\overset{CN}{CH}:^-} + \mathrm{H_2C{=}\overset{CN}{CH}} \longrightarrow \longrightarrow \longrightarrow \mathrm{H_2N\text{–}(\text{–}CH_2\text{–}\overset{CN}{CH}\text{–})_{\mathit{n}}\text{–}CH_2\overset{CN}{C}H_2:^-} \tag{5.32}$$

$$R_\mathrm{p} = k_\mathrm{p}[\mathrm{M}][\mathrm{M}^-] \tag{5.33}$$

with termination occurring through solvent transfer gives:



$$\mathrm{H_2N\text{–}(\text{–}CH_2\text{–}\overset{CN}{CH}\text{–})_{\mathit{n}}\text{–}CH_2\text{–}\overset{CN}{C}H_2:^-} + \mathrm{NH_3} \longrightarrow \mathrm{H_2N\text{–}(\text{–}CH_2\text{–}\overset{CN}{CH}\text{–})_{\mathit{n}}\text{–}CH_2\text{–}\overset{CN}{C}H_2} + \mathrm{:NH_2^-} \tag{5.34}$$

$$R_{\mathrm{tr}} = k_{\mathrm{tr}}[\mathrm{NH_3}][\mathrm{M^-}] \tag{5.35}$$

As in the case with cationic polymerizations, the number of growing chains is constant so that a steady state exists such as the $R_{\mathrm{i}} = R_{\mathrm{tr}}$. This is useful because it is difficult to determine the concentration of $[\mathrm{M^-}]$ so that it can be eliminated as follows:

$$k_{\mathrm{i}}[\mathrm{C}][\mathrm{M}] = k_{\mathrm{tr}}[\mathrm{NH_3}][\mathrm{M^-}] \tag{5.36}$$

and

$$[\mathrm{M^-}] = \frac{k_{\mathrm{i}}[\mathrm{C}][\mathrm{M}]}{k_{\mathrm{tr}}[\mathrm{NH_3}]} \tag{5.37}$$

Substitution into Equation 5.33 gives

$$R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}][\mathrm{M^-}] = \frac{k_{\mathrm{p}}[\mathrm{M}]k_{\mathrm{i}}[\mathrm{C}][\mathrm{M}]}{k_{\mathrm{tr}}[\mathrm{NH_3}]} = \frac{k'[\mathrm{M}]^2[\mathrm{C}]}{[\mathrm{NH_3}]} \tag{5.38}$$

$\overline{\mathrm{DP}}$ can be described as follows:

$$\overline{\mathrm{DP}} = R_{\mathrm{p}}/R_{\mathrm{tr}} = \frac{k_{\mathrm{p}}[\mathrm{M}][\mathrm{M^-}]}{k_{\mathrm{tr}}[\mathrm{NH_3}][\mathrm{M^-}]} = \frac{k'[\mathrm{M}]}{[\mathrm{NH_3}]} \tag{5.39}$$

Using the same approach did with the cationic polymerization, we have for the rate of propagation

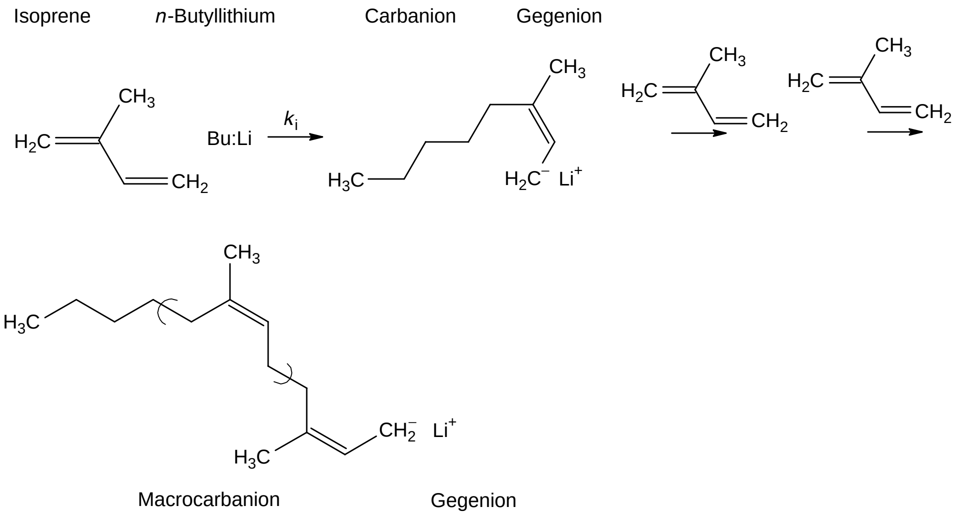
$$E_{\mathrm{(overall)}} = E_{\mathrm{p}} + E_{\mathrm{i}} - E_{\mathrm{tr}} \tag{5.40}$$

and for the dependence of chain length we have

$$E_{\mathrm{(overall)}} = E_{\mathrm{p}} - E_{\mathrm{tr}} \tag{5.41}$$

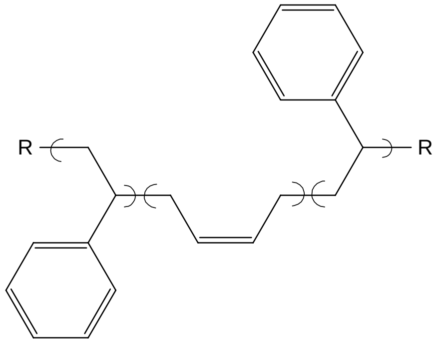
Thus, both the rate of propagation and the molecular weight are inversely related to the concentration of ammonia. The activation energy for chain transfer is higher than the activation energy for propagation. The overall activation energy is about 160 kJ/mol. The reaction rate increases and molecular weight decreases as the temperature is increased as shown in Figure 4.4. The reaction rate is dependent on the dielectric constant of the solvent and the degree of solvation of the gegenion. Weakly polar initiators, such as Grignard's reagent, may be used when strong electron-withdrawing groups are present on the monomer, but monomers with less electron-withdrawing groups require more highly polar initiators such as *n*-butyllithium.

Synthetic *cis*-1,4-polyisoprene (structure 5.42) is produced at an annual rate of about 100,000 t by the anionic polymerization of isoprene when a low dielectric solvent, such as hexane, and *n*-butyllithium are used. But, when a stronger dielectric solvent, such as diethylether, is used along with *n*-butyllithium, equal molar amount of *trans*-1,4-polyisoprene and *cis*-3,4-polyisoprene units is produced. It is believed that an intermediate cisoid conformation assures the formation of a *cis* product. An outline describing the formation of *cis*-1,4-polyisoprene is given in structure 5.42.



(5.42)

No formal termination is given in structure 5.42 because in the absence of contaminants the product is a stable macroanion. Szwarz named such stable active species “living polymers.” These macroanions or macrocarbanions have been used to produce block copolymers such as Kraton. Kraton is an ABA block copolymer of styrene (A) and butadiene (B) (structure 5.43). Termination is brought about by addition of water, ethanol, carbon dioxide, or oxygen.



(5.43)

Block ABA copolymer of styrene and butadiene

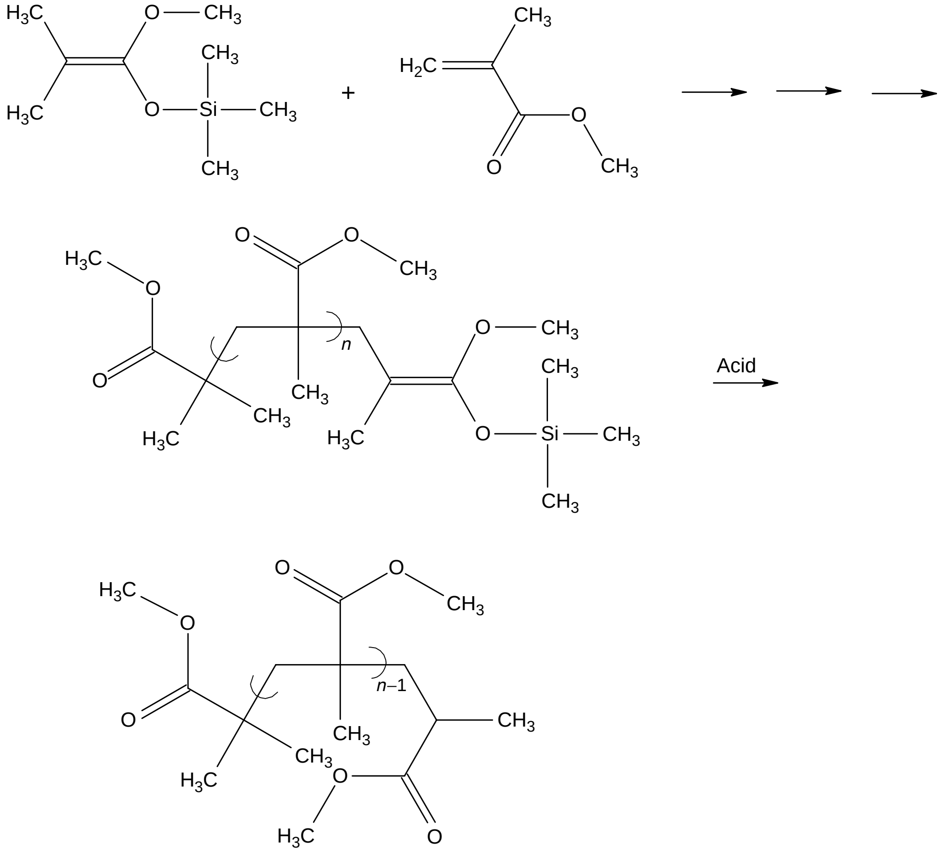
Living polymers are generally characterized by (1) an initiation rate that is much larger than the polymerization rate; (2) polymer molecular weight is related to [monomer]/[initiator]; (3) linear molecular weight–conversion relationship; (4) narrow molecular weight range; and (5) stabilization of the living end groups allowing the formation of telechelics, macromers, block copolymers, and star polymers.

Group-transfer polymerizations make use of a silicon-mediated Michael addition reaction. They allow the synthesis of isolatable, well-characterized living polymers whose reactive end groups can be converted into other functional groups. It allows the polymerization of alpha, beta-unsaturated esters, ketones, amides, or nitriles through the use of silyl ketenes in the presence of suitable nucleophilic catalysts such as soluble Lewis acids, fluorides, cyanides, azides, and bifluorides, HF_2^-.

As the polymerization occurs, the reactive ketene silyl acetal group is transferred to the head of each new monomer as it is added to the growing chain (Equation 5.44). Similar to anionic polymerization, the molecular weight is controlled by the ratio of the concentration of monomer to initiator. Reactions are generally carried out at low temperatures (about 0°C–50°C) in organic liquids such as THF. Compounds with "active" hydrogen atoms such as water and alcohol will stop the polymerization and their presence will curtain polymer chain length. Under the right conditions, polymerization will continue until all the monomer has been used up.

The trimethylsiloxy end group is a "living" end which continues to add units as long as monomer is available or until it is neutralized.

In addition to the use of salt combinations to produce nylons described in Chapter 4, nylons may also be produced by the anionic ROP of lactams. In fact, this method was largely developed to overcome patent rights held by DuPont based on the work of Carothers and his group. This is the preferred method for the production of nylon-6, structurally analogous to nylon-6,6, and is widely practiced in Europe.

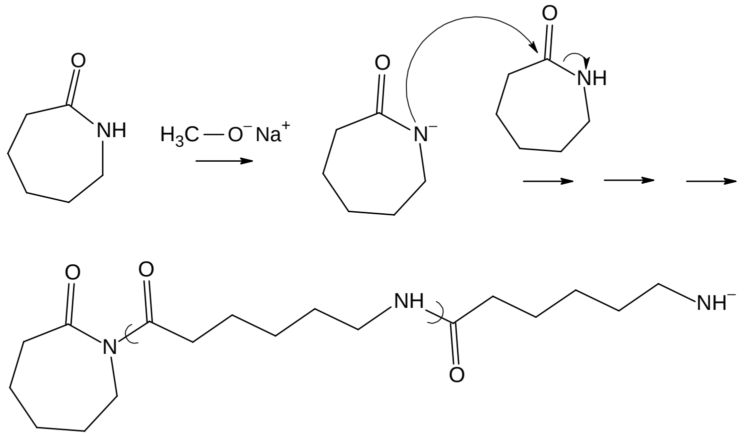


(5.44)

Nylon-6 is produced from the ROP of caprolactam (structure 5.45). Since each unit contains six carbon atoms it is named nylon-6 concurring to the naming of nylons. Along with having an analogous structure, it is not surprising that its physical and chemical properties are very similar to that of nylon-6,6 and they can generally be used to replace one another with almost no change in physical behavior. Structure 5.45 describes the synthesis of nylon-6 employing sodium methoxide as the initiator.

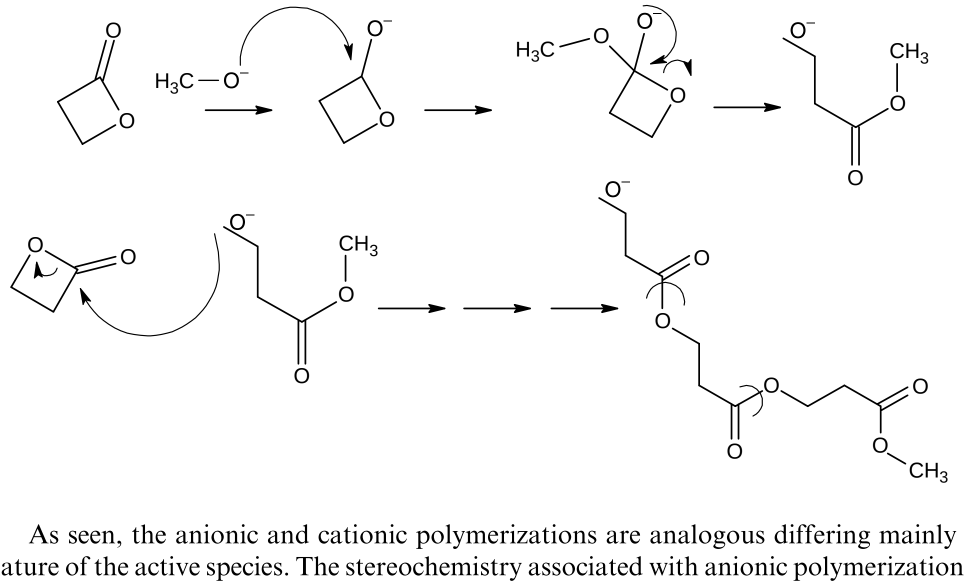
The term monadic is used to describe nylons such as nylon-6 that have been produced from one reactant. The term dyadic is used to describe nylons such as nylon-6,6 that have been produced from two reactants.

The initiation period in the lactam-opening polymerization may be shortened by addition of an activator, such as acetyl chloride. Nylon-4, nylon-8, and nylon-12 are commercially available and used as fibers and coatings.



(5.45)

Lactomes may also be polymerized by ring-opening anionic polymerization techniques. While the five-membered ring is not readily cleaved, the smaller rings polymerize easily producing linear polyesters (structure 5.46). These polymers are commercially used as biodegradable plastics and in PU foams.



(5.46)

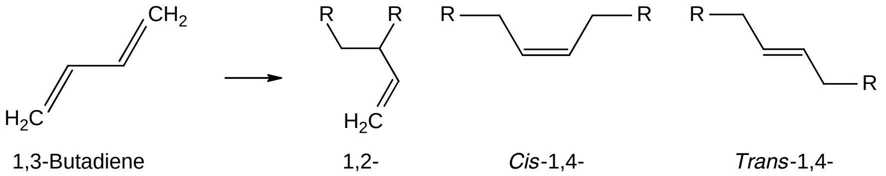
As seen, the anionic and cationic polymerizations are analogous differing mainly on the nature of the active species. The stereochemistry associated with anionic polymerization is also similar to that observed with cationic polymerization. For soluble anionic initiators at low temperatures, syndiotactic formation is favored in polar solvents, whereas isotactic formation is favored in nonpolar solvents. Thus, the stereochemistry of anionic polymerizations appears to be largely dependent on the amount of association the growing chain has with the counterion, analogous with the cationic polymerizations.

The stereochemistry of diene polymerizations is also affected by solvent polarity. For instance, the proportion of *cis*-1,4 units is increased by using organolithium or lithium itself as the initiator in the polymerization of isoprene or 1,3-butadiene in nonpolar solvents.

A polymer similar to natural hevea rubber is obtained using the anionic polymerization of isoprene under these conditions. In more polar solvents employing sodium and potassium initiators the amount of *cis*-1,4 units decreases and *trans*-1,4 and *trans*-3,4 units predominate.

5.4 STEREOREGULARITY AND STEREOGEOMETRY

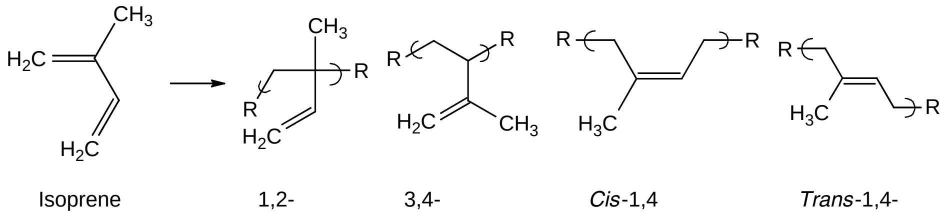
As noted in Chapter 2, there exists stereogeometry and stereoregularity in polymers. These differences have profound effects on the physical and, to a lesser degree, chemical properties of the polymers produced from the same monomer. There are three possible units that can be formed from the polymerization of butadiene as shown in structure 5.47.



(5.47)

For isoprene, there are four possible units formed (structure 5.48).

As shown in Figure 2.5, there are three possible stereoregular forms for monosubstituted vinyl polymers. These are isotactic, all of the pendant groups are on one side of the chiral carbon; syndiotactic, the pendant groups appear on alternate sides of the chiral carbon; and atactic, some mixture of geometries about the chiral carbon.



(5.48)

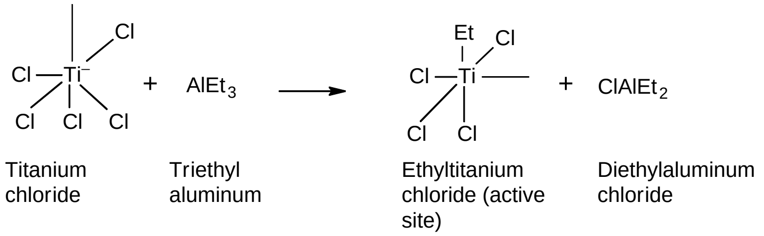
It is important to realize that polymer configuration and conformation are related. Thus, there is a great tendency for isotactic polymers (configuration) to form helical structures (conformation) in an effort to minimize steric constrains brought about because of the isotactic geometry.

5.5 POLYMERIZATION WITH COMPLEX COORDINATION CATALYSTS

Prior to 1950, the only commercial polymer of ethylene was a highly branched polymer called high-pressure polyethylene (HPPE) where extremely high pressures were used in the polymerization process. The technique for making linear polyethylene (PE) was discovered by Marvel and Hogan in the 1940s, by Banks in the 1950s, and by Nobel laureate Karl Ziegler in the early 1950s. Ziegler prepared HDPE by polymerizing ethylene at low pressure and ambient temperatures using mixtures of triethylaluminum and titanium tetrachloride. Another Nobel laureate, Giulio Natta, used Ziegler's complex coordination catalyst to produce crystalline, stereoregular PP. These catalysts are now known as Ziegler–Natta (or Natta–Ziegler) catalysts (ZNCs).

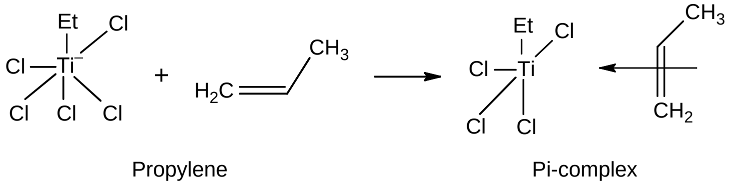
In general, a ZNC is a combination of a transition metal compound from Group IVB (4) to VIIIB (10) and an organometallic compound of a metal from Group IA (1) to IIIA (13) in the periodic table. It is customary to refer to the transition metal compounds as the catalyst (because reaction occurs at the transition metal atom site) and the organometallic compound as the cocatalyst.

Here, we will use titanium to illustrate the coordination polymerization process. Several exchange reactions between catalyst and cocatalyst occur with Ti(IV) reduced to Ti(III). The extent and kind of stereoregulation can be controlled through a choice of reaction conditions and catalyst or cocatalyst. The titanium salt is present as a solid. The precise mechanism probably varies a little depending on the catalyst or cocatalyst, and reaction conditions. Here, we will look at the polymerization of propylene using titanium chloride and triethylaluminum. In general, a monomeric molecule is inserted between the titanium atom and the terminal carbon atom in a growing chain. Propagation occurs at the solid titanium salt surface—probably at defect, corners, and edges. The monomer is always the terminal group on the chain. Triethylaluminum reacts producing ethyltitanium chloride as the active site for polymerization.



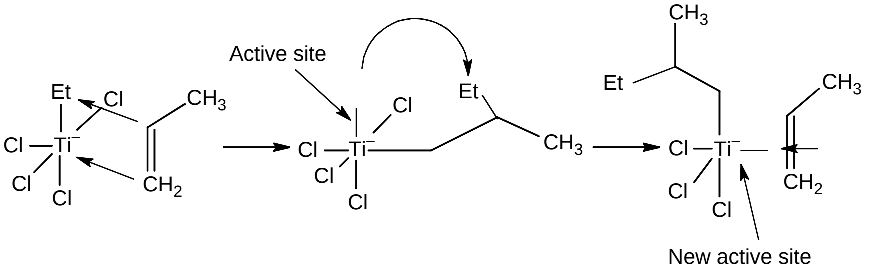
(5.49)

The propylene forms a pi-complex with the vacant d-orbital of titanium as shown in the following structure.



(5.50)

The ethyl groups transfer to the propylene opening up a new active site. The growing chain transfers to the site vacated by the ethyl group creating a new active site which attracts, through pi-interactions, another propylene monomer. This sequence is shown in structure 5.51. The edges of the solid titanium salt are believed to help provide the contour necessary to form the stereoregular chains.



(5.51)

Most vinyl monomers give a predominance of the isotactic product. Typically, the more exposed the catalytic site, the less the stereoregularity of the resulting polymer. The isotactic polypropylene (iPP) is produced using this technique, as is HDPE.

The versatility of such stereoregulating systems is demonstrated in the polymerization of 1,3-butadiene where all four of the potential structures, isotactic-1,2-, syndiotactic-1,2-, *trans*-1,4-, and *cis*-1,4-, can be synthesized in relatively pure form using different catalyst systems.

Molecular weight is regulated to some degree by control of the chain transfer with monomer and with the cocatalyst, plus internal hydride transfer. However, hydrogen is added in the commercial processes to terminate the reaction because many systems tend to form longer chains beyond the acceptable balance between desired processing conditions and chain size.

The stereochemistry of the products is often controlled through control of the reaction temperature. For instance, use of low temperatures, where the alkyl shift and migration is retarded, favors formation of syndiotactic polypropylene (sPP). Commercial iPP is produced at room temperatures.

HDPE is typically produced using some stereoregulating catalysts. Much of it is produced using a Phillips catalyst system such as chromia catalyst supported on silica. Some HDPE and PP are commercially produced employing a ZNC. This initiator is also employed for the production of polybutene and poly(-4-methyl-pentene-1) (TPX). TPX has high melting point of about 300°C but because of the presence of the bulky butyl groups, a relatively low specific gravity of 0.83. The percentage of polymer that is not soluble in *n*-hexane is called the isotactic index for some polymers where the atactic and syndiotactic forms are hexane soluble.

5.6 SOLUBLE STEREOREGULATING CATALYSIS

The 1940s were a time of studying the kinetics and mechanism of production of vinyl polymers that took "center stage" in the 1950s. The 1950s incubated the solid state stereoregulating catalysis that spawned a chemical revolution with the synthesis of stereoregular vinyl polymers in the 1960s. The 1980s and early 1990s served as a foundational time for soluble stereoregulating catalysis spawning another revolution related to the production of vinyl polymers with enhanced properties.

The solid state stereoregulating catalysts "suffered" from at least three problems. First, while stereoregular polymers were formed with good control of the stereogeometry, polymer properties still fell short of predicted (upper limit) values. This was probably due to the presence of the associated solid catalyst structure that accompanies the active catalytic site. This "excess baggage" restricts the motion of the growing chains so that stereoregular control was good, but the tendency to form good secondary structures was interrupted.

Second, in many cases the solid state catalysis was incorporated, as contaminants, within the growing polymer making an additional purification step necessary in the polymer processing to rid the polymer of this undesired material.

Third, many solid state catalysts offered several "active polymerization sites" due to differences in the precise structure at and about the active sites. This resulted in an average stereoregular product being formed.

The new soluble catalysts offer a solution to these three problems. First, the "smaller" size of the active site, and associated molecules, allows the growing chains to "take advantage" of a natural tendency for the growing polymer chain to form a regular helical structure (in comparison to polymers formed from solid state catalysts).

Second, the solution catalysts allow the synthesis of polymers that contain little or no catalytic agents, allowing the elimination of the typical additional "clean-up" steps necessary for polymers produced from solid state catalysts.

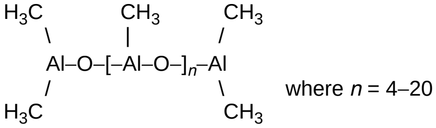
Third, the newer soluble catalytic sites are homogeneous offering the same electronic and stereostructure allowing the synthesis of more stereoregular, homogeneous polymers.

The new soluble stereoregulating polymerization catalysts require three features:

- A metal atom (active) site
- A cocatalyst or counterion
- A ligand system

While the major metal site is zirconium, other metals have been successfully used including Ti, Hf, Sc, Th, and rare earths (e.g., Nd, Yb, Y, Lu, and Sm). Cyclopentadienyls (Cps) have been the most commonly used ligands though a number of others have been successfully employed including substituted and bridged Cps. The most widely used metal–ligand grouping is zirconocene dichloride (zironocene dichloride has a distorted tetrahedral geometry about Zr).

Methylalumoxane (MAO) (structure 5.52) is the most widely utilized counterion. MAO is an oligomeric material with the following approximate structure:



$$(H_3C)_2Al-O-[-Al(CH_3)-O-]_n-Al(CH_3)_2 \quad \text{where } n = 4\text{–}20 \tag{5.52}$$

Methylalumoxane

It is believed that MAO plays several roles. MAO maintains the catalyst complex as a cation, but doing so without strongly coordinating to the active site. It also alkylates the metallocene chloride, replacing one of the chloride atoms with an alkyl group and removing the second chlorine, thus creating a coordinately unsaturated cation complex, Cp_2MR^+. As an olefin approaches the ion pair containing the active metal, a metallocene–alkyl–olefin complex forms. This complex is the intermediate stage for the insertion of the monomeric olefin into a growing polymer chain.

The structure of the catalyst complex controls activity, stereoselectivity, and selectivity toward monomers. The catalyst structure is sensitive to Lewis bases, such as water and alcohol, encouraging the use of strongly oxyphilic molecules, such as MAO, to discourage the inactivation (poisoning) of the catalyst.

These soluble catalysts are able to give vinyl polymers that have increased stereogeometry with respect to tacticity as well as allowing the growing chains to form more precise helical structures. Further, the homogeneity of the catalytic sites also allows for the production of polymers with narrow molecular weight "spreads."

The summation of these affects is the production of polymers with increased strength and tensile properties. For PE the use of these soluble catalysts allows the synthesis of PE chains with less branching compared to those produced using solid state catalysts such as the ZNCs. PE produced employing soluble catalysts also shows increased properties in comparison with PE produced by solid catalysts. Table 5.2 gives some comparisons of the PEs produced using the ZNCs with those produced with soluble catalysts.

Values of M_w/M_n of 2 or less are common for the soluble catalyst systems whereas values of 4–8 are usual for ZNC systems. The soluble catalyst systems also are able to polymerize a larger number and greater variety of vinyl monomers to form homogeneous polymers and copolymers in comparison with solid catalyst systems.

The active site is a cationic metallocene alkyl generated by reaction of a neutral metallocene formed from reaction with excess MAO or other suitable cocatalysts such as a borane Lewis acid. This sequence is shown in Figure 5.1 employing MAO with ethylene to form PE. Initiation and propagation occur through pre-coordination and insertion of the ethylene into the alkyl group polymer chain. Here, termination occurs through beta-hydride elimination

TABLE 5.2
Comparison of Properties of Polyethylene (PE) Using Solid (ZNC) and Soluble Catalysts

Property	Unit	Soluble	ZNC
Density	g/cm^3	0.967	0.964
Melt index		1.3	1.1
Haze		4.2	10.5
Tensile yield	psi	800	750
Tensile break	psi	9400	7300
Elongation break	%	630	670

Source: From Pain, C.F., *Proceedings of the Worldwide Metallocene Conference*, Catalyst Consultant Inc., Houston, TX, May 26–28, 1993.

producing a zirconium hydride and a long-chain alpha-olefin. These long-chain alpha-olefins can form linear HDPE or be used as comonomers with monomers such as 1-propylene, 1-hexene, or 1,5-hexadiene to give a variety of branched and linear products. These Group IVB metallocene catalysts are very active producing yields in excess of 1 t of PE per gram of catalyst per hour with a total efficiency on the order of 25 t of PE per gram of catalyst.

These catalyst systems are also used to form other hydrocarbon polymers such as a variety of PPs.

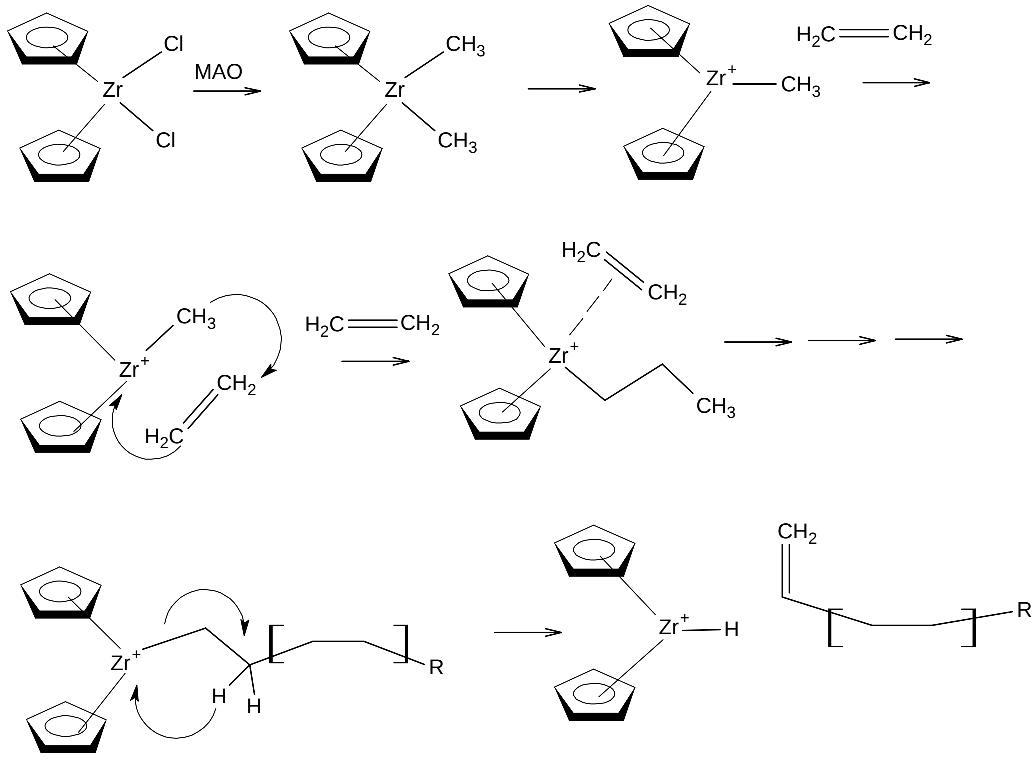


FIGURE 5.1 Proposed mechanism for soluble stereoregulating catalyst polymerizations.

A major limitation of such Group IVB metallocene catalysts is that they are air- and moisture-sensitive and not tolerant to heteroatom-containing monomers. In the case of heteroatom-containing monomers the unbonded electron pairs on the heteroatom, such as oxygen, preferentially coordinate to the Lewis acid metal center in place of the carbon–carbon double bond. Some so-called middle and late transition metal organometallics are more tolerant to the presence of such heteroatoms and can be used as effective cocatalysts. These include some palladium, iron, cobalt, and nickel initiators.

The use of transition and selected main group metal catalysis is increasing with the ability to design special catalytic systems for special polymer architecture and property production. These catalyst systems involve the transition metal as a site for active polymer growth. The new soluble stereoregulating catalysts are one example of these systems. These growing sites may be more or less ionic or covalent depending upon the catalyst used and such sites are not generally appreciably dissociated as is the case in classical cationic and anionic systems. The metal ligands can provide both electronic and steric structural control and are generally more robust in comparison with the anionic and cationic systems. Along with many advantages, there are some challenges. Because of their very nature, transition metal initiators can be very complex requiring several synthetic steps; they may be expensive and/or require costly cocatalysts; and control of the particular reaction conditions is very important since small, seemingly subtle changes can be magnified into larger polymer structural changes.

There are an increasingly large number of metal-catalyzed polymerizations including olefin metathesis reactions including ring-opening metathesis polymerizations (ROMPs), formation of polyketones from the copolymerization of carbon monoxide, group-transfer polymerizations, and step-growth addition and elimination (coupling) polymerizations. The study of metal catalytic sites is a vigorous area of ongoing research.

Polymers produced from single-site catalysts are increasingly being used in the marketplace. As noted earlier, the strength of the materials is increased because of the greater order in the individual polymer chains. For PE this means the number of branches is less and for substituted polymers such as PP this means that the order about the substituted carbon is increased allowing for a denser, tighter fit of the individual polymer chain segments resulting in increased overall polymer strengths and less permeability for materials.

Use of materials produced from single-site catalysts in areas employing thin films is increasing. For instance, bananas are generally produced at one location and shipped and stored at other locations for sale. Even when picked green, they ripen rapidly when exposed to oxygen. Regular LLDPE is generally employed as a thin film to protect bananas for shipment and storage. Regular LLDPE permits some transfer of oxygen and because of the somewhat pointed nature of bananas the film may be punctured. Single-site metallocene-based LLDPE is less permeable and less apt to tear and is now replacing regular LLDPE in this use. Its use is also increasing in the containment of heavier materials, such as topsoil and water-purification salt, which are using films. In both cases, thinner films and consequently less film material are necessary to give an equal or better job performance. Single-site produced materials also offer better clarity, toughness, and easy sealability.

5.7 POLYETHYLENES

Tupperware was the idea of Earl Silas Tupper, a New Hampshire tree surgeon and plastics innovator. He began experimenting with PE during the early part of World War II. In 1947, he designed and patented the famous "Tupper seal" that "sealed in" freshness. In order to close the container it had to be "burped" to remove air. Tupperware was also bug proof, spill proof, did not rot or rust, and did not break when dropped. Even with all of these advantages, few were sold. Enter Brownie Wise, a divorced single mother from Detroit who desperately needed to supplement her income as a secretary, who had the idea of "Tupperware Parties."

By 1951, Tupper had withdrawn all of the Tupperware from the stores and turned over their sales to Brownie Wise, making the Tupperware parties as the only source of the ware.

PE was probably initially synthesized by M.E.P. Friedrich, while a graduate student working for Carl S. Marvel in 1930, when it was an unwanted by-product from the reaction of ethylene and a lithium alkyl compound. In 1932, British scientists at the Imperial Chemical Industries (ICI) accidentally made PE while they were looking at what products could be produced from the high-pressure reaction of ethylene with various compounds. In March 1933, they found the formation of a white solid when they combined ethylene and benzaldehyde under high pressure (about 1400 atm pressure). They correctly identified the solid as PE. They attempted the reaction again, but with ethylene alone. Instead of getting the waxy white solid again, they got a violent reaction and the decomposition of the ethylene. They delayed their work until December 1935 when they had better high-pressure equipment. At 180°C, the pressure inside the reaction vessel containing the ethylene decreased consistently with the formation of a solid. Because they wanted to retain the high pressure, they pumped in more ethylene. The observed pressure drop could not be totally due to the formation of PE, but something else was contributing to the pressure loss. Eventually, they found that the pressure loss was also due to the presence of a small leak that allowed small amounts of oxygen to enter into the reaction vessel. The small amounts of oxygen turned out to be the right amount needed to catalyze the reaction of the additional ethylene that was pumped in subsequent to the initial pressure loss (another "accidental" discovery). The ICI scientists observed no real use for the new material. By chance, J.N. Dean of the British Telegraph Construction and Maintenance Company heard about the new polymer. He needed a material to encompass underwater cables. He reasoned that PE would be water resistant and suitable to coat the wire protecting it from the corrosion caused by the saltwater in the ocean. In July 1939, enough PE was made to coat one nautical mile of cable. Before it could be widely used, Germany invaded Poland and PE production was diverted to making flexible high-frequency insulated cable for ground and airborne radar equipment. PE was produced, at this time, by ICI and by DuPont and Union Carbide for the United States.

PE did not receive much commercial use until after the war when it was used in the manufacture of film and molded objects. PE film displaced cellophane in many applications being used for packaging produce, textiles, and frozen and perishable foods. This PE was branched and had a relatively low softening temperature, below 100°C, preventing its use for materials where boiling water was needed for sterilization.

The branched PE is called low-density HPPE because of the high pressures usually employed for its production, and because of the presence of the branches, the chains are not able to closely pack, leaving voids and subsequently producing a material that had a lower density in comparison with low-branched PE.

Karl Ziegler, director of the Max Planck Institute for Coal Research in Muelheim, Germany, was extending early work on PE attempting to get ethylene to form PE at lower pressures and temperatures. His group found that certain organometallics prevented the polymerization of ethylene. He then experimented with a number of other organometallic materials that inhibited PE formation. Along with finding compounds that inhibited PE formation, they found compounds that allowed the formation of PE under much lower pressures and temperatures. Further, these compounds produced a PE that had fewer branches and higher softening temperatures.

Natta, a consultant for the Montecatini company of Milan, Italy, applied the Zeigler catalysts to other vinyl monomers such as propylene and found that the polymers were of higher density, higher melting, and more linear than those produced by the then classical techniques such as free-radical-initiated polymerization. Ziegler and Natta shared the Nobel Prize in 1963 for their efforts in the production of vinyl polymers using what we know today as solid state stereoregulating catalysts.

Although many credit Natta and Ziegler as first having produced so-called HDPE and stereoregular polyolefins, Phillips' scientists first developed the conditions for producing stereospecific olefin polymers and HDPE. In 1952, Hogan and Banks discovered that ethylene and propylene polymerized into what we today know as HDPE and stereoregular PP. As with many other advancements, their initial studies involved other efforts, here to improve fuel yields by investigating catalysts that converted ethylene and propylene to higher molecular weight products. They found that chromium trioxide supported on a silica–alumina catalyst produced a hard solid rather than the usual waxy-like PE. They quickly looked at other olefins and soon discovered a crystalline PP, namely a stereoregular PP, specifically iPP.

Today, there exist a wide variety of "PEs" that vary in the extent and length of branching as well as molecular weight and MWD and amount of crystallinity. Some of these are pictured in Figure 5.2. Commercial LDPE typically has 40–150 short alkyl branches for every 1000 ethylene units. It is produced employing high pressure (15,000–50,000 psi and temperatures to 350°C). It has a density of about 0.912–0.935. Because of the branching, the LDPE is amorphous (about 50%) and sheets can allow the flow-through of liquids and gasses. Because of the branching and low amount of crystallinity, LDPE has a low melting point of about 100°C making it unsuitable for uses requiring sterilization through use of boiling water.

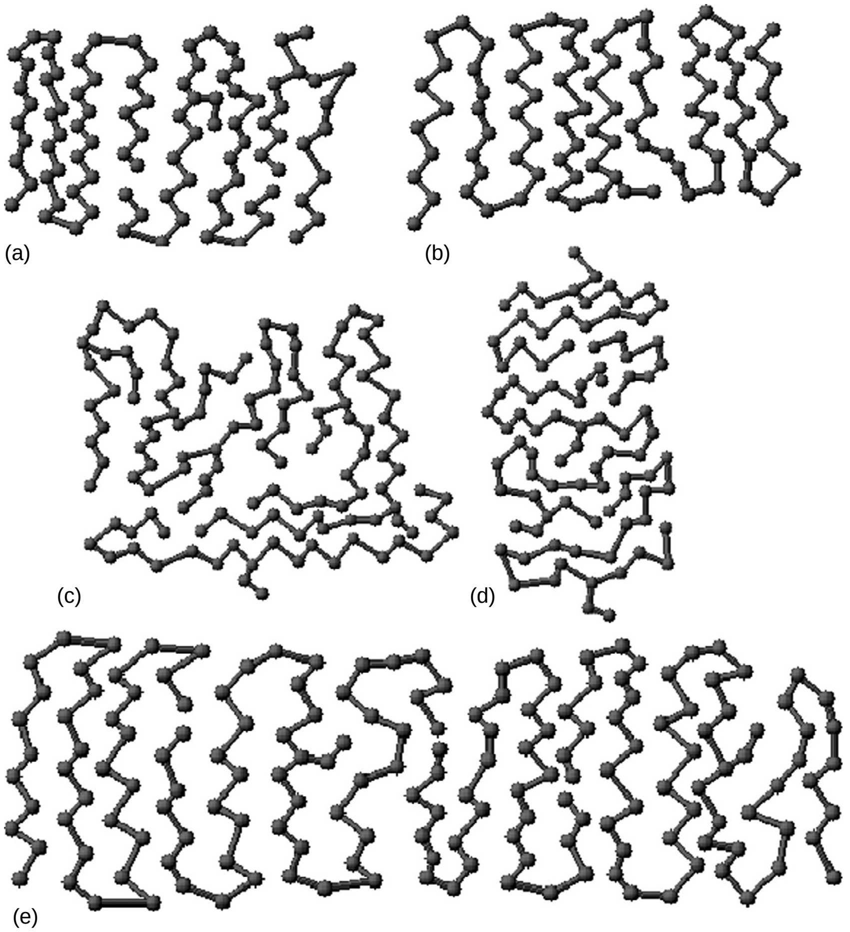


FIGURE 5.2 Ball-and-stick models of HDPE (a), UHMWPE (b), LDPE (c), LLDPE (d), and ULPE (e).

LDPE has a combination of short-to-long branches, with long branches occurring at a rate of about 10 short branches to every long branch.

HDPE produced using organometallic catalysts such as the ZNC or Phillips catalysts have less than 15 (normally within the range of 1–6) short alkyl branches (essentially no long branches) for 1000 ethylene units. Because of the regular structure of the ethylene units themselves and the low extent of branching, HDPE chains can pack more efficiently resulting in a material with greater crystallinity (generally up to 90%), higher density (0.96), with increased chemical resistance, hardness, stiffness, barrier properties, melting point (about 130°C), and tensile strength. Low-molecular weight (chain lengths in hundreds) HDPE is a "wax," while "typical" HDPE is a tough plastic.

LLDPE can be produced with less than 300 psi and at about 100°C. It is actually a copolymer of ethylene with about 8%–10% of an alpha-olefin such as 1-butene, 1-pentene, 1-hexene, or 1-octene. Through control of the nature and amount of alpha-olefin, we are able to produce materials with densities and properties between those of LDPE and HDPE. LLDPE does not contain the long branches found in LDPE.

UHMWPE is an HDPE with chain lengths over 100,000 ethylene units. Because of the great length of the chains, they "intertangle" causing physical cross-links, increasing the tensile strength, and related properties of these materials. (By comparison, HDPE rarely is longer than 2000 ethylene units.) UHMWPE is about 45% crystalline and offers outstanding resistance to corrosion and environmental stress-cracking, outstanding abrasion resistance and impact toughness, and good resistance to cyclical fatigue and radiation failure, and with a low surface friction. It is produced utilizing catalyst systems similar to those employed for the production of HDPE (i.e., ZNC and Phillips catalysts). It has a density of about 0.93.

Ultralinear polyethylene (ULPE) has recently become available through the use of soluble stereoregulating catalysts. Along with a decreased amount of short-chained alkyl branching, ULPE has a narrower molecular weight spread.

Polymethylene can be produced through several routes including the use of diazomethane or a mixture of carbon monoxide and hydrogen. This polymer has only a little branching.

It is well accepted that the history of a polymer, including polymer processing, influences polymer behavior. Some of these influences are just becoming known. Interestingly, as in much of science, once the critical parameters are known on a macrolevel, we are able to better understand them on a molecular and conceptual level. An example that illustrates this involves the processing of annealed PE. In general, for most linear PE, micelles, and associated spherulites are formed when it is melted and then slowly cooled. If no force is applied during the annealing process (simple melt crystallization), a high amount of force and large deformation is required to breakdown the initial spherulite structures with reformation occurring along the axis of the pull when high-strength PE rod, film, and sheet are produced. However, if the PE is crystallized under pressure applied in one direction, less energy and lower deformation are required to align the PE spherulites since the spherulites are already partly aligned. In both cases, stretching of the molecular network is required. For the simple melt-crystallized PE, the original spherulite structure is destroyed during the deformation followed by the formation of new fibrillar structures. For the pressure-associated annealing process, elongated micelles are formed that largely remain after the deformation process.

LDPE films are nearly clear even though they contain a mixture of crystalline and amorphous regions. This is because the crystalline portions are space filling and not isolated spherulites allowing a largely homogeneous structure with respect to refractive index resulting in a material that is transparent. In fact, the major reason that LDPE films appear hazy or not completely transparent is the roughness of the surface and is not due to the light scattering of the interior material.

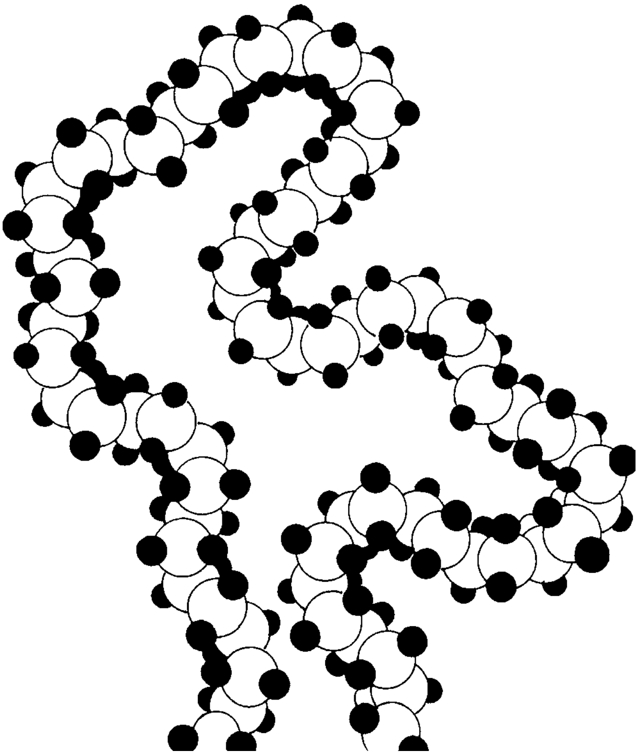


FIGURE 5.3 Space-filling structure of a portion of a linear amorphous polyethylene (PE) region.

Space-filling models of amorphous and crystalline linear PE are given in Figures 5.3 and 5.4. Typical uses of the various PEs include:

1. UHMWPE—battery separators, light-weight fibers, permanent solid lubricant materials in railcar manufacture, automobile parts, and truck liners; liners to hoppers, bins, and chutes; farm machinery as sprockets, idlers, wear plates, and wear shoes; sewage-treatment bearings, sprockets, wear shoes; lumbering-chute, sluice, and chain-drag liners; neutron shield
2. Typical HDPE—blow-molded products: bottles, cans, trays, drums, tanks, and pails; injection-molded products: housewares, toys, food containers, cases, pails, and crates; films, pipes, bags, conduit, wire and cable coating, foam, insulation for coaxial and communication cables
3. Low-molecular weight HDPE—spray coatings, emulsions, prinking inks, wax polishes, and crayons
4. LDPE—packaging products, bags, industrial sheeting, piping and tubing, films, garbage cans, industrial containers, household items
5. LLDPE—telephone jacketing, wire and cable insulation, piping and tubing, drum liners, bottles, films

Plastomers is the name given to copolymers of ethylene that have a little crystallinity, but are largely amorphous. They are also called very low-density polyethylene (VLDPE). They are more elastic than LLDPE but less stiff. They are used as a sealing layer in film applications and controlled permeation packaging for vegetables and fruits.

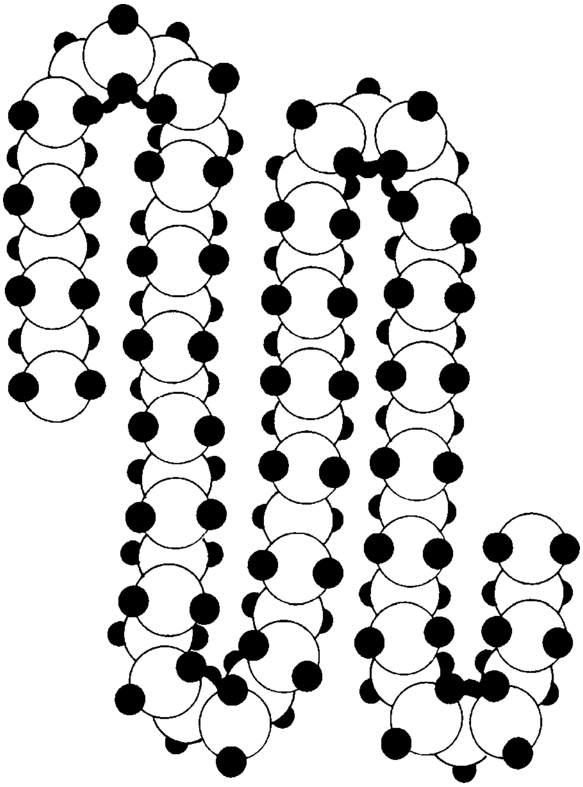


FIGURE 5.4 Space-filling structure of a portion of a linear crystalline polyethylene (PE) region.

LDPE, PP, and TPX are more susceptible to oxidation in comparison with HDPE because of the presence of tertiary carbon atoms in the former. The degradation of LDPE, PP, and TPX is retarded through the use of antioxidants.

General properties of some of the important PEs are given in Table 5.3.

5.8 POLYPROPYLENE

PP is one of the three most heavily produced polymers (Section 1.3). The abundance of PP is the result of the variety of PP produced, its versatility allowing a wide variety of products to

TABLE 5.3
General Physical Properties of Selected Polyethylenes (PEs)

Polyethylene →	LDPE	HDPE	UHMWPE
Heat deflection temperature (1820 kPa; °C)	40	50	85
Maximum resistance to continuous heat (°C)	40	80	80
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	10	12	12
Compressive strength (kPa)		2×10^4	
Impact strength (Izod: cm-N/cm of notch)	No break	30	No break
Tensile strength (kPa)	5×10^3	3×10^4	6×10^4
Density (g/mL)	0.91	0.96	0.93

be produced, availability of a large feedstock, and its inexpensiveness. Today, PP is used in such diverse applications as a film in disposable diapers and hospital gowns to geotextile liners; plastic applications as disposable food containers and automotive components; and fiber applications such as in carpets, furniture fabrics, and twine.

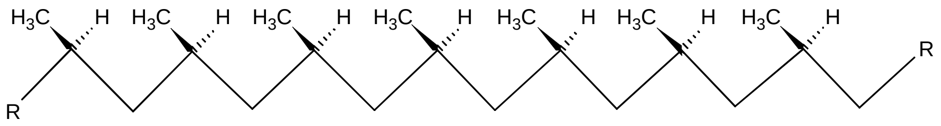
While PP was produced for sometime, it became commercially available only in the late 1950s with the production by Natta and coworkers at Phillips of somewhat stereoregular PP. The first PP was not highly crystalline because the tacticity, a measure of the stereoregularity, was only approximate. But, with the use of the ZNC and Phillips catalyst systems, PP with greater stereoregularity was produced giving PP with enhanced physical properties such as increased stiffness, better clarity, and a higher distortion temperature. Today, with better catalysts, including the soluble metallocene catalysts, the tacticity has been increased so that PP with 99% isotacticity can be produced. The more traditional ZNC has high catalyst efficiencies with 1 g of catalysts producing 1 kg of PP. This high catalytic efficiency eliminates the need for catalyst removal. Most iPP is made using bulk propylene, either as a gas or liquid.

A brief side trip allows some insight into industrial workings. Phillips Petroleum Company was busily working on ways to improve refinery processes because it was almost solely a fuel company in the 1950s. Two young chemists, Hogan and Banks, were trying to develop catalysts that would act as high-performance gasoline additives when one of the catalysts, mixed with the petroleum propylene present in a pipe, plugged up the pipe with a whitish, taffy-like material. While many companies might have told Hogan and Banks to get back to their original efforts that were the "bread and butter" of the company, instead they were told to investigate the formation of this off-white material. At this time, most of the known plastics were either too brittle or softened at too low a temperature for most practical uses. This off-white material, produced from propylene, could be hardened giving a flexible material that melted above 100°C. After some effort, it was discovered that this catalyst could also be used to give a PE that was superior to the "old" PE. Eventually, the old PE would be given the name of LDPE, and the new PE the name of HDPE.

In 1953, a patent was applied for covering both the synthesis of PP and PE under the trade name of Marlex. Even after a material is discovered many steps are needed before a product becomes available to the general public. Management was getting glowing reports about the potential for these new materials. Based on these assessments, $50 million was committed for the construction of a large-scale PE plant at Adams Terminal.

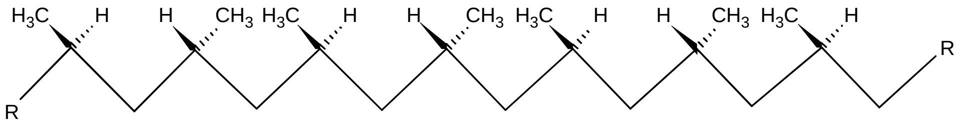
Several things were in operation that were not immediately apparent. First, the great investment of money and time needed to bring a product into the marketplace. At that time $50 million was a lot of money, on the order of $500 million today. Second, up to that time, technicians with little training were used in much of the chemical industry. The "educated" chemists were kept behind the research benches discovering "new" things. Most of the PhD chemists were, in fact, in universities rather than in industry. (Today, only about 11% of the professional chemists are teaching, the rest are in industry and government.) Because of the sensitivity of the catalyst system used to produce the new polymers, substantially greater training had to be given to workers who dealt with the production. Third, this was a venture into a new arena by Phillips, up to now solely a gasoline-producing company. Finally, while not initially apparent, the catalysts used to produce these new polymers were part of a new group of catalysts being investigated internationally by many companies that allowed the production of so-called stereoregular polymers.

As noted previously, PP and other alpha-olefins can reside in three main stereoregular forms differentiated from one another because of the precise geometry of the methyl group as the polymer is formed. When the methyl groups reside on the same side as one looks down a barrow of the chain, as below, it is called iPP.



(5.53)

The methyl group can also exist in alternate positions as shown in structure 5.54. This form is called sPP.



(5.54)

The third structure consists of mixtures of the syndiotactic and isotactic structures favoring neither structure. This mixture of structures is called the aPP, the “a” meaning having nothing to do with. Space-filling models of all three different tactic forms are given in Figure 5.5.

Each particular tactic form has its own physical properties. Table 5.4 contains representative values for iPP. The syndiotactic and isotactic forms are referred to as stereoregular forms and allow the chains to better fit together giving a material that is crystalline while the aPP is amorphous. Being crystalline causes the polymer to be stronger, denser, less porous to small molecules like water and oxygen, and to have a higher melting temperature. The old PP is of the atactic form and the form synthesized by Hogan and Banks is iPP. Only recently, using soluble stereoregulating systems has sPP become commercially available.

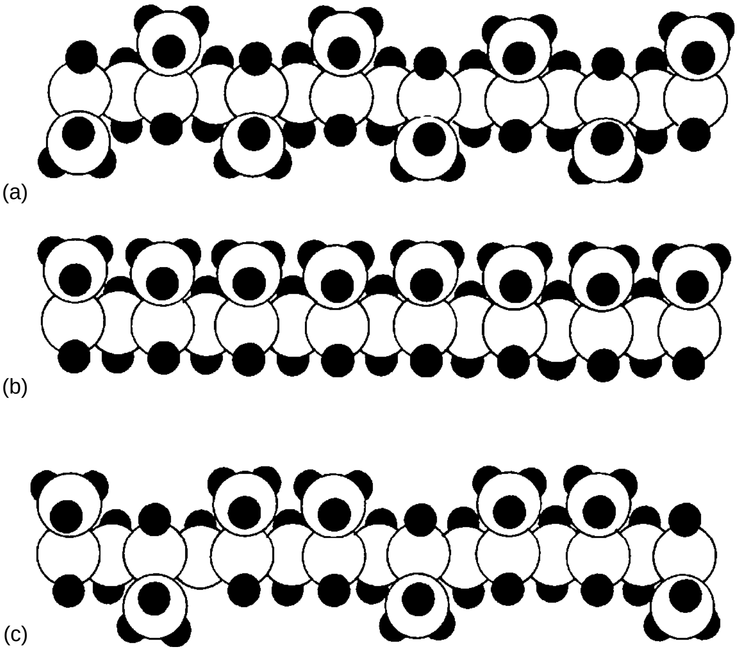


FIGURE 5.5 Space-filling models of syndiotactic (a), isotactic (b), and atactic (c) forms of polypropylene. (My children and now grandchildren believe that the isotactic polypropylene (iPP) is really a chorus line of dancing teddy bears.)

TABLE 5.4
General Physical Properties of iPP

Heat deflection temperature (1820 kPa; °C)	55
Maximum resistance to continuous heat (°C)	100
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	9
Compressive strength (kPa)	
Flexural strength (kPa)	5×10^4
Impact strength (Izod: cm-N/cm of notch)	27
Tensile strength (kPa)	3.5×10^4
Ultimate elongation (%)	100
Density (g/mL)	0.90

Other groups were working on developing these stereoregulating catalysts. In fact, more research dollars and effort were spent during the 1950s developing these stereoregulating catalysts than that spent on cancer research during that time. The competition was fierce and monetary stakes high. I was present at one of the initial presentations of the results from a number of different groups. Each group believed that their catalyst system gave the best results and each believed that the product they obtained was the same product that other companies obtained. There were several times during the presentations where the groups would yell at one another and physically wrench the microphone from another speaker calling one another various unkind words. It was later learned that each of the groups had different catalytic systems that gave different products. Thus, the presenters were most probably giving accurate information but based on slightly differing catalyst systems.

Jumping from a laboratory scale production to mass production is difficult because of the need to control the structure of the catalyst because only one form of the catalyst gave the desired iPP and PE while other forms gave mixtures of PP and PE structures. The first Marlex pellets came off the production line at the Adams plant and they were varied in color and size, and off-specification. It was hard for the sales staff to convince buyers that this was the miracle material that they had promised. The realization that the catalysts form was so important became painfully evident. The material was better than the old PE and PP, but it was not as good as that obtained in the laboratory. Warehouse after warehouse of somewhat inferior material was produced with few buyers.

Relief was spelled, not "R-E-L-I-E-F," but rather "H-U-L-A H-O-O-P" which was reinvented by Richard Knerr and Arthur "Spud" Melin who founded the Wham-O company that also reinvented another old toy, the Frisbee. American children fell in love with the hula hoop and the somewhat inferior Phillips material was good enough to give good hula hoops. Demand for these plastic rings was sufficient to take the Adams plant output for a half year and turn it into hula hoops. Phillips president, Paul Endacott, was so pleased that he kept a hula hoop in his office to remind him of his "savior." By the time that particular wave of hula hoop mania wound down in 1959, the problems in the product line at the Adam terminal were overcome and Marlex had found new markets. One of the first markets was the use of PE and PP baby bottles in hospitals to replace the old glass bottles. The Marlex bottles were less expensive, could be sterilized (remember, both the new PE and PP could be heated to boiling, 100°C, without melting), and would not shatter when dropped. The manufacture of Chiffon household liquid detergent took a chance on using plastic bottles rather than glass to hold their detergent. Their success caused other manufacturers to change to the lighter, nonbreakable, and less expensive plastic containers. Today, PP and PE hold the major share of the container market.

Copying the tubes used to make the hula hoop, plastic tubing for many varied application such as connecting air conditioners and ice makers, took off. Today, the three widely used synthetic polymers are LLDPE, HDPE, and PP. New catalysts and production procedures has allowed the physical properties and varied uses of these "big three" synthetic polymers to be continually increased.

While it was possible to produce sPP, employing the Zeigler–Natta solid systems, commercial sPP has only recently become commercial through the use of the soluble metallocene catalysts. These materials have a similar T_g as iPP, but they have a different balance between stiffness and toughness.

Atactic or amorphous forms of PP are also used. Initially, aPP was obtained as a by-product of the production of iPP. As an inexpensive by-product it is used as a modifier for asphalt for roofing and in adhesives. As the effectiveness of catalyst systems becomes better, less aPP is available so that today some aPP is intentionally made for these applications.

5.9 POLYMERS FROM 1,4-DIENES

There are three important 1,4-dienes employed to produce commercially important polymers. These monomers possess a conjugated pi-bond sequence of —C=C—C=C— that readily forms polymers with an average energy release of about 20 kcal/mol (80 kJ/mol) with the conversion of one of the double bonds into a lower (potential energy wise; generally more stable) energy single bond. For all of these products, cross-linking and grafting sites are available through the remaining double bond.

1,4-Butadiene can form three repeat units as described in structure 5.47: 1,2; *cis*-1,4; and *trans*-1,4. Commercial polybutadiene is mainly composed of 1,4-*cis* isomer and known as butadiene rubber (BR). In general, butadiene is polymerized using stereoregulating catalysts. The composition of the resulting polybutadiene is quite dependent on the nature of the catalyst such that almost total *trans*-1,4, *cis*-1,4, or 1,2 units can be formed as well as almost any combination of these units. The most important single application of polybutadiene polymers is its use in automotive tires where over 10^7 t are used yearly in the U.S. manufacture of automobile tires. BR is usually blended with NR or SBR to improve tire tread performance, particularly wear resistance.

A second use of butadiene is in the manufacture of ABS copolymers where the stereogeometry is also important. A polybutadiene composition of about 60% *trans*-1,4; 20% *cis*-1,4; and 20% 1,2 configuration is generally employed in the production of ABS. The good low-temperature impact strength is achieved in part because of the low T_g values for the compositions. For instance, the T_g for *trans*-1,4-polybutadiene is about −14°C, while that for *cis*-1,4-polybutadiene is about −108°C. Most of the ABS rubber is made employing an emulsion process where the butadiene is initially polymerized forming submicron particles. The SAN copolymer is then grafted onto the outside of the BR particles. ABS rubbers are generally tougher than HIPS rubbers but are more difficult to process. ABS rubbers are used in a number of appliances including luggage, power tool housings, vacuum cleaner housings, toys, household piping, and automotive components such as interior trim. Table 5.5 represents data for extrusion grade ABS.

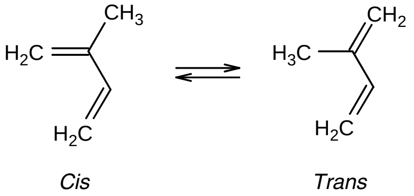
Another major use of butadiene polymer is in the manufacture of HIPS. Most HIPS has about 4%–12% polybutadiene in it so that HIPS is mainly a PS-intense material. Here, the polybutadiene polymer is dissolved in a liquid along with styrene monomer. The polymerization process is unusual in that both a matrix composition of PS and polybutadiene is formed as well as a graft between the growing PS onto the polybutadiene is formed. The grafting provides the needed compatibility between the matrix phase and the rubber phase. The grafting is also important in determining the structure and size of rubber particles that

TABLE 5.5
General Physical Properties of Extrusion Grade ABS

Heat deflection temperature (1820 kPa; °C)	90
Maximum resistance to continuous heat (°C)	90
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	9.5
Compressive strength (kPa)	4.8×10^4
Flexural strength (kPa)	6.2×10^4
Impact strength (Izod: cm-N/cm of notch)	320
Tensile strength (kPa)	3.4×10^4
Ultimate elongation (%)	60
Density (g/mL)	1.0

are formed. The grafting reaction occurs primarily by hydrogen abstraction from the polybutadiene backbone either by growing PS chains or alkoxy radicals if peroxide initiators are employed.

Interestingly isoprene, 2-methyl-1,3-butadiene, exists as an equilibrium mixture of *cis* and *trans* isomers.



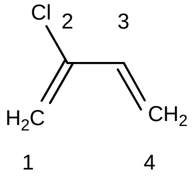
(5.55)

Polyisoprene is composed of four structures as shown in Equation 5.48. As in the case of polybutadiene, it is the *cis*-1,4 structure that is emphasized commercially. The *cis*-1,4-polyisoprene is similar to the *cis*-1,4-polybutadiene material except it is lighter in color, more uniform, and less expensive to process. Polyisoprene is composition-wise analogous to NR. The complete *cis*-1,4 product has a T_g of about −71°C. Interestingly, isomer mixtures generally have higher T_g values. Thus, an equal molar product containing *cis*-1,4; *trans*-1,4; and 3,4 units has a T_g of about −40°C.

As with many polymers, polyisoprene exhibits non-Newtonian flow behavior at shear rates normally used for processing. The double bond can undergo most of the typical reactions such as carbene additions, hydrogenation, epoxidation, ozonolysis, hydrohalogenation, and halogenation. As with the case of the other 1,4-diene monomers, many copolymers are derived from polyisoprene or isoprene itself.

Polyisoprene rubbers are used in the construction of passenger, truck, and bus tires and inner liners, as well as sealants and caulking compounds, sporting goods, gaskets, hoses, rubber sheeting, gloves, belts, and footwear.

Polychloroprene was the first commercially successful synthetic elastomer introduced in 1932 under the trade names of DuPrene and Neoprene by DuPont. It was discovered by Carothers and coworkers. Because of its early discovery good synthetic routes were worked out prior to the advent of good stereoregulating catalytic systems. Thus, polychloroprene is largely manufactured by emulsion polymerization using both batch and continuous systems. Free radical products contain mainly 1,4-*trans* units. Along with the four “main” structural units analogous to those of polyisoprene, sequence distributions are available for both polyisoprene and polychloroprene. Polymerization can occur with the growing end being the four-end or the one-end (structure 5.56). Generally, the 1,4-polymerization sequence is favored with the growing end being carbon 4.



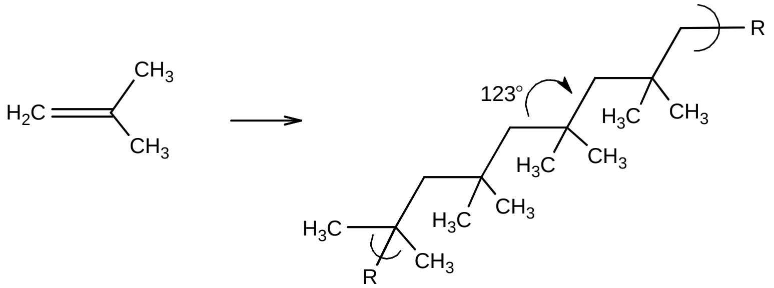
(5.56)

Structural regularity for inclusion of the 1,4-*trans* unit is inversely proportional to temperature. Thus, at 90°C the product contains about 85% of the *trans*-1,4 units while this increases to almost 100% at −150°C. Both uncured and cured polychloroprene exist as largely crystalline materials because of the high degree of stereoregularity. Cured polychloroprene has high tensile strength because of this, and application of stress to the material, either before or after curing, increases the tensile strength. The *trans*-1,4-polychloroprene has a T_g of about −49°C, while 1,4-*cis*-polychloroprene has a T_g of about −20°C.

Compounding of polychloroprene is similar to that of NR. Vulcanizing is achieved using a variety of agents including accelerators. Because of its durability, polychloroprene rubber is often used where deteriorating effects are present. It offers good resistance to oils, ozone, heat, oxygen, and flame (the latter because of the presence of the chlorine atom). Automotive uses include hoses, V-belts, and weather stripping. Rubber goods include diaphragms, hoses, seals, conveyer belts, and gaskets. It is also used in construction for highway joint seals, bridge mounts and expansion joints, soil-pipe gaskets, wet-laminating and contact-bond adhesives, in coatings and dipped goods, as modifiers in elasticized bitumens and cements, and in fiber binders.

5.10 POLYISOBUTYLENE

PIB (structure 5.57) was initially synthesized in the 1920s. It is one of the few examples of the use of cationic catalysis to produce commercial-scale polymers. Low-molecular weight (about 5000 Da) PIB can be produced at room temperature, but large chains (over 1,000,000 Da) are made at low temperatures where transfer reactions are suppressed.

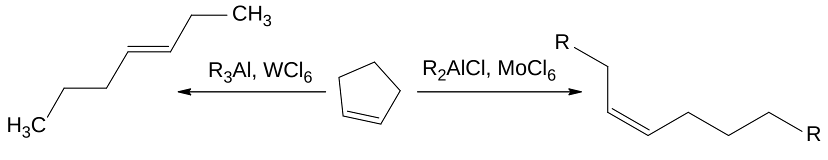


(5.57)

PIB and various copolymers are called butyl rubber. Butyl rubbers have lower permeability and higher damping than other elastomers making them ideal materials for tire inner liners and engine mounts.

Because of the symmetry of the monomer, it might be expected that the materials would be quite crystalline like linear PE. Although PIB crystallizes under stress conditions, but it does not crystallize under nonstressed conditions. This is because the geminal dimethyl groups on alternating carbons in the backbone cause the bond angles to be distorted from about the usual tetrahedral bond angle of 109.5° to 123° forcing the chain to straighten out. As a consequence of this the chains pack efficiently giving a relatively high-density material (density of 0.917 g/cm^3 compared to densities of about 0.85 g/cm^3 for many amorphous polymers) even when amorphous. This close packing reduces the incentive for crystallization, accounts for its low permeability, and produces an usually low T_g of −60°C for such a dense material.

Because PIB is fully saturated, it is cured as a thermoset elastomer through inclusion of about 1%–2% isoprene that supplies the needed double bonds used in the curing process. Other materials including brominated paramethyl styrene are replacing isoprene for this use. PIB is also used in sealing applications and medical closures and sealants.



Trans-polypentenamer (5.58)

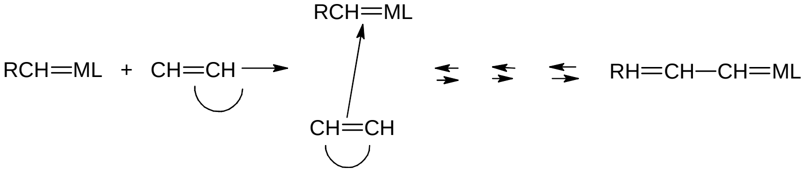
Cis-polypentenamer (5.59)

5.11 METATHESIS REACTIONS

Chauvin, Grubbs, and Schrock won the 2005 Nobel Prize for developing metathesis reactions. Olefin metathesis is a catalytically induced reaction wherein olefins, such as cyclobutene and cyclopentene, undergo bond reorganization resulting in the formation of so-called polyalkenamers. Because the resulting polymers contain double bonds that can be subsequently used to introduce cross-linking, these materials have been used to produce elastomeric materials as well as plastics. Transition metal catalysts are required for these reactions. Catalysts include typical Natta–Ziegler types and other similar catalyst–cocatalyst combinations. The reactions can be run at room temperature and the stereoregularity controlled through choice of reaction conditions and catalysts. For instance, the use of a molybdenum-based catalyst with cyclopentene gives the *cis* product, whereas the use of a tungsten-based catalyst gives the *trans* product.

As expected, the metathesis polymerization of more strained cycloalkenes, such as cyclobutene, occurs more rapidly than less strained structures such as cyclopentene.

It is believed that polymerization occurs via a chain polymerization where ring opening occurs via complete scission of the carbon–carbon double bond through the reaction with metal carbene precursors giving an active carbene species (structure 5.60).



(5.60)

where “L” is the ligand attached to the metal.

5.12 ZWITTERIONIC POLYMERIZATION

While most polymerizations require an initiator, catalyst, or some other form of activation, zwitterionic copolymerizations do not. These copolymerizations require a specific combination of one monomer that is nucleophilic and a second that is electrophilic in nature. The interaction of these two comonomers gives a zwitterion that is responsible for both the initiation and propagation.

Initiation $$\mathrm{MN} + \mathrm{ME} \rightarrow {}^{+}\mathrm{MN} - \mathrm{ME}^{-} \tag{5.61}$$

Propagation $$\begin{gathered} {}^{+}\mathrm{MN} - \mathrm{ME} + {}^{+}\mathrm{MN} - \mathrm{ME} \rightarrow {}^{+}\mathrm{MN} - \mathrm{ME} - \mathrm{MN} - \mathrm{ME} \\ \rightarrow\rightarrow\rightarrow\rightarrow {}^{+}\mathrm{MN} - (-\mathrm{ME}-\mathrm{MN}-) - \mathrm{ME} \end{gathered} \tag{5.62}$$

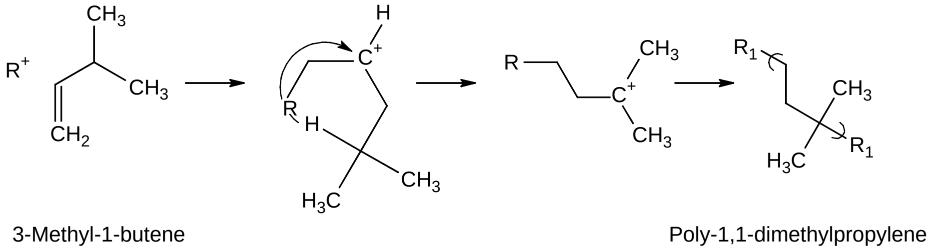
If growth involves only addition and condensation reactions, then an alternating copolymer is formed. Sometimes a lateral reaction occurs where the zwitterion interacts with one of the monomers giving a product that is a statistical copolymer.

5.13 ISOMERIZATION POLYMERIZATION

Isomerization polymerizations are polyaddition reactions where the propagating species rearranges to energetically preferred structures prior to subsequent chain growth.

$$n\mathrm{A} \rightarrow -(-\mathrm{B}-)_n- \tag{5.63}$$

In 1962, Kennedy reported the first isomerization polymerization using 3-methyl-1-butene to give a 1,1-dimethyl PP as below:



(5.64)

Isomerization polymerizations can be associated with coordination catalyst systems, ionic catalyst systems, and free radical systems. The cationic isomerization polymerization of 4-methyl-1-pentene is of interest because the product can be viewed as an alternating copolymer of ethylene and isobutylene. This structure cannot be obtained by conventional approaches.

In the presence of certain ZNCs, an equilibrium exists between *cis*- and *trans*-1,3-pentadiene. Here, the *cis*-1,4-polypentadiene is formed from *trans*-1,3-pentadiene or from a mixture of the *cis* and *trans* isomers.

Such isomerizations are sometimes desired and sometimes are the cause of or explanation for unwanted structures. In the cationic polymerization forming poly(1-butene), nine different structural units have been found. Classical 1,2-hydride and 1,2-methide shifts, hydride transfer, and proton elimination account for these structures.

Unwanted branching of many polymers probably occurs through such isomerizations. PP, formed using cationic polymerization, has methyl, ethyl, *n*-propyl, *n*-butyl, isopropyl, gem-dimethyl, isobutyl, and *t*-butyl groups connected to the main chain.

5.14 PRECIPITATION POLYMERIZATION

Precipitation polymerization, also called slurry polymerization, is a variety of solution polymerization where the monomer is soluble but the polymer precipitates as a fine flock. The formation of olefin polymers via coordination polymerization occurs by a slurry process. Here, the catalyst is prepared and polymerization is carried out under pressure and at low temperatures, generally less than 100°C. The polymer forms viscous slurries. Care is taken so that the polymer does not cake up on the sides and stirrer.

5.15 SUMMARY

1. Chain reactions, including ionic chain polymerization reactions, consist of at least three steps: initiation, propagation, and termination. Termination generally occurs through chain transfer producing a new ion and the dead polymer.
2. Cationic polymerizations occur with vinyl compounds that contain electron-donating groups using Lewis acids along with a cocatalyst as the initiators. Polymerizations generally occur at low temperatures in solvents with high dielectric constants. The DP is proportional to the concentration of monomer and overall rate of polymerization is proportional to the square of the monomer concentration. In general, the rate of polymerization is dependent on the dielectric constant of the solvent, resonance stability of the carbocation, the degree of solvation of the gegenion, and electropositivity of the initiator.
3. Monomers with electron-withdrawing groups can undergo anionic polymerization in the presence of anionic initiators. The rate of polymerization is dependent on the dielectric constant of the solvent, stability of the carbanion, electronegativity of the initiator, degree of solvation of the gegenion, and strength of the electron-withdrawing substituents.
4. Stereoregular polymers can be formed. These polymers can be divided into three general stereoregular unit combinations. When the pendent groups, such as methyl for PP, are all on one side of the polymer chain, the polymer combination is isotactic; when the methyl groups alternate from one side to the other, the polymer combination is syndiotactic; and when the position of the methyl group is somewhat random, it is atactic. The tacticity of polymers influence the physical properties of the products. In general, polymers with greater tacticity (order) have higher glass transition and melting temperatures, have a greater tendency to form crystalline products, are stronger, and are denser. Stereoregular polymers are produced at low temperatures in solvents that favor formation of ion pairs between the carbocation and the gegenion. One of the most widely used stereoregulating systems is called the ZNC system that generally employs a transition metal salt such as titanium chloride and a cocatalyst such as alkylaluminum. A proposed mechanism involves a reaction on the surface of $TiCl_3$, activated by the addition of an alkyl group from the cocatalyst. The monomer adds to this active site producing a pi-complex, which forms a new active center by insertion of the monomer between the titanium and carbon atoms. This step is repeated in the propagation reactions in which the alkyl group from the cocatalyst is the terminal group. Stereospecific polymers are also produced using the alfin and chromia on silica initiators. The alfin system consists of allyl sodium, sodium isopropoxide, and sodium chloride.
5. Soluble stereoregulating systems have been developed using an organometallic transition complex such as Cp_2TiCl_2 and a cocatalyst, often MAO. This system has advantages over the Ziegler–Natta and similar systems in that the polymers produced are more stereoregular, a wider range of monomers can be used, and little or no catalyst incorporated into the polymers allowing the polymer to be directly used without having to undergo a procedure to remove catalyst.

6. Two of the highest volume polymers are made using ionic polymerization—HDPE and iPP. There exist a number of commercially available PEs that vary in extent and kind of branching, chain length, and amount of crystallinity.
7. A number of polymers have been made using ROP. Nylon-6, similar to structure and properties to nylon-6,6, is made from the ring opening of the lactam caprolactam. PEO is made from the ring opening of ethylene oxide and is made more stable by capping the ends preventing ready depolymerization.

GLOSSARY

alfin catalyst Complex catalyst system consisting of allyl sodium, sodium isopropoxide, and sodium chloride.

anionic polymerization Polymerization initiated by an anion.

butyl rubber (IIR) Copolymer of isobutylene and isoprene.

capping Reacting the end groups to produce a stable polymer.

carbanion Negatively charged organic ion.

carbocation Positively charged organic ion, i.e., one lacking an electron pair on a carbon atom.

cationic polymerization Polymerization initiated by a cation and propagated by a carbonium ion.

ceiling temperature Threshold temperature above which a specific polymer is unstable and decomposes.

Celcon Trade name of copolymer of formaldehyde and dioxolane.

chain-reaction polymerization Rapid polymerization based on initiation, propagation, and termination steps.

chain transfer Process in which a growing chain becomes a dead polymer by abstracting a group from some other compounds, thereby generating another active site.

copolymer Polymer chain composed of units from more than one monomer.

copolymerization Polymerization of a mixture of more than one monomer.

coupling Joining of two active species.

gegenion Counterion.

initiation Start of a polymerization.

isomerization polymerization Polyaddition reaction in which the propagation species rearranges to energetically preferred structures prior to chain growth.

Kraton Trade name for an ABA block copolymer of styrene–butadiene–styrene.

lactam Heterocyclic amide with one nitrogen atom in the ring.

Leuchs' anhydride Cyclic anhydride that decomposes to carbon dioxide and an amino acid.

living polymers Macroanions or macrocarbanions.

macroions Charged polymer molecules.

metathesis reaction Catalytically induced reaction wherein olefins undergo bond reorganization resulting in the formation of polyalkenamers.

monadic Polyamide produced form one reactant.

Natta, Giulio Discoverer of stereospecific polymers.

oxirane Ethylene oxide.

polyacetal Polyoxymethylene (POM).

polychloral Polymer of trichloroacetaldehyde.

promoter Strained cyclic ethers that are readily cleaved.

propagation Continuous successive chain extension in a chain reaction.

soluble stereoregulating catalyst Soluble catalysts requiring a metal active site, cocatalyst or counterion, and a ligand system; capable of producing polymers with high stereoregularity and a minimum of branching.

termination Destruction of active growing chain in a chain reaction.

trioxane Trimer of formaldehyde.

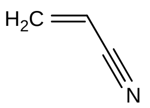
Ziegler, Karl Discoverer of complex coordination catalysts.

Ziegler–Natta (or Natta–Ziegler) catalyst (ZNC) Able to produce stereoregular polymers.

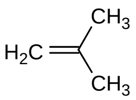
zwitterionic polymerization Copolymerization between nucleophilic and electrophilic comonomers.

EXERCISES

1. Describe the contents of the reaction flask 10 min after the polymerization of (a) reactants in a stepwise polymerization such as dimethyl terephthalate and ethylene glycol and (b) monomer in chain reactions, such as isobutylene.
2. What is the initiator in the polymerization of isobutylene?
3. What is the general name of the product produced by cationic initiation?
4. What reactant besides the monomer is present in cationic chain propagation reactions?
5. What name is used to describe the negatively charged counterion in cationic chain-reaction polymerizations?
6. Is a Lewis acid (a) an electrophile or (b) a nucleophile?
7. Is a Lewis base (a) an electrophile or (b) a nucleophile?
8. Why is not coupling a preferred termination step in the cationic chain polymerization of pure monomer?
9. Is the usual configuration of polymers produced by ionic chain polymerization (a) head-to-tail or (b) head-to-head?
10. Which condition would be more apt to produce stereoregular polymers in ionic chain polymerizations: (a) high temperature or (b) low temperatures?
11. Name (a) a thermoplastic, (b) an elastomer, and (c) a fiber that is produced commercially by ionic chain polymerization.
12. Which technique would you choose for producing a polymer of isobutyl vinyl ether: (a) cationic or (b) anionic?
13. Which technique would you choose for producing a polymer of acrylonitrile: (a) cationic or (b) anionic?
14. Which of the following could be used to initiate the polymerization of isobutylene: (a) sulfuric acid, (b) boron trifluoride etherate, (c) water, or (d) butyllithium?
15. Which of the following could be polymerized by cationic chain polymerization?



(a)



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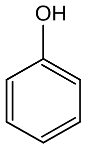

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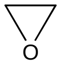

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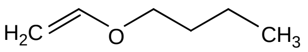

(e)

16. Which polymer is more susceptible to oxidation: (a) HDPE or (b) PP?
17. When termination is by chain transfer, what is the relationship of average DP and the kinetic chain length?
18. What would be the composition of the product obtained by the cationic low-temperature polymerization of a solution of isobutylene in ethylene?
19. What is the relationship between the rate of initiation to the monomer concentration in ionic chain polymerization?
20. What effect will the use of a solvent with a higher dielectric constant have on the rate of propagation in ionic chain polymerization?
21. How does the rate constant k_p change as the yield of polymer increases?
22. Which will have the higher T_g value: (a) PS or (b) PIB?
23. Which of the following could serve as an initiator for an anionic chain polymerization? (a) $AlCl_3 \cdot H_2O$, (b) $BF_3 \cdot H_2O$, (c) butyllithium, or (d) sodium metal?
24. What species, in addition to a dead polymer, is produced in a chain transfer reaction with a macrocarbocation in cationic chain polymerization?
25. What is the relationship between R_i and R_t under steady-state conditions?
26. What is the relationship between average DP and R_p and R_t?
27. Draw a structure of what iPP looks like.

28. What percentage of polymer is usually found when a polymer produced by chain-reaction polymerization is heated above its ceiling temperature?
29. What is the relationship between the average DP and initiator concentration in cationic chain polymerization.
30. Can the polymers found in the bottom of a bottle of insolubilized formaldehyde solution be useful?
31. How would you prepare stable polymers from formaldehyde?
32. Why is the thermal decomposition of polymers of formaldehyde called unzipping?
33. Discuss advantages of the soluble stereoregulating catalysts in comparison with the Natta–Zeigler catalysts.
34. Why are there so many widely used PEs?
35. How would you increase the flow rate of water in a fire hose?
36. Why is poly-3,3-bischloromethyloxybutylene crystalline?
37. Why are PP and PE the most widely used polymers?
38. What kind of polymers are made from lactones?
39. How could you remove unsaturated hydrocarbons from petroleum or coal tar distillates?
40. What species is produced by the reaction of an anionic chain polymerization initiator and the monomer?
41. What are the propagation species in anionic chain polymerizations?
42. Why are polymers produced by the anionic polymerization of pure monomers called living polymers?
43. Using the symbols A and B for repeating units in the polymer chain, which of the following is a block copolymer: (a) ABAABABBABAAB, (b) ABABABABAB, or (c) AAAAAABBBBBB?
44. What is the most widely used monadic nylon?
45. What is the repeating unit for nylon-4?
46. What is the catalyst and cocatalyst in the most widely used ZNC?
47. Name two structures that are possible from the polymerization of 1,3-butadiene.
48. What is the principle difference between propagation reactions with butyllithium and a ZNC?
49. What are some physical properties that iPP would have in comparison with aPP?
50. Show the skeletal structures of *cis*- and *trans*-polyisoprene.
51. Write formulae for repeating units in the chains of (a) poly-1,4-isoprene and (b) poly-1,2-isoprene.
52. What is the most widely used catalyst for the production of HDPE?
53. What elastomer is produced by anionic chain polymerization?
54. What elastomer is produced by use of a ZNC?
55. What are the difficulties associated with the use of solid state catalysts in the production of polymers?
56. How are the difficulties associated with the use of solid state catalysts overcome by the use of soluble stereoregulating catalysts?
57. What are some considerations in determining which PE is used to produce bags for a lawn and garden store?
58. How will you produce a polymer with good flexibility from crystalline HDPE that is strong but does not have the desired flexibility?
59. One table lists the ultimate elongation of a material as 60% and another lists the supposedly same general material with an ultimate elongation of 6000. How can you account for this large difference?
60. Would you expect a copolymer rubber formed from styrene and 1,4-butadiene to be easily cross-linkable? Why?

FURTHER READING

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6 Free Radical Chain Polymerization (Addition Polymerization)

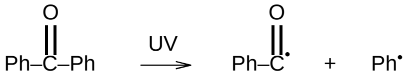
Since many synthetic plastics and elastomers and some fibers are prepared by free radical polymerization, this method is important. Table 6.1 contains a listing of commercially important addition polymers including those that will be emphasized in this chapter because they are prepared using the free radical process.

As with other chain reactions, free radical polymerization is a rapid reaction which consists of the characteristic steps of initiation, propagation, and termination. Free radical initiators are produced by the homolytic cleavage of covalent bonds as well as numerous radiation-associated methods.

6.1 INITIATORS FOR FREE RADICAL CHAIN POLYMERIZATION

Free radical initiation can occur through application of heat (thermal), UV and visible light (photochemical), ionizing light, redox reagents, electricity (electrochemical), etc., that is any process that creates the essential free radicals.

Light in the UV and visible range can disrupt selected bonds forming free radicals. Such disruption occurs when we are exposed to sunlight. Suntan treatments often contain certain compounds that can accept this damaging radiation. Related compounds are also used in foods to give them longer shelf life. They are generally known as antioxidants. Synthetic antioxidants include benzophenones, benzyls, and certain organic ketones. Thus, diphenylketone decomposes on exposure of UV radiation of the appropriate wavelength forming two free radicals.



$$\text{Ph–}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{–Ph} \xrightarrow{\text{UV}} \text{Ph–}\overset{\overset{\text{O}}{\|}}{\text{C}}{}^{\bullet} + \text{Ph}^{\bullet} \qquad (6.1)$$

The advantage of using such photochemical initiations is that polymerization can be carried out at room temperature.

When molecules are exposed to light of higher energy, shorter wavelength, or higher frequency, electrons can be removed or added depending on the specific conditions. Usual forms of ionizing radiation employed industrially and experimentally include neutrons, x-rays, protons, and alpha and beta particles. Oxidation–reduction—redox—reactions are also often employed to initiate free radical polymerizations in solution or heterogeneous organic–aqueous systems. Free radicals can be created by passing a current through a reaction system sufficient to initiate free radical polymerizations.

TABLE 6.1
Industrially Important Addition Polymers

Polymer Name	Typical Properties	Typical Uses
Polyacrylonitrile	High strength; good stiffness; tough, abrasion resistant; good flex life; good resistance to moisture, stains, fungi, chemicals, insects; good weatherability	Carpeting, sweaters, skirts, socks, slacks, baby garments
Poly(vinyl acetate)	Water sensitive with respect to physical properties, such as adhesion and strength; good weatherability, fair adhesion	Lower molecular weight used in chewing gum, intermediate in production of poly(vinyl alcohol); water-based emulsion paints
Poly(vinyl alcohol)	Water soluble; unstable in acid and base system; fair adhesion	Thickening agent for various suspension and emulsion systems; packaging film, wet-strength adhesive
Poly(vinyl butyral)	Good adhesion to glass; tough, good stability to sunlight; good clarity; insensitive to moisture	Automotive safety glass as the interlayer
Poly(vinyl chloride) and poly(vinyidene chloride); (called "the vinyls or vinyl resins")	Relatively unstable to heat and light; resistant to fire, insects, fungi, moisture	Calendered products, such as film, sheets, floor coverings; shower curtains, food covers, rainwear, handbags, coated fabrics, insulation for electrical cable and wire; old records
Poly(tetrafluoroethylene)	Insoluble in most solvents, chemically inert, low dielectric loss, high dielectric strength, uniquely nonadhesive, low friction, constant electrical and mechanical properties from 20°C–250°C; high impact strength	Coatings for frying pans, wire, cable; insulation for motors, oils, transformers, generators; gaskets; pump and valve packings; nonlubricated bearings, biomedical
Polyethylene (LDPE)	Good toughness and pliability over wide temperature range; outstanding electrical properties; good transparency in thin films; resistant to chemicals, acids, bases; ages poorly in sunlight and oxygen; low density, flexible, resilient, high tear strength, moisture resistant	Films, sheeting used as bags, textile materials, pouches, frozen foods, produce wrapping, etc.; drapes, table cloths, covers for ponds, greenhouses, trash can liners, etc.; electrical wire and cable insulator; coating for foils, papers, other films, squeeze bottles
Polypropylene	Lightest major plastic; iPP is major form sold; high tensile strength, stiffness, hardness, resistance to marring; good gloss, high T_g allows it to be sterilized; good electrical properties, chemical inertness, moisture resistance	Filament-rope, webbing, cordage, carpeting, injection molding applications in appliances, small housewares, and automotive fields
Polyisoprene (*cis*-1,4-polyisoprene)	Structurally close to natural rubber (NR); properties similar to those of NR; good elasticity, rebound	Replacement of NR; often preferred because of greater uniformity and cleanliness
Styrene–butadiene rubber (SBR)	Random copolymer; generally slightly poorer physical properties than those of NR	Tire treads for cars; inferior to NR with respect to heat buildup and resilience, thus not used for truck tires; belting, molded goods, gum, flooring, rubber shoe soles, hoses, electrical insulation
Butyl rubber (copolymer of isobutylene)	Amorphous isoprene largely 1,4 isomer; good chemical inertness, low gas permeability, high viscoelastic response to stresses, less sensitive to oxidative aging than most isoprene rubbers; better ozone stability than NR; good solvent resistance	About 60%–70% used for inner tubes for tires

TABLE 6.1 (continued)
Industrially Important Addition Polymers

Polymer Name	Typical Properties	Typical Uses
Polychloroprene (mostly 1,4 isomer)	Outstanding oil and chemical resistance; high tensile strength; outstanding resistance to oxidative degradation, aging; good ozone and weathering response; dynamic properties same or better than most synthetic rubbers	Can replace NR in most applications; gloves, coated fabrics, cable and wire coatings, hoses, belts, shoe heels, solid tires
Polystyrene	Clear, easily colored; easily fabricated; transparent; fair mechanical and thermal properties; good resistance to acids, bases, oxidizing, and reducing agents; readily attacked by many organic solvents; good electrical insulator	Production of ion-exchange resins, heat- and impact-resistant copolymer, ABS, resins, etc.; foams, toys, plastic optical components, lighting Fixtures, housewares, packaging, home furnishings
Poly(methyl methacrylate)	Clear, transparent, colorless, good weatherability, good impact strength, resistant to dilute basic and acidic solutions; easily colored; good mechanical and thermal properties; good fabricability; poor abrasion resistance compared to glass	Used in cast sheets, rods, tubes, molding, extrusion compositions, tail- and signal-light lenses, dials, medallions, brush backs, jewelry, signs, lenses, skylight "glass," generally used where good light transmission is needed

Although application of heat or some other method can rupture the pi-bond in the vinyl monomer causing the formation of a two-headed free radical that can act as a free radical initiator, peroxides and dinitriles are generally employed as initiators. This is a consequence of the general bond dissociation energy trend of C—H > C—C > C—N > O—O. Dinitrile or azo compounds, such as 2,2′-azo-bis-isobutyronitrile (AIBN), require temperatures of about 70°C–80°C to produce decomposition with free radical formation. Peroxides such as benzoyl peroxide (BPO) require temperatures higher than 60°C for decomposition and free radical formation. While the dissociation bond energy for C—N is generally greater than for O—O, the formation of a stable N_2 molecule is the thermodynamic driving force due to an entropy effect allowing dissociation to occur at typically lower temperatures.

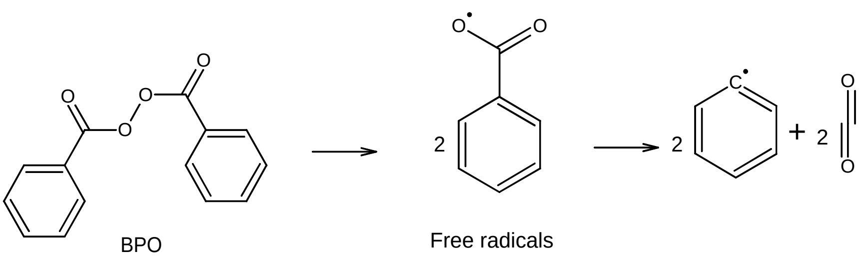
Although initiation can occur via a number of routes, we will emphasize the use of chemical initiators for the formation of the free radicals necessary to begin the free radical polymerization process.

The rate of decomposition of initiators usually follows first-order kinetics and is dependent on the solvent present and the temperature of polymerization. The rate is usually expressed as a half-life time ($t_{1/2}$), where $t_{1/2} = \text{In}\ 2/k_d = 0.693/k_d$. The rate constant ($k_d$) changes with temperature in accordance with the Arrhenius equation as shown below:

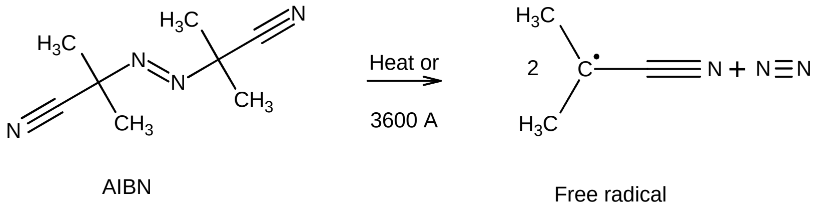
$$k_d = A e^{-E_a/RT} \tag{6.2}$$

Typical equations for the dissociation of AIBN and BPO are shown below. It should be pointed out that because of recombination, which is solvent-dependent, and other side reactions of the created free radical ($R^\bullet$), the initiator efficiency is seldom 100%. Hence, an efficiency factor (f) is employed to show the fraction of effective free radicals produced.

The decomposition of AIBN and BPO to form radicals is given in Equations 6.3 and 6.4.



(6.3)



(6.4)

The precise structure of the initiating agent and initial addition to the monomer varies according to the reaction conditions, monomer, and initiator. For illustration, we will look at the products formed from BPO. Generally, BPO is reported to break forming two benzoyl free radicals (Equation 6.3). In reality, the initial step is complex and involves the formation of a number of products as shown in Figure 6.1 for styrene. The major reaction involves direct

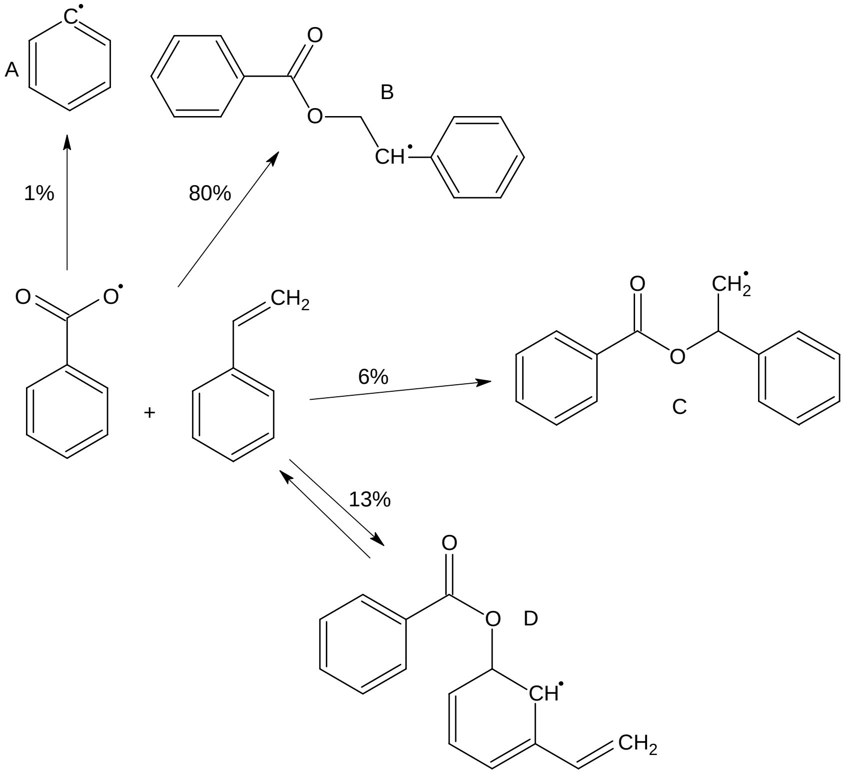
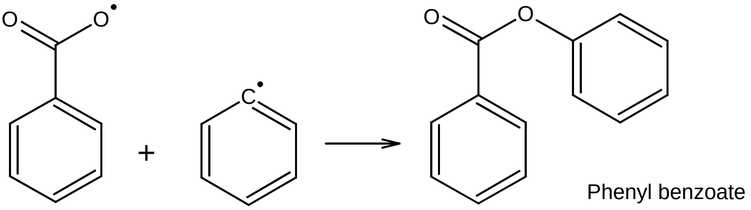


FIGURE 6.1 Initial reaction products of benzoyl peroxide (BPO) and styrene monomer.

addition of the benzoyl radical to the tail end of the styrene monomer creating a molecule where the radical resides at the head or more sterically demanding and more radical-stabilizing site (B). A lesser amount adds to the head end (C). Some adds to the ring forming a variety of compounds including D. A small amount decomposes forming the phenyl radical and carbon dioxide (A). For simplicity we will employ structure A as the initiating structure but all initiating structures give similar products differing only in the nature of the end group.

The BPO decomposes with a specific rate constant of about 10^{-8}/sec, an Arrhenius constant (A) of about 10^{16}, and an activation energy of about 28 kcal/mol (about 115 kJ/mol). As noted earlier, not all radicals initiate new chains. Some terminate prior to initiation forming inactive products, mainly phenyl benzoate (Equation 6.5). Thus, as noted, an efficiency constant (f) is used that reflects the ratio of BPO that actually form chains.



(6.5)

6.2 MECHANISM FOR FREE RADICAL CHAIN POLYMERIZATION

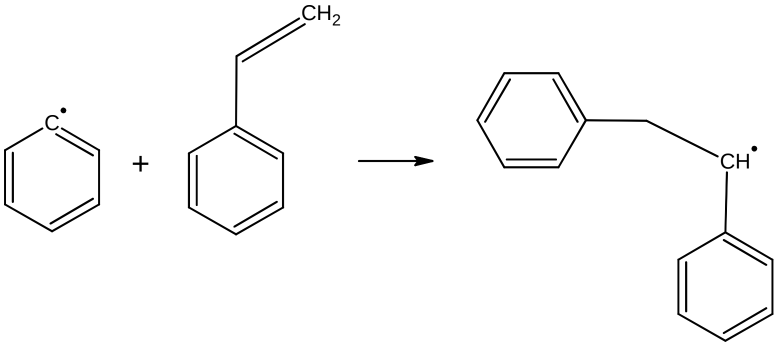
In general, the decomposition of the initiator (I) may be expressed by the following equation in which k_d is the specific rate or decay constant.

$$I \rightarrow 2R^{\bullet} \tag{6.6}$$

$$R_d = -d[I]/dt = k_d[I] \tag{6.7}$$

where R_d is the rate of decomposition.

Initiation of a free radical chain takes place by addition of a free radical ($R^{\bullet}$) to a vinyl monomer (Equation 6.8). Polystyrene (PS) will be used to illustrate the typical reaction sequences. (Styrene, like many aromatic compounds, is toxic, and concentrations that come into contact with us should be severely limited.) It is important to note that the free radical ($R^{\bullet}$) is a companion of all polymerizing species and is part of the polymer chain acting as an end group and hence should not be called a catalyst even though it is often referred to as such. It is most properly referred to as an initiator.



(6.8)

$$R^{\bullet} + M \rightarrow RM^{\bullet} \tag{6.9}$$

$$R_\mathrm{i} = \mathrm{d}[\mathrm{RM}^{\bullet}]/\mathrm{d}t = k_\mathrm{i}[\mathrm{R}^{\bullet}][\mathrm{M}] \tag{6.10}$$

where R_i is the rate of initiation and $\mathrm{R}^{\bullet}$ is the free radical from BPO.

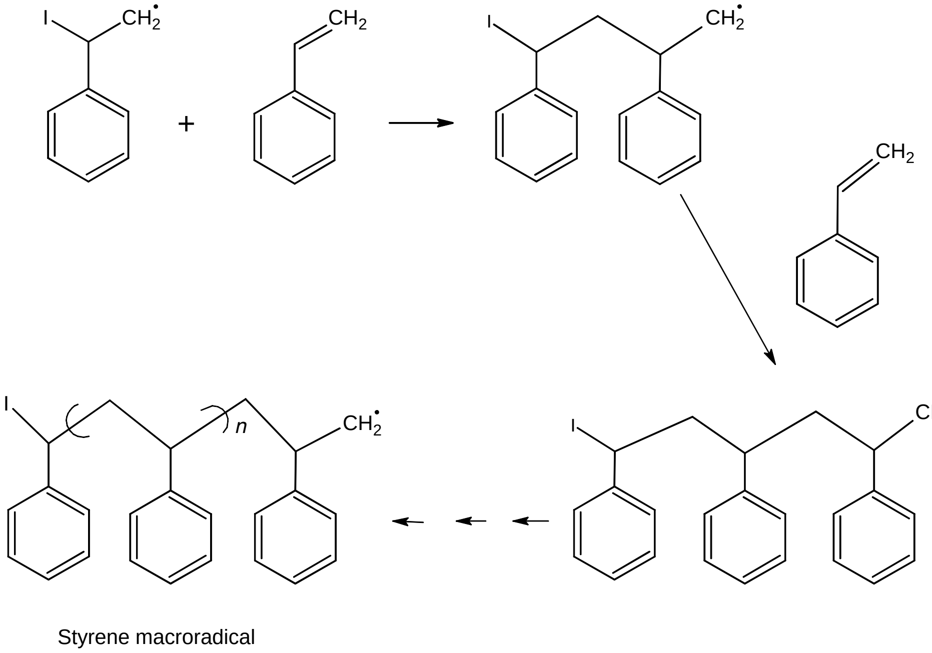
The rate of decomposition of the initiator (I) (Equation 6.6) is the rate-controlling step in the free radical polymerization as well as formation of growing chains. Thus, the overall expression describing the rate of initiation can be given as

$$R_\mathrm{i} = 2k_\mathrm{d}f[\mathrm{I}] \tag{6.11}$$

where "*f*" is the *efficiency factor* (a measure of the fraction of initiator radicals that produce growing radical chains, i.e., are able to react with monomer).

A "2" is inserted in Equation 6.11 because, in this presentation, for each initiator molecule that decomposes, two radicals are formed. The "2" is omitted from Equation 6.6 because this rate expression describes the rate of decomposition of the initiator, but not the rate of formation of free radicals $\mathrm{R}^{\bullet}$. Similarly, in Equations 6.18 and 6.20, each termination results in the loss of two growing chains, thus a "2" appears in the descriptions.

Propagation is a bimolecular reaction (Equations 6.12 and 6.13), occurring through addition of a new free radical ($\mathrm{RM}^{\bullet}$) to another molecule of monomer (M). This step is repeated many times resulting in the formation of the polymer chain. It is experimentally found that there may be slight changes in the propagation rate constant (k_p) in the first few steps, but the rate constant is generally considered to be independent of chain length. Hence, the symbols $\mathrm{M}^{\bullet}$, $\mathrm{RM}^{\bullet}$, and $\mathrm{RM}_n\mathrm{M}^{\bullet}$ may be considered equivalent in rate equations for free radical polymerization.



(6.12)

(6.13)

Since the specific rate constants are approximately independent of the length of the growing chain, one specific rate constant is used to represent all of the propagation steps, k_p.

The rate of demise of monomer with time is described as

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{M}^{\bullet}][\mathrm{M}] + k_\mathrm{i}[\mathrm{R}^{\bullet}][\mathrm{M}] \tag{6.14}$$

i.e., monomer consumption only occurs in reactions described by Equations 6.8 and 6.13.

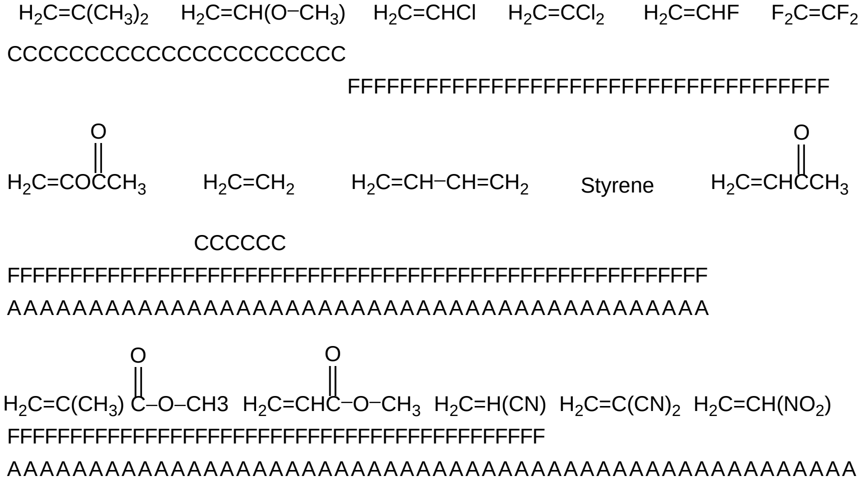


FIGURE 6.2 Type of chain initiation for some common monomers in order of general decrease in electron density associated with the double bond and their tendency to undergo chain polymerization where A = anionic, C = cationic, and F = free radical.

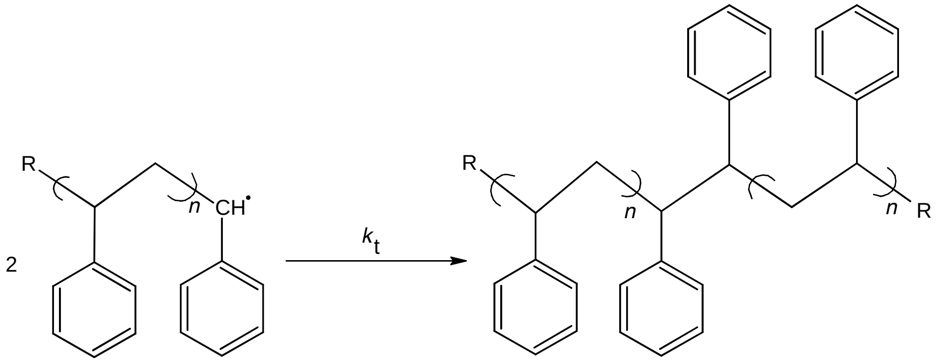
For long chains, the consumption of monomer by the initiation step (Equation 6.13) is small and can be neglected allowing Equation 6.14 to be rewritten as

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_{\mathrm{p}}[\mathrm{M}^{\bullet}][\mathrm{M}] \tag{6.15}$$

$$R_{\mathrm{p}} = k_{\mathrm{p}}[\mathrm{M}^{\bullet}][\mathrm{M}] \tag{6.16}$$

The polarity of the functional group in the monomers polymerized by free radical chain polymerization is between the positively inclined monomers characterized by undergoing cationic polymerization, and the negatively inclined monomers characterized by undergoing anionic polymerization. Figure 6.2 contains a listing of the addition polymerization routes taken by various monomers. As true for the configuration of ionic growing chains, free radical polymers are also formed so that addition gives a head-to-tail configuration because functional groups on the vinyl monomers are better at stabilizing the free radical than are hydrogen atoms and because this balances the steric requirements present as addition occurs.

Unlike ionic polymerizations, the termination of the growing free radical chains usually occurs by coupling of two macroradicals. Thus, the kinetic chain length (v) is equal to $\overline{DP}/2$. The chemical and kinetic equations for bimolecular termination are shown below (Equations 6.17 and 6.18).

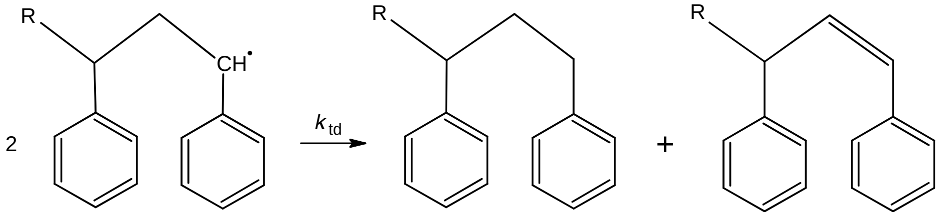


(6.17)

Termination is a head-to-head configuration at the juncture of the two macroradicals. The extent of coupling termination can then be obtained by determining the extent of head-to-head configuration in the product. The kinetic equation for coupling termination is shown in the following equation:

$$R_t = -\mathrm{d}[\mathrm{M}^\bullet]/\mathrm{d}t = 2k_t[\mathrm{M}^\bullet][\mathrm{M}^\bullet] = 2k_t[\mathrm{M}^\bullet]^2 \tag{6.18}$$

In certain situations, termination occurs by disproportionation. This termination process involves chain transfer to a hydrogen atom from one chain end to the free radical chain end of another growing chain, resulting in one of the "dead" polymer chains having an unsaturated chain end (Equations 6.19 and 6.20).



(6.19)

$$R_{td} = 2k_{td}[\mathrm{M}^\bullet]^2 \tag{6.20}$$

The kinetic chain length for termination by disproportionation is $\overline{DP} = v$ (compared with the relationship for coupling of $\overline{DP} = 2v$. The extent of the two types of termination is experimentally found by determining the number of head-to-head sites [coupling] and unsaturated end groups [disproportionation]).

The mode of termination varies with monomer and reaction conditions. While styrene macroradicals typically terminate by coupling, methyl methacrylate macroradicals terminate by coupling at temperatures below 60°C, but by disproportionation at higher temperatures.

The *kinetic chain length* (v) is described in the following equation:

$$v = \frac{R_p}{R_i} = \frac{R_p}{R_{td}} = \frac{k_p[\mathrm{M}][\mathrm{M}^\bullet]}{2k_{td}[\mathrm{M}^\bullet]^2} = \frac{k_p[\mathrm{M}]}{2k_{td}[\mathrm{M}^\bullet]} = k'\frac{[\mathrm{M}]}{[\mathrm{M}^\bullet]} \tag{6.21}$$

As it is experimentally found that the number of growing chains is constant, there exists a steady state in $\mathrm{M}^\bullet$ so that $R_i = R_{td}$ (a similar scenario can be used to develop rate expressions for coupling).

Although Equations 6.15, 6.18, 6.20, and 6.21 are theoretically important, they contain $[\mathrm{M}^\bullet]$, which is difficult to experimentally determine and are thus practically of little use. The following is an approach to render such equations more useful by generating a description of $[\mathrm{M}^\bullet]$ that involves experimentally accessible terms.

The rate of monomer–radical *change* is described by

$$\begin{aligned}\mathrm{d}[\mathrm{M}^\bullet]/\mathrm{d}t &= [\text{monomer} - \text{radical formed}] - [\text{monomer} - \text{radical utilized}]\\ &= k_i[\mathrm{R}^\bullet][\mathrm{M}] - 2k_t[\mathrm{M}^\bullet]^2\end{aligned} \tag{6.22}$$

As noted earlier, it is experimentally found that the number of growing chains is approximately constant over a large extent of reaction. This situation is referred to as a "steady state." For Equation 6.22 this results in $\mathrm{d}[\mathrm{M}^\bullet]/\mathrm{d}t = 0$ and

$$k_i[\mathrm{R}^\bullet][\mathrm{M}] = 2k_t[\mathrm{M}^\bullet]^2 \tag{6.23}$$

Additionally, a steady state value for the concentration of [R•] exists giving

$$d[R^\bullet]/dt = 2k_d f[I] - k_i[R^\bullet][M] = 0 \tag{6.24}$$

Solving for [M•] from Equation 6.23 gives

$$[M^\bullet] = (k_i[R^\bullet][M]/2k_t)^{1/2} \tag{6.25}$$

and [R•] from Equation 6.24 gives

$$[R^\bullet] = 2k_d f[I]/k_i[M] \tag{6.26}$$

Substituting into Equation 6.25 the expression for [R•], we obtain an expression for [M•] (Equation 6.27) that contains experimentally determinable terms.

$$[M^\bullet] = (k_d f[I]/k_t)^{1/2} \tag{6.27}$$

Using this relationship for [M•] we get more useful rate (Equation 6.28) and kinetic chain length (Equation 6.30) equations that are free from the hard to measure [M•].

$$R_p = k_p[M][M^\bullet] = k_p[M](k_d f[I]/k_t)^{1/2} = (k_p^2 k_d f/k_t)^{1/2}[M][I]^{1/2} = k''[M][I]^{1/2} \tag{6.28}$$

Thus, the rate of propagation, or polymerization, is directly proportional to the concentration of the monomer and square root concentration of initiator.

In preparation of describing the kinetic chain length, we can also describe the rate of termination using the new description for [M•].

$$R_t = 2k_t[M^\bullet]^2 = 2k_t k_d f[I]/k_t = 2k_d f[I] \tag{6.29}$$

$$DP = \frac{R_p}{R_i} = \frac{k_p[M](k_d f[I]/k_t)^{1/2}}{2k_d f[I]} = \frac{k_p[M]}{2(k_d k_t f[I])^{1/2}} = \frac{k'[M]}{[I]^{1/2}} \tag{6.30}$$

Thus, chain length is directly proportional to monomer concentration and inversely proportional to the square root of initiator concentration.

Typical energies of activation for propagation and termination are given in Table 6.2 and typical free radical kinetic values in Table 6.3.

TABLE 6.2
Energies of Activation for Propagation (E_p) and Termination (E_t) in Free Radical Chain Polymerization

Monomer	E_p(kJ/mol)	E_t(kJ/mol)
Methyl acrylate	30	22
Acrylonitrile	17	23
Butadiene	39	—
Ethylene	34	—
Methyl methacrylate	26	12
Styrene	33	12
Vinyl acetate	31	22
Vinyl chloride	15	18

TABLE 6.3
Typical Free Radical Kinetic Values

Specific Rate Constant		Activation Energies (kJ/mol)	
k_d	$10^{-3}/\sec$	E_d	80–160
k_i	10^3 L/mol/sec	E_i	20–30
k_p	10^3 L/mol/sec	E_p	20–40
k_t	10^7 L/mol/sec	E_t	0–20

As done in Chapter 5, the effect of temperature can be determined using average activation of the various steps. Again, the rates of all single step reactions increase as the temperature increases but the overall result may be different for complex reactions. For free radical polymerizations the activation energies are generally of the order $E_d > E_i \cong E_p > E_t$. Remembering that the description of the specific rate constant is

$$k = A\mathrm{e}^{-E_a/RT} \tag{6.31}$$

the overall or "net" activation energy is

$$E_{(\text{overall})} = E_t + E_i + E_p + E_d \tag{6.32}$$

Using only the specific rate constants involved with propagation, from Equation 6.28 we have

$$R_p \propto k_p^2 k_d / k_t \tag{6.33}$$

so that the overall activation energy using average values is a positive value (Equation 6.34), hence the overall rate of polymerization increases as temperature increases.

$$E_{p(\text{overall})} \propto 2E_p + E_d - E_t = 2 \times 30 + 120 - 10 = 170 \tag{6.34}$$

For chain length, from Equation 6.30 we have

$$DP \propto k_p / 2k_d k_t \tag{6.35}$$

so that the overall activation energy using average values is

$$DP_{(\text{overall})} \propto E_p - E_d - E_t = 30 - 120 - 10 = -100 \tag{6.36}$$

so that $\overline{DP}$ decreases when temperature increases as pictured in Figure 4.4.

The Gibbs free energy relationship for a reversible process at constant temperature for polymerization is described by

$$\Delta G_p = \Delta H_p - T\Delta S_p \tag{6.37}$$

where ΔH_p is the heat of polymerization defined by

$$\Delta H_p = E_p - E_{dp} \tag{6.38}$$

where E_p is the activation energy for propagation and E_{dp} is the activation energy for depolymerization.

The entropy term is negative so that it is the enthalpy or energy term that "drives" the polymerization. At low temperatures, the enthalpy term is larger than the $T\Delta S_p$ term so that polymer growth occurs. At some temperature, called the *ceiling temperature*, the enthalpy and the entropy terms are the same and $\Delta G_p = 0$. Above this temperature depolymerization occurs more rapidly than polymer formation so that polymer formation does not occur. At the ceiling temperature depolymerization and polymerization rates are equal. The ceiling temperature is then defined as

$$T_c = \Delta H_p/\Delta S_p \tag{6.39}$$

since $\Delta G_p = 0$.

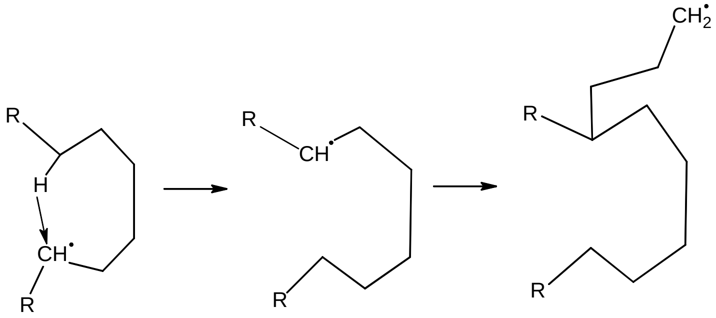
The ceiling temperature for styrene is about 310°C, for ethylene 400°C, for propylene 300°C, for methyl methacrylate 220°C, for tetrafluoroethylene 580°C, and for α-methylstyrene 61°C.

It is interesting to note that due to their industrial importance, free radical polymerizations are the most studied reactions in chemistry. Furthermore, the kinetic approaches taken in this chapter are experimentally verified for essentially all typical free radical vinyl polymerizations.

There is a tendency for the formation of stereoregular sequences, particularly at low temperatures, but ionic and coordination catalysts are far superior in this aspect and are used to create stereoregular macromolecules.

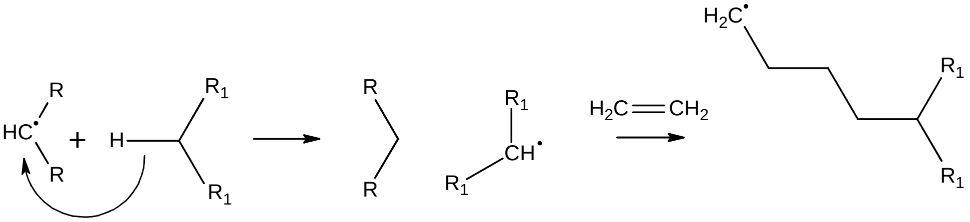
6.3 CHAIN TRANSFER

Transfer of the free radical to another molecule serves as one of the termination steps for general polymer growth. Thus, transfer of a hydrogen atom at one end of the chain to a free radical end of another chain is a chain transfer process we dealt with in Section 6.2 under termination via disproportionation. When abstraction occurs intramolecularly or intermolecularly by a hydrogen atom some distance away from the chain end, branching results. Each chain transfer process causes the termination of one macroradical and produces another macroradical. The new radical sites serve as branch points for chain extension or branching. As noted above, such chain transfer can occur within the same chain as shown below.



(6.40)

Chain transfer can also occur between chains.



(6.41)

Chain transfer can also occur with initiator, impurity, solvent, or other additive present in the polymerization system. While the average chain length is equal to R_p divided by the sum of all termination reactions, it is customary to control all termination steps except the one that is being studied. Chain transfer to all other molecules, except solvent or some special additive, is typically negligible.

The chain transfer reaction decreases the average chain length in accordance with the concentration of the chain-transfer agent (S) and the tendency to chain transfer. The resulting $\overline{DP}$ is equal to that which would have been obtained without the solvent or additive plus a factor related to the product of the ratio of the rate of propagation (R_p) and the rate of chain transfer (R_{tr}), and the ratio of the concentration of the monomer [M] to the concentration of chain-transfer agent [S].

The Mayo equation (Equation 6.42) that gives positive slopes when the data is plotted (such as Figure 6.3) is the reciprocal relationship derived from the expression cited earlier. The ratio of the rate of cessation or termination by transfer to the rate of propagation is called the chain transfer constant (C_s).

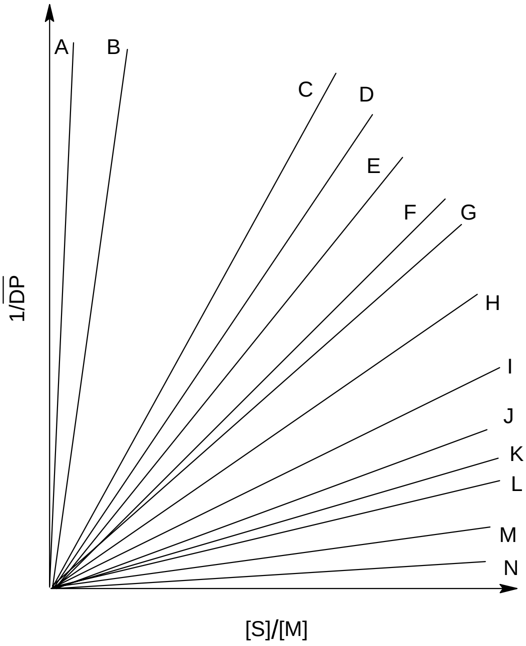


FIGURE 6.3 Molecular weight of polystyrene (PS) as a function of solvent and solvent concentration: A = *n*-butylmercaptan, B = carbon tetrabromide, C = carbon tetrachloride, D = *o*-cresol, E = *p*-cresol, F = *m*-cresol, G = phenol, H = *sec*-butylbenzene, I = cumene, J = ethylbenzene, K = chloroform, L = *n*-heptant, M = toluene, N = benzene, where [S] = concentration of chain-transfer agent and [M] = concentration of styrene monomer.

TABLE 6.4
Chain Transfer Constants of Solvent to Styrene in Free Radical Chain Polymerization at 60°C

Transfer Agent	$C_s \times 10^4$	Transfer Agent	$C_s \times 10^4$
Acetic acid	2.0	1-Dodecanethiol	148,000
Benzene	0.01	Hexane	0.90
Butyl alcohol	0.06	*N,N*-Dimethylaniline	12.00
t-Butyl alcohol	6.70	1-Naphthalenethiol	1,500.00
Butyl disulfide	0.24	1-Octanethiol	190,000.00
Carbon tetrabromide	18,000	*p*-Methoxyphenol	260.00
Carbon tetrachloride	84.00	Phenol	8.10
Chloroform	0.50	Triethylamine	1.40
o-Chlorophenol	6.00	Toluene	0.105
2,6-Di-*tert*-butylphenol	49.00	Water	0.00

$$1/DP = 1/DP_o + C_s \frac{[S]}{[M]} \tag{6.42}$$

The chain transfer constant is given as

$$C_s = k_{tr}/k_p \tag{6.43}$$

As shown in Figure 6.3, the molecular weight of PS is reduced when it is polymerized in solvents, and the reduction or increase in slope is related to the chain transfer efficiency of the solvent. The slopes in this figure are equal to C_s.

Chain transfer constants of various solvents, including those given in Figure 6.3, are given in Table 6.4.

Chain-transfer agents have been called and employed as regulators (of molecular weight). When used in large proportions, they are called *telogens*, since they produce low-molecular weight polymers (*telomers*).

6.4 POLYMERIZATION TECHNIQUES

The principle free radical polymerization techniques are bulk, solution, suspension, and emulsion. Tables 6.5 and 6.6 briefly describe these techniques.

6.4.1 BULK POLYMERIZATION

Bulk polymerization of a liquid monomer such as methyl methacrylate is relatively simple in the absence of oxygen where small bottles or test tubes can be used as the reaction vessel.

TABLE 6.5
Types of Polymerization Systems

Monomer–Polymer Phase Relationship	Monomer Location	
	Continuous	Dispersed
Homogeneous (same phase)	Bulk, solid state, solution	Suspension
Heterogeneous (different phase)	Bulk with polymer precipitating	Emulsion; suspension with polymer precipitating

TABLE 6.6
Summary of Popular Polymerization Techniques

Bulk

Simplest of the techniques requiring only monomer and monomer-soluble initiator, and perhaps a chain-transfer agent for molecular weight control. Characterized, on the positive side, by high polymer yield per volume of reaction, easy polymer recovery. Difficulty of removing unreacted monomer and heat control are negative features. Examples of polymers produced by bulk polymerization include poly(methyl methacrylate), polystyrene, and low-density (high pressure) polyethylene.

Solution

Monomer and initiator must be soluble in the liquid and the solvent must have the desired chain-transfer characteristics, boiling point (above the temperature necessary to carry out the polymerization and low enough to allow for ready removal if the polymer is recovered by solvent evaporation). The presence of the solvent assists in heat removal and control (as it also does for suspension and emulsion polymerization systems). Polymer yield per reaction volume is lower than for bulk reactions. Also, solvent recovery and removal (from the polymer) is necessary. Many free radical and ionic polymerizations are carried out utilizing solution polymerization including water-soluble polymers prepared in aqueous solution (namely poly(acrylic acid), polyacrylamide, and poly(*N*-vinylpyrrolidinone). Polystyrene, poly(methyl methacrylate), poly(vinyl chloride), and polybutadiene are prepared from organic solution polymerizations.

Suspension

A water insoluble monomer and initiator are used. Again, a chain-transfer agent may be used to control chain size. Stirring is usual. Droplets of monomer containing initiator and chain-transfer agent are formed. A protective colloidal agent, often poly(vinyl alcohol), is added to prevent coalescence of the droplets. Near the end, the particles become hard and are recovered by filtration. Because the liquid is water-based, solvent recovery and treatment problems are minimal. The products may contain a number of impurities including any of the agents added to assist in the polymerization process. Polymers produced by suspension polymerization include poly(vinyl chloride), polystyrene resins, and copolymers such as poly(styrene-coacrylonitrile), SAN, and poly(vinyl chloride-covinylidene chloride).

Emulsion

The system usually contains a water-soluble initiator (in contrast to the requirement that the initiator must not be water soluble in suspension polymerizations), chain-transfer agent, and a surfactant. The hydrophobic monomer forms large droplets that are stabilized by the surfactant. At a certain surfactant concentration, the surfactant molecules form micelles that contain 50–100 surfactant molecules. During polymerization, the monomer, that has a small but real water solubility, migrates from the monomer droplets through the water and into these micelles. Polymerization begins when the water-soluble initiator enters into the monomer-containing micelle. Because the concentration of micelles (about 10^{21}/L) is high compared with the concentration of monomer droplets (about 10^{13}/L) the initiator is more likely to enter a micelle than a monomer droplet. As polymerization continues, monomer is transferred to the growing micelles. At about 50%–80% conversion the monomer droplets disappear and the micelles become large polymer-containing droplets. This suspension is called a latex. The latex is stable and can be used as is or the polymer recovered by coagulation. In inverse emulsion polymerization, the monomer, which is hydrophilic, is dispersed in an organic liquid. Here, the monomer is usually contained in an aqueous solution.

The monomer can be heated in the presence of an initiator giving a clear plastic shaped like the container, but a little smaller because of shrinkage. The volume of the monomers is generally larger than the final polymers; thus, the density of the polymer is greater than that of the original monomer.

The rate of bulk polymerization can be followed by monitoring the change in volume or increase in viscosity. When the viscosity is high, the termination reaction is hindered since the macroradicals are unable to diffuse readily in the viscous medium. Thus, the number of growing chains increases. This *autoacceleration*, called the Norris–Trommsdorff, Tranmsdorff, or gel effect, causes the formation of unusually high molecular weight chains. Since vinyl polymerizations are exothermic, there is a buildup of heat, which further causes an additional autoacceleration of the reaction. If the temperature buildup is not controlled, it is possible that an explosion will occur. Although the temperature can be easily controlled within a small test tube, it is more difficult in a large batch process. Stirring and external cooling are employed to control the polymerization process.

6.4.2 SUSPENSION POLYMERIZATION

Water insoluble monomers such as vinyl chloride may be polymerized as suspended droplets (10–1000 nm in diameter) in a process called *suspension* (pearl) *polymerizations*. Coalescence of droplets is prevented by the use of small amounts of water-soluble polymers, such as PVA. The suspension process is characterized by good heat control and ease of removal of the discrete polymer particles.

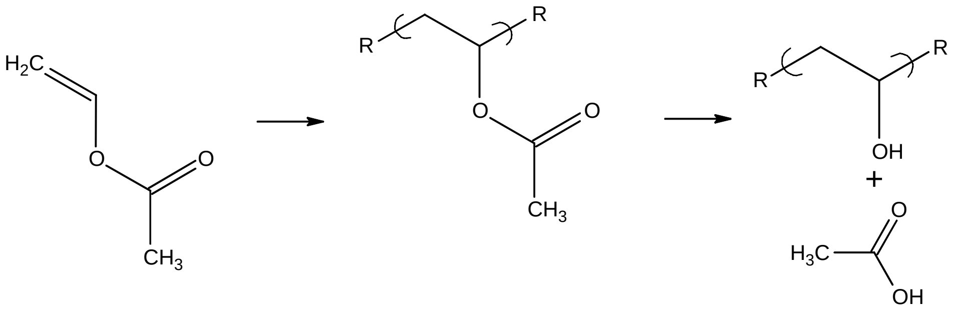
Since PVC is insoluble in its monomer, it precipitates as formed in the droplet. This is actually advantageous, since it permits ready removal of any residual carcinogenic monomer from the solid beads by stripping under reduced pressure.

6.4.3 SOLUTION POLYMERIZATION

Monomers may also be polymerized in solution using good or poor solvents for homogeneous and heterogeneous systems, respectively. In solution polymerizations, solvents with low chain transfer constants are used to minimize reduction in chain length.

PVAc may be produced by the polymerization of vinyl acetate (Equation 6.47). The viscosity of the solution continues to increase until the reaction is complete. Dilute polymer solutions are used to prevent the onset of autoacceleration because of the gel effect.

PVAc is used in adhesives and coatings and is hydrolyzed producing water-soluble PVA (Equation 6.44). The PVA may be reacted with butyraldehyde to produce poly(vinyl butyral) used as the inner lining of safety glass.



(6.44)

When a monomer such as acrylonitrile is polymerized in a poor solvent, macroradicals precipitate as they are formed. Since these are “living polymers,” polymerization continues as more acrylonitrile diffuses into the precipitated particles. This heterogeneous solution polymerization has been called *precipitation polymerization*.

6.4.4 EMULSION POLYMERIZATION

Many water-soluble vinyl monomers may be polymerized by the *emulsion polymerization* technique. This technique, which differs from suspension polymerization in the size of the suspended particles and in mechanism, is widely used for the production of a number of commercial plastics and elastomers. While the particles in the suspension range from 10 to 1000 nm, those in the emulsion process range from 0.05 to 5 nm in diameter. The small beads produced in the suspension process may be separated by filtering, but the latex produced in emulsion polymerization is a stable system in which the charged particles cannot be recovered by ordinary separation procedures.

Since relatively stable macroradicals are produced in the emulsion process, the termination rate decreases and a high molecular weight product is rapidly produced. It is customary to use a water-soluble initiator such as potassium persulfate and an anionic surfactant

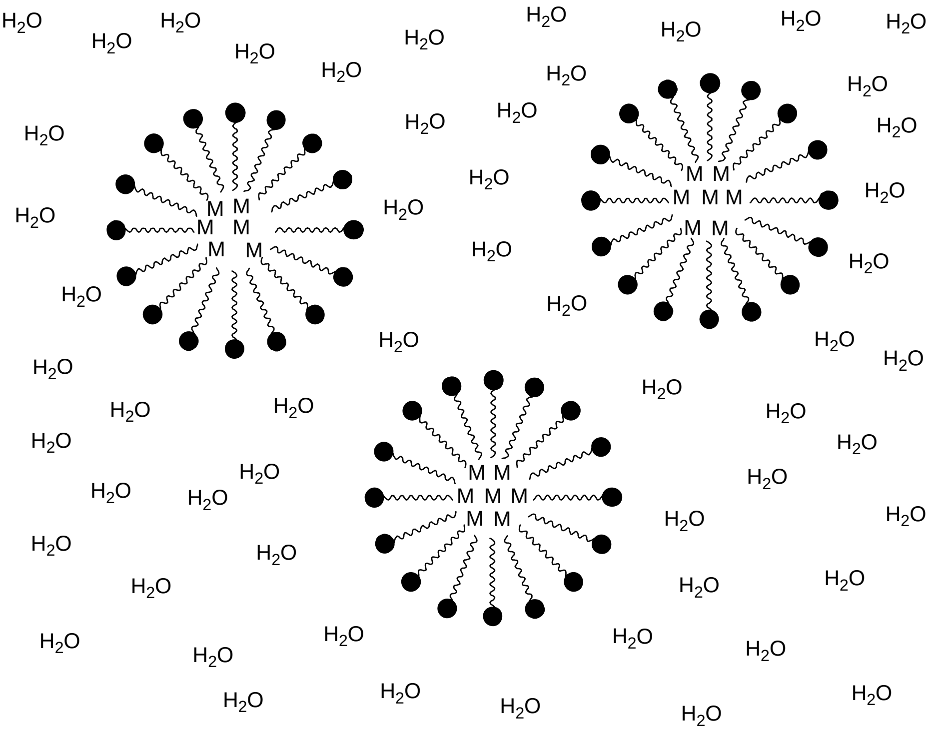


FIGURE 6.4 Micelles swollen with solubilized monomer. As the concentration increases the micelles change from spherical, as shown, to more rod-like in appearance.

such as sodium sterate, and to stir the aqueous mixture of monomer, initiator, and surfactant in the absence of oxygen at 40°C–70°C. When the concentration of soap exceeds the critical micelle concentration, the molecules are present as micelles in which the hydrophilic carboxylic acid ends are oriented toward the water–micelle interface, and the lyophilic hydrocarbon ends are oriented toward the center of the micelle. The micelles are present as spheres with a diameter of 5–10 nm when the soap concentration is less than 2%. However, with the higher concentrations typically employed, the micelles resemble aggregates of rods, which are 100–300 nm in length.

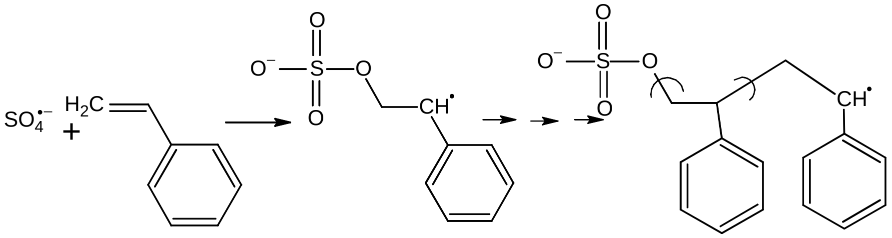
As shown in Figure 6.4, the water-insoluble monomer (M) is attracted to the lyophilic ends in the micelles, causing the micelles to swell. The number of swollen micelles per milliliter of water is on the order of 10^{18}. However, at the initial stages of polymerization (phase I) most of the monomer is present as globules that resemble those observed in suspension polymerization.

Since the initiation of polymerization takes place in the aqueous phase, essentially no polymerization occurs in the globules. Thus, they serve primarily as a reservoir of monomer supplied to the micelles to replace monomer converted to polymer. The number of droplets per milliliter of water is on the order of 10^{11}. Since there are 10 million times as many micelles as droplets, the chance of initiation of monomer in a droplet is very small and the chance that more than one growing chain occurs within the same droplet is very small.

The persulfate ion undergoes homolytic cleavage producing two sulfate ion radicals.

$$S_2O_8^{-2} \rightarrow 2SO_4^{\bullet -} \tag{6.45}$$

The sulfate ion radical then initiates polymerization, here with a styrene monomer eventually forming a PS oligomer radical and eventually a PS radical.



(6.46)

According to a theory proposed by Harkins and refined by Smith and Ewart, the first stages of propagation in an emulsion system also take place in the aqueous phase to produce a more lyophilic surface oligoradical. When the $\overline{DP}$ of the PS oligoradical is 3–5, its solubility is much like that of styrene, and it migrates to the swollen micelle where propagation continues with the styrene molecules already present. According to the accepted theories, each micelle can accommodate only one free radical, as noted earlier, and until a second one enters and terminates the propagation reaction through coupling, propagation continues to take place in the micelles. From a statistical point of view, only one half of the micelles ($N/2$) will contain growing chains at any one time. It should also be noted that since propagation occurs in the micelles, the rate of polymerization will be proportional to the number of micelles present, i.e., the rate is proportional to the soap concentration.

As the micelles grow by absorption of more monomer and formation of polymer, they become relatively large particles that absorb soap from micelles that have not been inoculated or stung by oligoradicals. Thus, in stage II, when about 20% of the monomer has been converted to polymer, the micelles disappear and are replaced by large, but fewer, monomer–polymer particles.

Polymerization continues in stage II, and monomer continues to be supplied to the particles by the droplets in the aqueous phase. These droplets disappear when about 30% of the monomers has been converted to polymers. Polymerization continues in stage III after about 60% conversion, but all monomers must now be supplied to the macroradicals by a diffusion process in the micelles.

The rate of sulfate decomposition is described as

$$R_d = k_d[S_2O_8^{-2}] \tag{6.47}$$

The rate of initiation is then

$$R_i = k_i[SO_4^{\bullet -}][M] = 2k_d f[S_2O_8^{-2}] \tag{6.48}$$

The rate of propagation in the micelles is similar to that described for other free radical chain growth, but since the free radical concentration is equal to the number of active micelles, the value of $N/2$ is used instead of $[M^\bullet]$. Thus, the rate of propagation is dependent on the number of micelles present.

$$R_p = k_p[M][M^\bullet] = k_p[M](N/2) \tag{6.49}$$

The rate of production of free radicals at 50°C is about 10^{13} radicals/mL/sec. Thus, since there are 10^5 micelles for every free radical produced in 1 sec, inoculation of any of the 10^{18} micelles/mL is infrequent. Hence, since propagation is a very fast reaction, long chains are produced before termination by coupling, which takes place as the result of the entrance of a new oligoradical in the active micelle. The $\overline{DP}$ is also proportional to the number of active micelles ($N/2$).

$$DP = R_p/R_i = k_p(N/2)/k_i[SO_4^{\bullet -}] \tag{6.50}$$

6.5 FLUORINE-CONTAINING POLYMERS

Polytetrafluoroethylene (PTFE), better known by its trade name Teflon, was accidentally discovered by Roy J. Plunkett, a DuPont chemist who had just received his PhD from Ohio State University 2 years earlier. He was part of a group searching for nontoxic refrigerant gases. On April 6, 1938, he and his assistant, Jack Rebok, had filled a tank with tetrafluoroethylene. After some time, they opened the valve but no gas came out. The tank weight indicated that there was no weight loss—so what happened to the tetrafluoroethylene. Using a hacksaw, they cut the cylinder into half and found a waxy white powder. He correctly surmized that the tetrafluoroethylene had polymerized. The waxy white powder had some interesting properties. It was quite inert toward strong acids, bases, and heat, and was not soluble in any attempted liquid. It appeared to be quite "slippery."

Little was done with this new material until the military, working on the atomic bomb, needed a special material for gaskets that would resist the corrosive gas uranium hexafluoride, which was one of the materials used to make the atomic bomb. General Leslie Groves, responsible for the U.S. Army's part in the atomic bomb project, had learned of DuPont's new inert polymer and had DuPont manufacture it for them.

Teflon was introduced to the public in 1960 when the first Teflon-coated muffin pans and frying pans were sold. Like many new materials, problems were encountered. Bonding to the surfaces was uncertain at first. Eventually the bonding problem was solved. Teflon is now used for many other applications including acting as a biomedical material in artificial corneas, substitute bones for nose, skull, hip, nose, and knees; ear parts, heart valves, tendons, sutures, dentures, and artificial tracheas. It has also been used in the nose cones and heat shield for space vehicles and for their fuel tanks.

Over half a million vascular graft replacements are performed yearly. Most of these grafts are made of PET and PTFE. These relatively large diameter grafts work when blood flow is rapid, but they generally fail for smaller vessels.

PTFE is produced by the free radical polymerization process. While it has outstanding thermal and corrosive resistance, it is a marginal engineering material because it is not easily machinable. PTFE has low tensile strength, resistance to wear, and low creep resistance. Molding powders are processed by press and sinter methods used in powder metallurgy. It can also be extruded using ram extruder techniques.

PTFE is a crystalline polymer with melting typically occurring above 327°C. Because it is highly crystalline, PTFE does not generally exhibit a noticeable T_g.

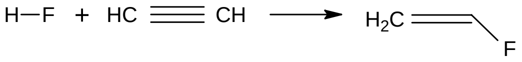
The C–F bond is one of the strongest single bonds known with a bond energy of 485 kJ/mol. Although it is structurally similar to linear PE it has marked differences. Because of the small size of hydrogen, PE exists as a crankshaft backbone structure. Fluorine is a little larger (atomic radius of F $=$ 71 pm and H $=$ 37 pm) than hydrogen causing the Teflon backbone to be helical forming a complete twist every 13 carbon atoms. The size of fluorine is sufficient to form a smooth "protective" sheath around the carbon backbone. The concentration of fluorine end groups is low in ultra-high molecular weight PTFE contributing to its tendency to form crystals.

The electron density of PE and PTFE is also different. The electronegativity value for C $=$ 2.5, F $=$ 4.0, and H $=$ 2.1. Thus, the electron density on the fluorine surface of PTFE is greater than that for PE.

For high molecular weight linear PE, the repeat unit length is about 0.254 nm forming crystalline portions with a characteristic thickness of about 10 nm. The chain length for tough solids from PE is about 4.5 times the crystalline thickness. Thus, tough solids occur at molecular weights greater than 5000 g/mol or chain lengths greater than about 45 nm. In comparison, the repeat unit length for PTFE is about 0.259 nm. The crystalline thickness for PTFE is about 100–200 nm or much thicker than for PE. Chain lengths for tough solids are about 4.5 times the crystalline thickness. Thus, much greater chain sizes, about 200,000–400,000 Da, are required to produce tough solids. The greater size of the crystalline portions also probably contributes to its higher T_m and greater difficulty in processing. The crystal thickness of PTFE is about 10–20 times the crystal thickness found for most other semicrystalline polymers such as PE.

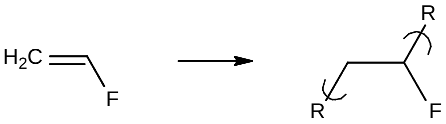
At low-molecular weights, PTFE is waxy and brittle. To achieve good mechanical properties ultra-high molecular weights on the order of 10 million daltons are usually needed. These long chains disrupt crystal formation because they are longer than a single crystal. Moreover, the long chain lengths connect the crystals together adding to their strength. But these long chains result in extremely high viscosities so that ultra-high molecular weight PTFE does not flow when melted and is thus, not melt processable. Form-restrictive and costly methods are used to produce products from PTFE.

Although vinyl fluoride was prepared around 1900, it was believed to be resistant to typical "vinyl" polymerization. German scientists prepared vinyl fluoride through reaction of acetylene with hydrogen fluoride in the presence of catalysts in 1933.



(6.51)

It was not until 1958 that DuPont scientists announced the polymerization of vinyl fluoride forming poly(vinyl fluoride)—PVF (Equation 6.52). Polymerization is accomplished using peroxide catalysts in water solutions under high pressure.



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In comparison to PTFE, PVF is easily processable using a variety of techniques used for most thermoplastic materials. It offers good flame retardancy, presumably due to the formation of hydrogen fluoride that assists in the control of the fire. Thermally induced formation of hydrogen fluoride is also a negative factor because of its toxicity. As in the case of PVC, elimination of the hydrogen halide (HF) promotes formation of aromatic polycyclic products that are toxic.

The difference in electronegativity between the adjacent carbons because of the differing electronegativities of hydrogen and fluorine results in the C–F bond being particularly polar resulting in it being susceptible to attack by strong acids. The alternating bond polarities on the PVF chain give a tight structure resulting in PVF films having a low permeability. This tight structure also results in good solvent resistance, resistance to cracking, and resistance to fading.

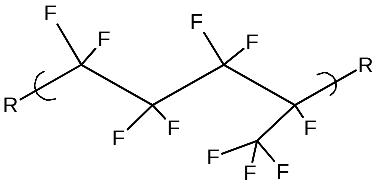
Friction and wear are important related characteristics. If a material has a high friction, it will generally have a shorter wear time because water or other friction event chemicals pass over the material with the higher friction causing greater wear. The friction eventually "wears" away polymer chains layer-by-layer. The engineering laws of sliding friction are simple. According to Amontons' laws, the friction (F) between a body (raindrop, wind, or board rubbing against the material) and a plane surface (the polymeric material) is proportional to the load (L) and independent to the area of contact (A). The friction of moving bodies is generally less than that of a static body. The kinetic friction is considered independent of the velocity. The coefficient of friction is defined as F/L. Polymers show a wide range of coefficients of friction so that rubbers exhibit relatively high values (BR $=$ 0.4–1.5 and SBR $=$ 0.5–3.0), whereas some polymers such as PTFE (0.04–0.15) and PVF (0.10–0.30) have low values.

The low coefficient of friction for PVF results in materials coated with it remaining somewhat free of dirt and other typical contaminants allowing PVF-coated materials to be less frequently cleaned. It is essentially self-cleaning as rain carries away dust and other particulates including bird droppings, acid rain, and graffiti. The low friction also results in longer lifetimes for materials coated with the PVF and for the PVF coating itself.

PVF has a T_g of about -20°C remaining flexible over a wide temperature range (from about -20°C to 150°C), even under cold temperatures. Because of its low coefficient of friction and tightly bound structure, it retains good strength as it weathers. Films, in Florida, retain much of their thickness even after about a decade losing less than 20% of their thickness. To increase their useful lifetimes, relatively thick films, such as 1 mil, are generally employed. The "slickness" also acts to give the material a "natural" mildew resistance.

Unlike PVC that requires plasticizers to be flexible, PVF contains no plasticizers and does not "dry out" like PVC. PVF, because of its higher cost in comparison to PE and PP, is used as a coating and selected "high end" bulk applications, such as films. Films are sold by DuPont under the trade name Tedlar. Teldar is used in awnings, outdoor signs, roofing, highway sound barriers, commercial building panels, and solar collectors. It is used as a fabric coating, protecting the fabric from the elements. PVF is resistant to UV-related degradation and unlike PVC, it is inherently flexible. While transparent, pigments can be added to give films and coatings with varying colors. Protective coatings are used on plywood, automotive parts, metal siding, lawn-mower housings, house shutters, gutters, electrical insulation, and in packaging of corrosive chemicals. PVF has pizeoelectric properties generating current when compressed.

The processability of fluorine-containing polymers is improved by replacement of one or more of the fluorine atoms. Replacing one of the eight fluorine atoms with a trifluoromethyl group gives a product called FEP or Viton, actually a copolymer of tetrafluoroethylene and hexafluoropropylene (Equation 6.53). Polytrifluoromonochloroethylene (PCTFE, Kel F) (Equation 6.54), in which one fluorine atom has been replaced by a chlorine atom, has a less regular structure and is thus more easily processed. Poly(vinylidene fluoride) (PVDF, Kynar) (Equation 6.55) is also more easily processable but less resistant to solvents and corrosives.



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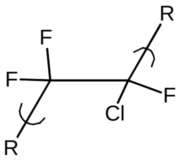


(6.54)

Gore-Tex is named after its inventors W.L. Gore and R.W. Gore and the nature of the material, a textile. Gore-Tex materials are based on expanded PTFE and other fluoropolymers. They are used in a variety of areas including gaskets, sealants, insulation for wires and cables, filter media, and medical implants and their most widely used area as high performance fabrics. Gore-Tex is a thin, highly porous fluoropolymer membrane bonded generally to a nylon or polyester fabric. The membrane has about 9 billion pores per square inch. Each of these pores is

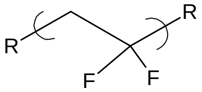
TABLE 6.7
General Physical Properties of Selected Fluorine-Containing Polymers

Polymer	PTFE	PCTFE	PVDF	PVF
Heat deflection temperature (1820 kPa; °C)	100	100	80	90
Maximum resistance to continuous heat (°C)	250	200	150	125
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	10	14	8.5	10
Compressive strength (kPa)	2.7×10^4	3.8×10^4	—	—
Flexural strength (kPa)	—	6×10^4	—	—
Impact strength (Izod: cm–N/cm of notch)	160	130	—	—
Tensile strength (kPa)	2.4×10^4	3.4×10^4	5.5×10^4	—
Ultimate elongation (%)	200	100	200	—
Density (g/mL)	2.16	2.1	1.76	1.4

about 20,000 times smaller than a drop of water preventing liquid water from penetrating but allowing individual water molecules to pass through. This results in a material that is breathable but also waterproof and wind resistant. This is in contrast to most raincoats that are waterproof but not breathable. Along with garments, Gore-Tex is also used to make tents and other outdoors goods.

A slice of quartz develops a net positive charge on one side and a net negative charge on the other side when pressure is applied. The same effect is found when pressure is applied by means of an alternating electric field. This effect is known as the piezoelectric effect and is used for quartz watches and clocks, TVs, hearing aids, etc.

Several polymers also are effective piezoelectric materials. The best known of these is PVDF (Equation 6.55), which is employed in loud speakers, fire and burglar alarm systems, earphones, and microphones.



(6.55)

Table 6.7 contains physical properties of selected fluorine-containing polymers described above.

Nylon 11 (Equation 6.56) is also a piezoelectric material that can be aligned when placed in a strong electromagnetic field giving films used in infrared-sensitive cameras, underwater detection devices, and in electronic devices since it can be overlaid with printed circuits.

$$\underset{\text{11-Aminoundecanoic acid}}{H_2N—(CH_2)_{10}—COOH} \rightarrow \underset{\text{Nylon 11}}{—(—HN—(CH_2)_{10}—COO—)—} \qquad (6.56)$$

6.6 POLYSTYRENE

Styrene monomer was discovered by Newman in 1786. The initial formation of PS was by Simon in 1839. Although PS was formed almost 175 years ago, the mechanism of formation, described in Sections 6.1 through 6.3, was not discovered until the early 20th century. Staudinger, using styrene as the principle model, identified the general free radical polymerization process in 1920. Initially commercialization of PS, as in many cases, awaited the ready availability of the monomer. While there was available ethyl benzene, it underwent thermal cracking rather than dehydrogenation until the appropriate conditions and catalysts were discovered. Dow first successfully commercialized PS formation in 1938. While most commercial PS has only a low degree of stereoregularity, it is rigid and brittle because of the resistance of the more bulky phenyl-containing units to move in comparison, e.g., to the methyl-containing units of PP. This is reflected in a relatively high T_g of about 100°C for PS. It is transparent because of the low degree of crystalline formation.

Although PS is largely commercially produced using free radical polymerization, it can be produced by all four major techniques—anionic, cationic, free radical, and coordination-type systems. All of the tactic forms can be formed employing these systems. The most important of the tactic forms is syndiotactic polystyrene (sPS). Metallocene-produced sPS is a semi-crystalline material with a T_m of 270°C. It was initially produced by Dow in 1997 under the trade name Questra. It has good chemical and solvent resistance in contrast to "regular" PS that has generally poor chemical and solvent resistance because of the presence of voids that are exploited by the solvents and chemicals.

Physical properties of PS are dependent on the molecular weight and presence of additives. While higher molecular weight PS offers better strength and toughness, it also offers poorer processability. Low-molecular weight PS allows good processability but poorer strength and toughness. Generally, a balance is sought where intermediate chain lengths are used. Typically employed chain lengths are on the order of 1500–3500 with standard MWDs of about 2.2–3.5. Small amounts of plasticizers are often used to improve processability.

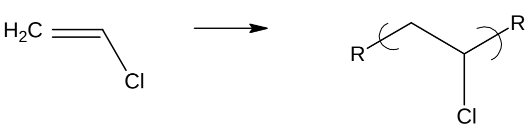
Styrene is employed in the formation of a number of co- and terpolymers. The best known is the terpolymer ABS.

Major uses of PS are in packaging and containers, toys and recreational equipment, insulation, disposable food containers, electrical and electronics, housewares, and appliance parts. Expandable PS is used to pack electronic equipment, such as TVs, computers, and stereo equipment. Legislation was put in place in some states to insure the recycling of PS. Interestingly some of this legislation was written such that all PS had to be recycled within some period of time, such as a year. This legislation was changed to reflect the real concern of fast food containers when it was pointed out that less than 10% PS is used in this manner and that well over twice as much was used as house insulation that should not be recycled every year or so.

6.7 POLY(VINYL CHLORIDE)

PVC is one of the three most abundantly produced synthetic polymers. PVC is one of the earliest produced polymers. In 1835, Justus von Liebig and his research student, Victor Regnault, reacted ethylene dichloride with alcoholic potash forming the monomer vinyl chloride. Regnault believed he polymerized vinyl chloride but latter studies showed it to be PVC. In 1872, E. Baumann exposed vinyl chloride sealed in a tube to sunlight and produced a solid, PVC. Klasse, in Germany, found that vinyl chloride could be made by the addition of hydrogen chloride to acetylene in a system that could be scaled up for commercial production. (Today most vinyl chloride is made from the oxychlorination reaction with ethylene.) As Germany was already producing a number of flexible and rigid PVC products, during World War I it used PVC as a replacement for corrosion-prone metals.

Today, PVC is made from the polymerization of vinyl chloride as shown in the following equation:



(6.57)

Waldo Semon was responsible for bringing many of the PVC products to market. As a young scientist at BF Goodrich, he worked on ways to synthesize rubber and to bind the rubber to metal. In his spare time, he discovered that PVC, when mixed with certain liquids, gave an elastic-like, pliable material that was rainproof, fire resistant, and did not conduct electricity. Under the trade name Koroseal, the rubbery material came into the marketplace, beginning around 1926, as shower curtains, raincoats, and umbrellas. During World War II, PVC became the material of choice to protest electrical wires for the Air Force and Navy. Another of his inventions was the SR patented under the name Ameripol that was dubbed "liberty rubber" since it replaced NR in the production of tires, gas masks, and other military equipment. Ameripol was a butadiene-type material.

Because of its versatility, some unique performance characteristics, ready availability, and low cost PVC is now the third largest produced synthetic polymer behind PE and PP.

As a side note, there is today a debate concerning the use of chlorine-containing materials and their effect on the atmosphere. This is a real concern and one that is being addressed by industry. PVC and other chloride-containing materials have in the past been simply disposed of through combustion that often created unwanted hydrogen chloride. This practice has largely been stopped, but care should be continued to see that such materials are disposed of properly. Further, simply outlawing of all chloride-containing materials is not possible or practical. For instance, we need common salt for life, which is sodium chloride. Chlorine is widely used as a water disinfectant both commercially (for our drinking water) as well as for pools. Further, PVC is an important material that is not easily replaced. Finally, the amount of chloride-containing residue that is introduced into the atmosphere naturally is large in comparison to that introduced by PVC. Even so, we must exercise care as we want to leave a better world for our children and grandchildren so a knowledge-based approach must be taken. As with most significant problems, it is better to err in the direction of caution.

PVC materials are often defined to contain 50% or more vinyl chloride units by weight. PVC is generally a mixture of a number of additives and often other units, such as ethylene, propylene, vinylidene chloride, and vinyl acetate. Structurally similar products, but with differing properties, are made from the chlorination of PE but almost all PVC is made from the polymerization of vinyl chloride. Typical homopolymers are about 400–1000 units long.

PVC is commercially produced by a number of techniques but mainly by suspension, emulsion, bulk, and solution polymerization. Typically, product properties and form can be tailored through the use of a particular synthetic process and conditions. Particulate architecture is then controlled to achieve materials with specific sizes and distributions for specific uses and applications. Because of the tendency of PVC to split off hydrogen chloride, forming materials with high char at relatively low general processing temperatures, special care is taken with respect to temperature control and particulate architecture that allows ready processing of PVC by most of the common processing techniques.

Tacticity of the PVC varies according to the particular reaction conditions but generally manufactures favor a syndiotactic form with many PVC materials being about 50% sPVC. The reported amount of crystallinity is in the range of 5%–10%. This allows for a material with some strength, but one with sufficient amorphous regions to retain good flexibility.

PVC, in comparison with many other polymers, employs an especially wide variety of additives. For instance, a sample recipe or formulation for common stiff PVC pipe such as that used in housing and irrigation applications may contain, in addition to the PVC resin, tin stabilizer, acrylic processing aid, acrylic lubricant-processing aid, acrylic impact modifier, calcium carbonate, titanium dioxide, calcium sterate, and paraffin wax. Such formulations vary according to the intended processing and end use. In such nonflexible PVC materials, the weight amount of additive is on the order of 5%–10%.

Plasticizers weaken the intermolecular forces in the PVC reducing crystallinity. A relatively stable suspension, called a plastisol, of finely divided PVC in a liquid plasticizer, can be poured into a mod and heated to about 175°C producing a solid flexible plastic as a result of fusion of the plasticizer in the PVC.

As noted earlier, there is a tendency for PVC to undergo elimination of hydrogen chloride when heated. The most labile chlorine atoms are those at tertiary or terminal sites. Once the initial chloride is eliminated, continued unzipping occurs with the formation of unsaturated backbone sites and the evolution of hydrogen chloride. The purpose of the stabilizer is to cap unzipping sites by substitution of more stable groups for the evolved chloride as depicted in the following equation:

$$\text{—C—Cl} + \text{Sn—R} \rightarrow \text{—C—R} + \text{Sn—Cl} \tag{6.58}$$

Some of the tin stabilizers are based on oligomeric materials first made by Carraher and coworkers. These oligomeric materials are essentially "nonmigrateable."

A sample formula for a flexible upholstery fabric covering might contain PVC resin, medium molecular weight polymeric plasticizer, stearic acid lubricant, calcium carbonate, pigment, antimony oxide, linear phthalate ester, epoxidized soy bean oil, and linear phthalate ester. Here the weight of the amount of additive is in the range of 40%–70% by weight with the plasticizer often being on the order of about 60%.

PVC has a built-in advantage over many other polymers in that it is itself flame resistant. About 50% of PVC is used as rigid pipes. Other uses of rigid PVC are as pipe fittings, electrical outlet boxes, and automotive parts. Uses of flexible PVC include in gasoline-resistant hose, hospital sheeting, shoe soles, electrical tape, stretch film, pool liners, vinyl-coated fabrics, roof coatings, refrigerator gaskets, floor sheeting, and electrical insulation and jacketing. A wide number of vinyl chloride copolymers are commercially used. Many vinyl floor tiles are copolymers of PVC.

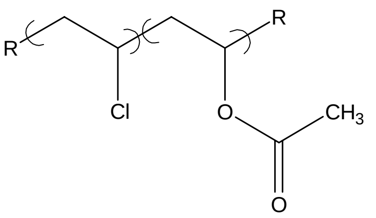
Table 6.8 contains general physical properties of PVC. Because of the variety of additives, the values for the plasticized PVC are approximate.

PVC is flexibilized by addition of plasticizers as already noted. It is also made more flexible through blending with elastomers that act as impact modifiers. These blends are used when impact resistance is essential.

A number of copolymers are formed employing vinyl chloride. Because of the presence of the comonomer, these copolymers are more flexible than PVC itself. Vinylite (Equation 6.59) is a random copolymer of vinyl chloride (87%) and vinyl acetate. While vinylite is not as strong as PVC, it is more easily processed.

TABLE 6.8
General Physical Properties of PVC

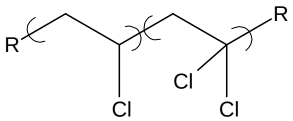
	Rigid PVC	**Plasticized PVC**
Heat deflection temperature (1820 kPa; °C)	75	—
Maximum resistance to continuous heat (°C)	60	35
Crystalline melting point (°C)	170	—
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	6	12
Compressive strength (kPa)	6.8×10^4	6×10^3
Flexural strength (kPa)	9×10^4	—
Impact strength (Izod: cm–N/cm of notch)	27	—
Tensile strength (kPa)	4.4×10^4	1×10^4
Ultimate elongation (%)	50	200
Density (g/mL)	1.4	1.3



(6.59)

Copolymers of vinyl chloride with vinyl acetate and maleic anhydride are made more adhesive to metals through hydrolysis of the ester and anhydride units.

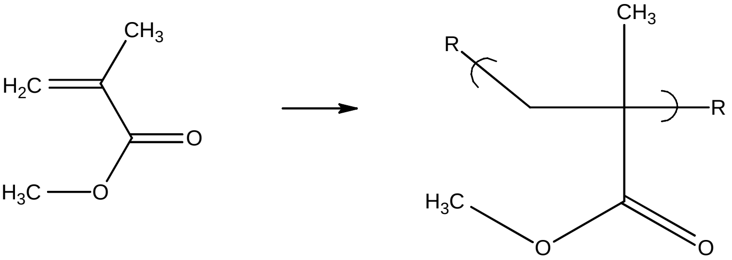
Copolymers of vinyl chloride and vinylidene chloride are widely used (Equation 6.60). Two extremes are employed. The lesser known has a high vinyl chloride content compared with the vinylidene chloride comonomer. These copolymers are more easily dissolved and have greater flexibility. The most widely known copolymer has about 90% vinylidene chloride and 10% vinyl chloride and is known as Saran. This copolymer has low permeability to gases and vapors and is transparent. Films are sold as Saran Wrap.



(6.60)

6.8 POLY(METHYL METHACRYLATE)

Poly(methyl methacrylate) (PMMA) (Equation 6.61) is the most widely employed of the alkyl methacrylates. For the most part, commercial PMMA is sold as an atactic amorphous polymer that has good light transparency (92%) and gives transparent moldings and films. General properties are given in Table 6.9. The presence of two substituents on every alternate carbon atom restricts chain mobility so PMMA is less flexible than the corresponding poly(alkyl acrylates). The presence of the alpha methyl group increases the stability of PMMA toward light-associated and chemical degradation.



(6.61)

TABLE 6.9
General Physical Properties of PMMA

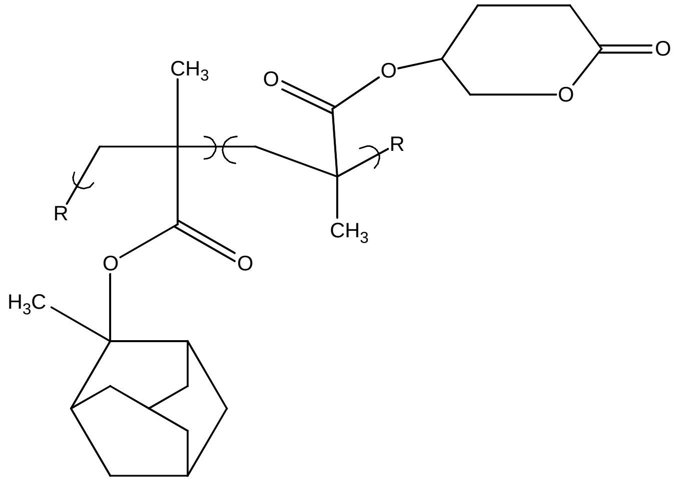
Heat deflection temperature (1820 kPa; °C)	95
Maximum resistance to continuous heat (°C)	75
Coefficient of linear expansion (cm/cm-°C, 10^{-5})	7.0
Compressive strength (kPa)	1×10^5
Flexural strength (kPa)	9.6×10^4
Impact strength (Izod: cm–N/cm of notch)	21
Tensile strength (kPa)	6.5×10^4
Ultimate elongation (%)	4
Density (g/mL)	1.2

Unlike the poly(alkyl methacrylates) that degrade by random chain scission, PMMA undergoes degradation through unzipping when heated.

The most widely used acrylic plastics are PMMA (such as Lucite) and copolymers of methyl methacrylate that contain small amounts (2%–18%) of methyl or ethyl acrylate (such as Plexiglas). These materials are available as sheets and molding powders. PMMA is more resistant to impact than PS or glass but its scratch-resistance is inferior to glass. PMMA is widely used in the creation of automotive (light) lenses for tail lights and some front light casings.

PMMA is resistant to nonoxidizing acids, bases, and salts at ordinary temperatures but is attacked by oxidizing acids at room temperature. It is resistant to highly polar solvents, such as ethanol, but is soluble in less polar solvents, such as toluene.

Polymers such as the methacrylates play an essential role as *photoresists*. To make a photoresist, the methacrylate polymer is deposited onto silicon dioxide. A mask, that shields specific regions from subsequent exposure to light, is placed over the methacrylate polymer resist. The combination is exposed to light of such strength as to induce methacrylate polymer bond breakage producing a somewhat degraded methacrylate product that is more soluble in organic liquids allowing the preferential removal of the exposed photoresist. These methacrylate polymers are especially designed to allow both easy degradation and subsequent easy removal of the exposed photoresist. One of these is a copolymer with adamantane and lactone-containing units.

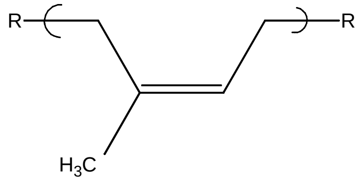


(6.62)

Modified methacrylate copolymer

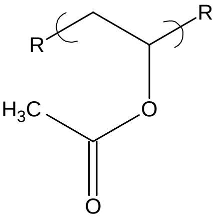
This type of photoresist is called a "positive photoresist" since it is the exposed area that is removed.

Negative photoresists are formed from polymers that undergo reactions that decrease their solubility when exposed to radiation. Thus, polymers such as *cis*-1,4-polyisoprene (Equation 6.63) cross-link when exposed to the appropriate radiation giving insoluble products.

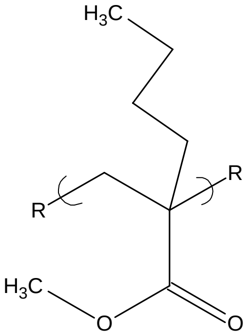


(6.63)

Since the 1950s, synthetic polymers have been used as art binders. The most common groups are referred to as the vinyls and acrylics by artists. Both groupings represent a wide variety of polymers and copolymers and are inaccurately, or at best not accurately, named. For polymer scientists, the term vinyl generally refers to PVC, but to artists it may refer to many other materials. Even so, most of the synthetic paint market today is based on acrylics. Acrylic paints are typically water emulsions of synthetic polymers. In art, the term acrylic is used to describe a wide variety of polymers and copolymers that can be considered as derivatives of acrylic acids. Most acrylics used in art binders are PMMA (Equation 6.61), PVAc (Equation 6.64), poly(*n*-butyl methacrylate) (Equation 6.65), and copolymers such as poly(ethyl acrylate-comethacrylate).



(6.64)



(6.65)

Acrylic emulsions tend to flow nicely "leveling out" rather than giving a three-dimensional effect sometimes offered in various oils. In the absence of a pigment, acrylic emulsions give a milky white appearance. As the water evaporates, the binder particles coalesce forming a tight film. When dried, the film is clear and becomes water insoluble.

As noted above, acrylics are colorless when hardened so that the color comes from the addition of the coloring agents, pigments. When thick, acrylics form plastics, but when applied to give thin coatings, they give flexible films. Unlike many of the natural coatings, such as oil-based paints that crack and are not flexible, acrylic coatings are more flexible and do not crack easily. On the contrary, the permanence of the acrylic coatings has not been field tested since they are only about half a century old, whereas oil-based paintings have remained for almost half a millennium. Even so, many artists claim that acrylic paints are more permanent than the natural-based paints. Only the test of time will truly give us the answer.

Acrylic paints have compositions similar to water-based house paints. Since they are synthetic, manufactures can design paints that fulfill specific requirements and that are the same from tube to tube. Because water is the main vehicle such paints are largely odorless. They are not completely odorless because while the overwhelming majority of the vehicle is water, there are often minute amounts, generally 1%–10%, of organic liquid added to help the particles of polymer remain sufficiently flexible so that they will "lay down" a thin smooth coating.

Unlike oils that take days and weeks to dry "to the touch," acrylics dry in minutes to several hours. They are also considered nonyellowing.

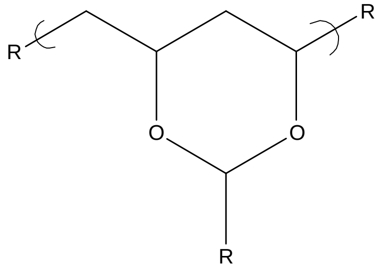
Acrylics are also the most used paint for baked polymer clay.

6.9 POLY(VINYL ALCOHOL) AND POLY(VINYL ACETALS)

PVA is produced by the hydrolysis of PVAc (Equation 6.44). Because of the ability to hydrogen bond and small size of the hydroxyl grouping, PVA is a crystalline atactic material.

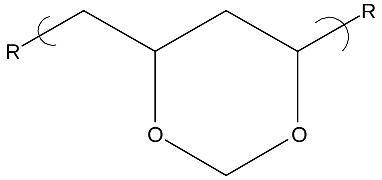
Because of the formation of strong internal hydrogen bonds, completely hydrolyzed PVAc is not water soluble. Thus, hydrolysis of PVAc is stopped giving a material that is about 88% hydrolyzed and water soluble. PVA is resistant to most organic solvents, such as gasoline. PVA fibers (Kuralon) are strong and insoluble in water because of a surface treatment with formaldehyde that reacts with the surface hydroxyl groups producing poly(vinyl formal) on the polymer surface.

PVA is used in the treatment of textiles and paper. PVA also acts as the starting material for the synthesis of a number of poly(vinyl acetals) with the general structure as given in Equation 6.66. The acetal rings on these random amorphous polymer chains restrict flexibility and increase the heat deflection temperature to a value higher than that of PVAc.



(6.66)

The deflection temperature of poly(vinyl formal) is about 90°C. Because of the presence of residual hydroxyl groups, commercial poly(vinyl formal) has a water absorption of about 1%. Poly(vinyl formal) (Equation 6.67) has a T_g of about 105°C and is soluble in moderately polar solvents, such as acetone.

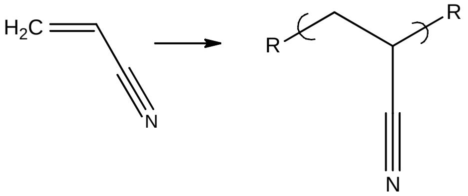


(6.67)

The most widely used poly(vinyl acetal) is poly(vinyl butyral) discussed in Section 6.4. As already noted, this plastic is used as the inner lining of safety windshield glass. Because of the presence of unreacted hydroxyl groups, poly(vinyl butyral) has excellent adhesion to glass.

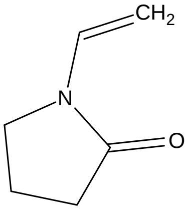
6.10 POLY(ACRYLONITRILE)

Poly(acrylonitrile) (PAN) (Equation 6.68) forms the basis for a number of fibers and copolymers. As fibers, they are referred to as acrylics or acrylic fibers. The development of acrylic fibers began in the early 1930s in Germany, but they were first commercially produced in the United States by DuPont (Orlon) and Monsanto (Acrilan) around 1950.

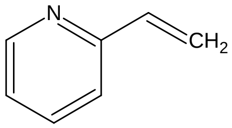


(6.68)

Because of the repulsion of the cyanide groups the polymer backbone assumes a rod-like conformation. The fibers derive their basic properties from this stiff structure of PAN where the nitrile groups are randomly distributed about the backbone rod. Because of strong bonding between the chains, they tend to form bundles. Most acrylic fibers actually contain small amounts of other monomers, such as methyl acrylate and methyl methacrylate. As they are difficult to dye, small amounts of ionic monomers, such as sodium styrene sulfonate, are often added to improve their dyeability. Other monomers are also employed to improve dyeability. These include small amounts (about 4%) of more hydrophilic monomers, such as *n*-vinyl-2-pyrrolidone (Equation 6.69), methacrylic acid, or 2-vinylpyridine (Equation 6.70).



(6.69)



(6.70)

Acrylic fibers are used as an alternative to wool for sweaters. PAN is also used in the production of blouses, blankets, rugs, curtains, shirts, craft yarns, and pile fabrics used to simulate fur.

At temperatures above 160°C, PAN begins forming cyclic imines that dehydrogenate forming dark-colored, heat-resistant, fused ring polymers with conjugated C=C and C=N bonding. This is described in Section 12.17.

Fibers with more than 85% acrylonitrile units are called acrylic fibers but those containing 35%–85% acrylonitrile units are referred to as modacrylic fibers. The remainder of the modacrylic fibers are derived from comonomers, such as vinyl chloride or vinylidene chloride, that are specifically added to improve flame resistance.

6.11 SOLID STATE IRRADIATION POLYMERIZATION

There are numerous examples of solid state polymerizations. Here we will briefly describe examples based on addition polymers. Generally, the crystalline monomer is irradiated with electrons or some form of high-energy radiation, such as gamma or x-rays. Since many monomers are solids only below room temperature, it is customary to begin irradiation at lower temperatures with the temperature raised only after initial polymerization occurs. (Some reactions are carried to completion at the lower temperature.) After polymerization, the monomer is removed. Table 6.10 contains a list of some of the common monomers that undergo solid-state irradiation polymerization.

TABLE 6.10
Monomers That Undergo Solid-State Irradiation Polymerization

Styrene
Acetaldehyde
Methacrylic acid (and salts)
1,3-Butadiene
Isoprene
Acrylamide
Diacetylenes
Formaldehyde
Acrylic acid (and salts)
Trioxane
3,3-Bischloromethyl cyclooxabutane
Acrylonitrile
Beta-propiolactone
—

This approach can offer several advantages. First, polymers can be formed from monomers that do not give polymer under more typical reaction conditions. Second, under some cases, the crystalline structure acts as a template giving the order that might otherwise be difficult to achieve. Third, removal and interference by solvent or additives is eliminated as they are not present. Fourth, the polymers produced by this technique are often different from those from the same monomer except that produced using typical reaction techniques.

6.12 PLASMA POLYMERIZATIONS

Organic and inorganic molecules can be placed in the vapor state either through heating, low pressure, simply spraying, or some combination of these. These molecules are then subjected to some ionizing energy that forms active species that react with one another eventually depositing themselves on a surface. Often the products are polymeric with complex structures. The term plasma polymerization is generally used to describe the process resulting in surface film formation, whereas the term deposition is generally used to describe the deposition of powdery particles formed in the gas phase. Others describe plasma polymerization as that which occurs at high rates in the gas phase resulting in powder formation and deposition as any sorption occurring on the surface. In truth, it is difficult to separate the two reaction sequences because active molecules can react both in the gaseous phase upon collision and on the surface.

Plasma environments are often created using plasma jets, ion beams, glow discharges, corona discharges, laser-induced plasmas, and electron beams. Low temperature plasmas can also be created using radio frequency, audio frequency, microwave, or direct current energy sources. In general terms, the molecules enter the reactor as neutral species. They become reactive species as electronic energy is transferred to them. The reactive species can be ions, free radicals, or excited molecules. Reaction can occur in the gaseous phase and/or at the solid surface. Commercially, reactors often consist of a low pressure glow discharge of reactive species. Because a small amount of electromagnetic radiation is emitted in the visible region, the term glow discharge was derived.

This approach allows the deposition of thin films at low temperatures. By comparison, polymer deposition generally requires very high temperatures. For instance, the chemical vapor deposition of silicon nitride requires a temperature of about 900°C, whereas the plasma chemical deposition requires a temperature of only 350°C.

A number of typical polymer-forming monomers have been polymerized using plasma polymerization including tetrafluoroethylene, styrene, acrylic acid, methyl methacrylate, isoprene, and ethylene. Polymerization of many nontypical monomers has also occurred including toluene, benzene, and simple hydrocarbons.

Plasma films are usually highly cross-linked, resistant to higher temperatures, resistant to abrasion and chemical attack, and are highly adherent to the surface. Adhesion to the surface is generally high both because the growing polymer complex can fit the surface contour and thus “lock-itself in” (physical adhesion), and because in many instances, the species are active enough to chemically react with the surface molecules to chemically bond to the surface. The surface can be prepared so that the chemical reaction is enhanced.

Plasma surface treatment of many polymers, including fabrics, plastics, and composites, often occurs. The production of ultra-thin films via plasma deposition is important in microelectronics, biomaterials, corrosion protection, permeation control, and for adhesion control. Plasma coatings are often on the order of 1–100 nm thick.

6.13 SUMMARY

1. For classical free radical polymerizations the rate of propagation is proportional to the concentration of monomer and the square root of the initiator concentration. Termination usually occurs through a coupling of two live radical chains but can occur through disproportionation. The rate of termination for coupling is directly proportional to initiator concentration. The $\overline{DP}$ is directly proportional to monomer concentration and inversely proportional to the square root of the initiator concentration.
2. The first chains produce high molecular weight products. Within the polymerizing system, the most abundant species are the monomer and polymers chains.
3. Increasing the temperature increases the concentration of free radicals thus decreasing the chain length. Increasing the temperature increases the rate of polymer formation.
4. The rate-controlling step is the rate of initiation.
5. There is a steady-state concentration of growing chains.
6. The kinetic chain length ν is equal to $\overline{DP}$ for disproportionation termination, but $\overline{DP} = 2\nu$ for termination by coupling.
7. Chain transfer reactions almost always decrease $\overline{DP}$ and will often introduce branching as it occurs within or between polymer chains. Solvent can also act as effective chain-transfer agents lowering chain length.
8. Vinyl monomers can be polymerized using solution, bulk, suspension, and emulsion techniques. Each has its own characteristic strengths and weaknesses.
9. When polymerizations become viscous, termination slows allowing an increase in the number of growing chains and rate of polymerization. This is known as the gel of Trommsdorff effect. If such reactions are allowed to continue without cooling, explosions are possible.
10. Monomers may be polymerized using a water-soluble initiator while dispersed, by agitation, in a concentrated soap solution. In this emulsion system initiation occurs in the aqueous phase and propagation occurs in the soap micelles. Since the growing macroradicals are not terminated until a new free radical enters the micelle, high molecular weight products are rapidly obtained. The rate of polymerization and $\overline{DP}$ is proportional to the number of activated micelles.
11. Polyfluorocarbons are resistant to heat, solvent, and corrosives. The resistance is greatest in the regularly structured PTFE and decreases as the geometry is upset by substitution of other atoms for fluorine.
12. PVC is an important polymer used for many commercial purposes, e.g., pipes for water delivery systems within homes.

GLOSSARY

backbiting Hydrogen atom abstraction that occurs when a chain end of a macroradical doubles back on itself forming a more stable hexagonal conformation.

branch point Point on a polymer chain where additional chain extension occurs producing a branch.

bulk polymerization Polymerization of monomer without added solvents or water; also called neat.

ceiling temperature (T_c) Characteristic temperature above which polymerization occurs but the polymer decomposes before it is recovered.

chain stopper Chain-transfer agent that produces inactive free radicals.

chain transfer Process in which a free radical abstracts an atom or group of atoms from a solvent, telogen, or polymer.

chain transfer constant (C_s) Ratio of cessation or termination of transfer to the rate of propagation.

critical micelle concentration (CMC) Minimum concentration of soap in water that will produce micelles.

dead polymer Polymer in which chain growth has been terminated.

disproportionation Process by which termination occurs as a result of chain transfer between two macroradicals yielding dead polymers.
half-life Time required for half the reactants to be consumed (generally for a first-order reaction).
heterolytic cleavage Cleavage of a covalent bond that leaves one electron with each of the two atoms. The products are free radicals.
homopolymer Polymer composed of only one repeating unit.
Kel F Trade name for polytrifluorochloroethylene.
kinetic chain length Length of the polymer chain initiated by one free radical.
macroradicals Electron-deficient polymers having a free radical present on the chain.
micelles Ordered groups of soap molecules in water.
oligoradical Low-molecular weight macroradical.
piezoelectric Conversion of mechanical force, such as pressure, into electrical energy.
plasticizer High-boiling compatible liquid that lowers T_g and flexibilizes the polymer.
retarder Additive that acts as a chain-transfer agent producing less active free radicals.
Saran Trade name for copolymers of vinyl chloride and vinylidene chloride.
SBR Rubbery copolymer of styrene and butadiene.
suspension polymerization Process in which liquid monomers are polymerized in liquid droplets suspended in water.
telogen Additive that readily undergoes chain transfer with a macroradical.
telomer Low-molecular weight polymer resulting from chain transfer of a macroradical with a telogen.
telomerization Process in which telomers are produced by chain transfer reactions.
Trommsdorff effect Decrease in termination rate in viscous media that results in higher molecular weight polymers being formed.

EXERCISES

1. Use a slanted line to show the cleavage of (a) boron trifluoride–water (BF_3–H_2O), (b) sodamide, and (c) AIBN in cationic, anionic, and free radical initiations, respectively.
2. Which type of chain-reaction polymerization is most likely to terminate by coupling?
3. If an initiator has a half-life of 4 h, what percentage of this initiator will remain after 12 h?
4. If some head-to-head configuration is detected in a polymer chain known to propagate by head-to-tail addition, what type of termination has occurred?
5. Which is the better way to increase polymer production rates: (a) increasing the temperature or (b) increasing the initiator concentration?
6. Name three widely used thermoplastics produced by free radical chain polymerization?
7. What effect does the increase of polarity of the solvent have on free radical polymerization?
8. Show the repeat units for (a) PS, (b) PVC, and (c) PMMA.
9. Can you think of any advantage of the Trommsdorff effect?
10. What is the limiting step in free radical chain polymerization?
11. In general, which is more rapid: (a) free radical chain reactions or (b) step reaction polymerizations?
12. If one obtained a yield of 10% polymer after 10 min of polymerizing styrene by a free radical mechanism, what would be the composition of the other 90%?
13. Why is $t_{1/2}$ for all first-order reactions equal to $0.693/k_d$?
14. How could you follow the rate of decomposition of AIBN without directly measuring the rate of polymerization?
15. What is the usual value for the energy of activation of free radical initiation?
16. What is the advantage of producing free radicals by UV radiation?
17. Why is PVC considered negative by some environmentally?
18. If $[M^\bullet]$ is equal to 1×10^{-11} mol/L under steady-state conditions, what will $[M^\bullet]$ equal after (a) 30, (b) 60, and (c) 90 min?
19. In general, what is the activation energy in free radical chain propagation of polymer chains?
20. What is the relationship between the rate of propagation and the concentration of initiators [I]?
21. When chain transfer with solvent occurs, what effect does this have on the average DP?
22. In the free radical polymerization name two steady-state assumptions.

23. What monomer is used to produce PVA?
24. Name one advantage and one disadvantage for the bulk-batch polymerization of PS.
25. Does k_p increase or decrease when the average $\overline{DP}$ for a single growing chain goes from 10 to 10^4?
26. Why is ethylene more readily polymerized by free radical chain polymerization than isobutylene?
27. What is the termination mechanism in free radical polymerization is the average $\overline{DP} = v$?
28. The value of v increases as the polymerization temperature of a specific monomer is increased. What does this tell you about the termination process?
29. In general, what is the activation energy of termination?
30. Why would you not recommend the use of poly-α-methylstyrene for the handle of a cooking utensil?
31. Why is polyfluoroethylene generally known by the public as Teflon.
32. Which would you expect to have the higher chain transfer constant: (a) carbon tetrafluoride or (b) carbon tetrachloride?
33. While the addition of dodecyl mercaptan to styrene causes a reduction in DP, the rate of polymerization is essentially unchanged. Explain.
34. Would it be safe to polymerize styrene by bulk polymerization in a 55 gal drum?
35. How do the kinetics of polymerization differ in the bulk and suspension polymerization methods?
36. Since the monomers are carcinogenic, should the polymerization of styrene, acrylonitrile, and vinyl chloride be banned?
37. What are some unusual properties of polyfluoroethylene?
38. Why does polymerization not take place in the droplets instead of in the micelles in emulsion polymerization?
39. Why does initiation not occur in the micelles in emulsion polymerization?
40. What would happen if one added a small amount of an inhibitor to styrene before bulk polymerization?
41. Name several places you might "run across" PS daily.
42. Why is the T_g of PTFE higher than that of FEP?
43. Why does an increase in soap concentration increase the average $\overline{DP}$ and R_p in emulsion polymerizations?
44. Which will have the higher specific gravity (density): (a) PVC or (b) PVDC?
45. By bulk, why are vinyl-derived polymers used in greater amounts than synthetic condensation polymers?
46. How might the kinetics change is an initiator with an E_a of 30 kJ/mol were employed?
47. Why were free radicals polymerizations studied so well?
48. What is an engineering plastic and is Teflon an engineering plastic?
49. Describe how a plastisol is made.
50. How is PAN made so it can be colored?

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7 Copolymerization

Although the mechanism of copolymerization is similar to that discussed for the polymerization of one reactant (homopolymerization), the reactivities of monomers may differ when more than one is present in the feed, i.e., reaction mixture. Copolymers may be produced by step-reaction or by chain reaction polymerization. It is important to note that if the reactant species are M_1 and M_2, then the composition of the copolymer is not a physical mixture or blend, though the topic of blends will be dealt with in this chapter.

Most naturally occurring polymers are largely homopolymers, but proteins and nucleic acids are copolymers composed of a number of different mers. While many synthetic polymers are homopolymers, the most widely used synthetic rubber, SBR, is a copolymer of styrene (S) and butadiene (B), with the "R" representing "rubber." There are many other important copolymers. Here we will restrict ourselves to vinyl-derived copolymers.

Copolymers may be *random* in the placement of units,

$$-M_1M_2M_1M_2M_2M_1M_1M_2M_1M_1M_2M_1M_2M_2M_1M_1M_2M_2M_2M_1M_1M_2M_1M_1- \tag{7.1}$$

alternating in the placement of units,

$$-M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2M_1M_2- \tag{7.2}$$

block in either or both of the different units in which there are long sequences of the same repeating unit in the chain,

$$-M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2M_2M_2M_2M_2M_1M_1M_1M_1M_1M_1M_1M_1M_1M_2M_2M_2M_2- \tag{7.3}$$

or *graft* copolymers in which the chain extension of the second monomer is present as branches.

$$\begin{array}{cccccccccccccccccccccc}
- & M_1 & - \\
 & & & M_2 & & & & & M_2 & & & & & & & & M_2 & & & & & \\
 & & & M_2 & & & & & M_2 & & & & & & & & M_2 & & & & & \\
 & & & M_2 & & & & & M_2 & & & & & & & & M_2 & & & & & \\
 & & & M_2 & & & & & M_2 & & & & & & & & M_2 & & & & & \\
 & & & M_2 & & & & & M_2 & & & & & & & & & & & & & \\
 & & & & & & & & M_2 & & & & & & & & & & & & &
\end{array} \tag{7.4}$$

Each of these types of copolymers offers different physical properties for a particular copolymer combination. It is interesting to note that block copolymers may be produced from one monomer only if the arrangement around the chiral carbon atom changes sequentially. These copolymers are called *stereoblock* copolymers.

7.1 KINETICS OF COPOLYMERIZATION

Because of a difference in the reactivity of monomers, expressed as reactivity ratios (r), the composition of the copolymer (n) may be different from that of the reactant mixture or feed (x). When x equals n, the product is said to be an *azeotropic copolymer*.

In the early 1930s, Nobel laureate Staundinger analyzed the product obtained from the copolymerization of equimolar quantities of VC and VAc. He found that the first product produced was high in VC, but as the composition of the reactant mixture changed because of a preferential depletion of VC, the product was becoming higher in VAc. This phenomenon is called the *composition drift*.

Wall studied the composition drift and derived what is now called the Wall equation, where n was equal to rx when the reactivity ratio r was equal to the ratio of the propagation rate constants. Thus, r was the slope of the line obtained when the ratio of monomers in the copolymer (M_1/M_2) was plotted against the ratio of monomers in the feed (m_1/m_2). The Wall equation is not general:

$$n = M_1/M_2 = r\ (m_1/m_2) = rx \tag{7.5}$$

The copolymer equation that is now accepted was developed in the late 1930s by a group of investigators including Wall, Dostal, Lewis, Alfrey, Simha, and Mayo. These workers considered the four possible extension reactions when monomers M_1 and M_2 were present in the feed. As shown below, two of these reactions are homopolymerizations or self-propagating steps (Equations 7.6 and 7.8), and the other two are heteropolymerizations or cross-propagating steps (Equations 7.7 and 7.9). The ratio of the propagating rate constants is expressed as *monomer reactivity ratios* (or simply reactivity ratios), where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. $M_1^\bullet$ and $M_2^\bullet$ are used as symbols for the macroradicals with $M_1^\bullet$ and $M_2^\bullet$ terminal groups, respectively.

Reaction	Rate constant	Rate expression	
$M_1^\bullet + M_1 \rightarrow M_1M_1^\bullet$	k_{11}	$r_{11} = k_{11}[M_1^\bullet][M_1]$	(7.6)
$M_1^\bullet + M_2 \rightarrow M_1M_2^\bullet$	k_{12}	$r_{12} = k_{12}[M_1^\bullet][M_2]$	(7.7)
$M_2^\bullet + M_2 \rightarrow M_2M_2^\bullet$	k_{22}	$r_{22} = k_{22}[M_2^\bullet][M_2]$	(7.8)
$M_2^\bullet + M_1 \rightarrow M_2M_1^\bullet$	k_{21}	$r_{21} = k_{21}[M_2^\bullet][M_1]$	(7.9)

Experimentally, it is found that the specific rate constants for the various reaction steps described above are essentially independent of chain length, with the rate of monomer addition primarily dependent only on the adding monomer unit and the growing end. Thus, the four reactions between two comonomers can be described using only these four equations.

As is the case with the other chain processes, determining the concentration of the active species is difficult so that expressions that do not contain the concentration of the active species are derived. The change in monomer concentration, i.e., the rate of addition of monomer to growing copolymer chains, is described as follows:

$$\text{Disappearance of } M_1\text{: } -d[M_1]/dt = k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1] \tag{7.10}$$

$$\text{Disappearance of } M_2\text{: } -d[M_2]/dt = k_{22}[M_2^\bullet][M_2] + k_{12}[M_1^\bullet][M_2] \tag{7.11}$$

Since it is experimentally observed that the number of growing chains remains approximately constant throughout the duration of most copolymerizations (i.e., a steady state in the number of growing chains), the concentrations of $M_1^{\bullet}$ and $M_2^{\bullet}$ are constant, and the rate of conversion of $M_1^{\bullet}$ to $M_2^{\bullet}$ is equal to the conversion of $M_2^{\bullet}$ to $M_1^{\bullet}$; i.e., $k_{12}[M_1^{\bullet}][M_2] = k_{21}[M_2^{\bullet}][M_1]$. Solving for $M_1^{\bullet}$ gives

$$[M_1^{\bullet}] = k_{21}[M_2^{\bullet}][M_1]/k_{12}[M_2] \tag{7.12}$$

The ratio of disappearance of monomers M_1/M_2 is described by Equation 7.13 from Equations 7.10 and 7.11. Remember that this is also the average composition of the growing chains and resulting polymer.

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^{\bullet}][M_1] + k_{21}[M_2^{\bullet}][M_1]}{k_{22}[M_2^{\bullet}][M_2] + k_{12}[M_1^{\bullet}][M_2]} = \frac{[M_1](k_{11}[M_1^{\bullet}] + k_{21}[M_2^{\bullet}])}{[M_2](k_{22}[M_2^{\bullet}] + k_{12}[M_1^{\bullet}])} \tag{7.13}$$

Substitution of $[M_1^{\bullet}]$ into Equation 7.13 gives

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left\{\frac{(k_{11}k_{21}[M_2^{\bullet}][M_1]/k_{21}[M_2]) + k_{21}[M_2^{\bullet}]}{(k_{12}k_{21}[M_2^{\bullet}][M_1]/k_{21}[M_2]) + k_{22}[M_2^{\bullet}]}\right\} \tag{7.14}$$

Division by k_{12} and cancellation of the appropriate ks give

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left\{\frac{(k_{11}[M_2^{\bullet}][M_1]/k_{12}[M_2]) + [M_2^{\bullet}]}{([M_2^{\bullet}][M_1]/[M_2]) + k_{22}[M_2^{\bullet}]/k_{21}}\right\} \tag{7.15}$$

Substitution of $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ and cancellation of $[M_2^{\bullet}]$ give

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}\left\{\frac{(r_1[M_1]/[M_2]) + 1}{([M_1]/[M_2]) + r_2}\right\} \tag{7.16}$$

Multiplication by $[M_2]$ gives what are generally referred to as the "copolymerization equations," Equations 7.17 and 7.19, which gives the copolymer composition without the need to know any free radical concentration, and which gives the composition of the growing polymer as a function of monomer feed (Equation 7.19).

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \tag{7.17}$$

Equation 7.17 is also presented in another form that allows greater ease of seeing the relationship between the monomer feed (x) and copolymer composition (n). This is achieved by the following steps:

Multiplying throughout by $[M_1]$ and $[M_2]$ gives

$$n = \frac{d[M_1]}{d[M_2]} = \frac{[M_1]r_1[M_1] + [M_1][M_2]}{[M_2][M_1] + [M_2]r_2[M_2]} \tag{7.18}$$

Division of both the numerator and denominator by $[M_1][M_2]$ gives the second form, Equation 7.19, of the copolymerization equation, but in terms of the composition of the feed (x) on the composition of the copolymer (n) as shown below:

$$n = \frac{d[M_1]}{d[M_2]} = \frac{r_1([M_1]/[M_2]) + 1}{r_2([M_2]/[M_1]) + 1} = \frac{r_1 x + 1}{r_2/x + 1} \tag{7.19}$$

The reactivity ratios are determined by an analysis of the change in the composition of the feed during the early stages of polymerization. Typical free radical chain copolymerization reactivity ratios are given in Table 7.1. The copolymer composition and type can be predicted by looking at the values of r_1 and r_2. If the value of r_1 is greater than 1, then M_1 tends to react with itself producing homopolymers, or block copolymers in M_1. When r_1 is greater than 1 and r_2 less than 1, then a copolymer is formed with blocks in M_1 (A).

AAAAAABAAAAAAABAAAAAABAAAAAAABAAAAAAAABABAAAAAAA (7.20)

If both r_1 and r_2 are greater than 1, then a copolymer is formed with blocks of M_1 (A) and blocks of M_2 (B).

AAAAAABBBBBAAAAAABBBBBBBAAAAAABBBBBBAAAAABBBAAAA (7.21)

TABLE 7.1
Typical Free Radical Chain Copolymerization Reactivity Ratios at 60°C

M_1	M_2	r_1	r_2	r_1r_2
Acrylamide	Acrylic acid	1.38	0.36	0.5
	Methyl acrylate	1.30	0.05	0.07
	Vinylidene chloride	4.9	0.15	0.74
Acrylic acid	Acrylonitrile (50°C)[a]	1.15	0.35	0.40
	Styrene	0.25	0.50	0.04
	Vinyl acetate (70°C)	2	0.1	0.2
Acrylonitrile	Butadiene	0.25	0.33	0.08
	Ethyl acetate (50°C)	1.17	0.67	0.78
	Maleic anhydride	6	0	0
	Methyl methacrylate	0.13	1.16	0.15
	Styrene	0.04	0.41	0.16
	Vinyl acetate	4	0.06	0.24
	Vinyl chloride	3.3	0.02	0.07
Butadiene	Methyl methacrylate	0.70	0.32	0.22
	Styrene	1.4	0.78	1.1
Isoprene	Styrene	2	0.44	0.88
Maleic anhydride	Methyl acrylate	0	2.5	0
	Methyl methacrylate	0.03	3.5	0.11
	Styrene	0	0.02	0
	Vinyl acetate (70°C)	0.003	0.055	0.0002
Methyl acrylate	Acrylonitrile	0.67	1.3	0.84
	Styrene	0.18	0.75	0.14
	Vinyl acetate	9.0	0.10	0.90
	Vinyl chloride	5	0	0
Methyl methacrylate	Styrene	0.50	0.50	0.25
	Vinyl acetate	20	0.015	0.3
	Vinyl chloride	12.5	0	0
Styrene	p-Chlorostyrene	0.74	1.03	0.76
	p-Methoxystyrene	1.2	0.82	0.95
	Vinyl acetate	55	0.01	0.55
	Vinyl chloride	17	0.02	0.34
	2-Vinylpyridine	0.56	0.9	0.50
Vinyl acetate	Vinyl chloride	0.23	1.7	0.39
	Vinyl laurate	1.4	0.7	0.98
Vinyl chloride	Dimethyl maleate	0.77	0.009	0.007

Source: From Brandrup and Immergut, 1975.

[a] Temperatures other than 60°C are shown in parentheses.

The length of each block will be of some statistical average with the statistical length dependent on how large the reactivity ratios are. In general, the larger the value of the reactivity ratio the larger the block will be.

Preference for reaction with the unlike monomer occurs when r_1 is less than 1. When r_1 and r_2 are approximately equal to 1, the conditions are said to be ideal, with a random (not alternating) copolymer produced, in accordance with the Wall equation. Thus, a random copolymer (ideal copolymer) would be produced when chlorotrifluoroethylene is copolymerized with tetrafluoroethylene (Table 7.1).

When r_1 and r_2 are both approximately zero, as in the case with the copolymerization of maleic anhydride and styrene, an alternating copolymer is produced (Equation 7.22). In general, there will be a tendency towards alternation when the product r_1r_2 approaches zero.

$$\text{ABABABABABABABABABABABABABABABABABABA} \tag{7.22}$$

In contrast, as noted above if the values of r_1 and r_2 are similar and the product r_1r_2 approaches 1, tendency will be to produce random copolymers.

$$\text{ABABBABAABABBAABABBBABAABAABBAABABBAABABBABAAABABBA} \tag{7.23}$$

In batch reactions, where the yield is high and no additional monomer is added, at the end of the reaction the average content of each monomer unit in the total copolymer formed will necessarily be directly related to the initial ratio of the two monomers. Thus, the copolymer content will vary depending on when the particular chains are formed but the final overall product will have an average of units in it reflective of the initial monomer concentrations.

The values for r_1 and r_2 are used to help guide the ratio of reactants necessary to achieve a specific copolymer composition. When a desired copolymer composition is required and either reactivity ratio is unlike and not near zero, continuous flow processes or batch process where monomer is continuously added, are employed. Considering the reaction between VAc and VC, r_1 is 0.23 meaning growing chains with VAc radicals at their ends have a greater tendency to react with a VC monomer than a VAc monomer. The value for r_2 is 1.68 meaning that there is a tendency for growing chains with VC radical ends to add to VC monomer rather than VAc monomer. Thus, given both monomers present in equal molar amounts, the polymer formed first will be rich in VC-derived units. As the amount of VC is depleted, the copolymer chains formed will have greater amounts of VAc, until all of the VC is almost used up and chains with almost only VAc units are formed. If a copolymer composition that favors a copolymer rich in VC is desired, then the concentration of VC will have to be maintained sufficient to give copolymers that have high VC-derived unit content. This is done by simply adding VC as the reaction proceeds.

The resonance stability of the macroradical is an important factor in polymer propagation. Thus, for free radical polymerization, a conjugated monomer such as styrene is at least 30 times as apt to form a resonance-stabilized macroradical as VAc, resulting in a copolymer rich in styrene-derived units when these two are copolymerized.

Strongly electrophilic or nucleophilic monomers will polymerize exclusively by anionic or cationic mechanisms. However, monomers that are neither strongly electrophilic nor nucleophilic generally polymerize by ionic and free radical processes. The contrast between anionic, cationic, and free radical methods of addition copolymerization is clearly illustrated by the results of copolymerization utilizing the three modes of initiation (Figure 7.1). Such results illustrate the variations of reactivities and copolymer composition that are possible from employing the different initiation modes. The free radical "tie-line" resides near the middle since free radical polymerizations are less dependent on the electronic nature of the comonomers relative to the ionic modes of chain propagation.

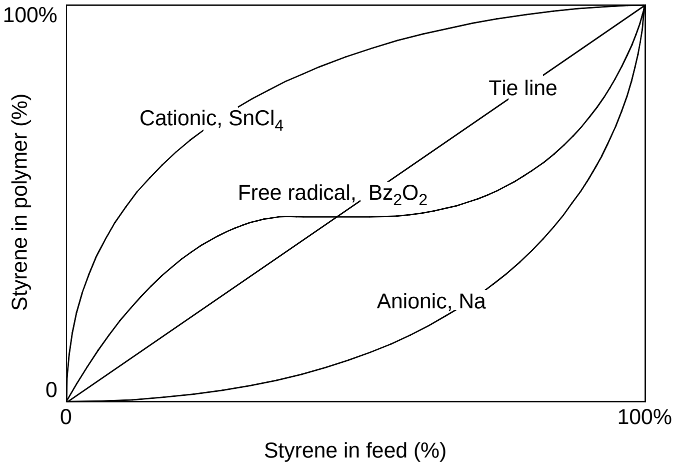


FIGURE 7.1 Instantaneous copolymer composition as a function of monomer composition and initiator employed for the comonomer system of styrene and methyl methacrylate using different modes of initiation. (Adapted from Landler, Y., *Comptes Rendus*, 230, 539, 1950. With permission.)

As noted earlier, copolymerization can be controlled by regulating the monomer feed in accordance with, for example, Equations 7.17 and 7.19.

7.2 THE *Q–e* SCHEME

A useful scheme for predicting r_1 and r_2 values for free radical copolymerizations was developed by Alfrey and Price in 1947. The Alfrey–Price *Q–e* scheme is similar to the Hammett equation approach, except that it is not primarily limited to substituted aromatic compounds. In the semiempirical *Q–e* scheme, the reactivities or resonance effects of the monomers and macroradicals are evaluated empirically by *Q* and *P* values. The polar properties of both monomers and macroradicals are designated by arbitrary "*e*" values. Thus, as shown in Table 7.2, Q_1 and Q_2 are related to reactivity, and e_1 and e_2 are related to the polarity of monomers M_1 and M_2, respectively. Styrene is assigned the *Q* value of 1 and an *e* value of −0.80. Higher *Q* values indicate greater resonance stability or reactivity, and higher *e* values (less negative) indicate greater electron-withdrawing power of the α-substituents on the vinyl monomer (in comparison to the phenyl substituent in styrene).

The *Q–e* scheme neglects steric factors, but it is a useful guide when data for r_1 and r_2 are not available. Following is an approach that relates the reactivity ratios to the Alfrey–Price *e* values:

$$k_{11} = P_1 Q_1 e^{-e_1^2} \tag{7.24}$$

$$k_{12} = P_1 Q_2 e^{-e_1 e_2} \tag{7.25}$$

and

$$r_1 = k_{11}/k_{12} = [Q_1/Q_2] e^{-e_1(e_1 - e_2)} \tag{7.25}$$

Similarly,

$$k_{22} = P_2 Q_2 e^{-e_2^2} \tag{7.26}$$

$$k_{21} = P_2 Q_1 e^{-e_1 e_2} \tag{7.27}$$

TABLE 7.2
Typical *Q* and *e* Values for Monomers

Monomer	*Q*	*e*
Benzyl methacrylate	3.64	0.36
Methacrylic acid	2.34	0.65
2-Fluoro-1,3-butadiene	2.08	−0.43
p-Cyanostyrene	1.86	−0.21
p-Nitrostyrene	1.63	0.39
2,5-Dichlorostyrene	1.60	0.09
Methacrylamide	1.46	2.24
p-Methoxystyrene	1.36	−1.11
2-Vinylpyridine	1.30	−0.50
p-Methylstyrene	1.27	−0.98
Methacrylonitrile	1.12	0.81
p-Bromostyrene	1.04	−0.32
Styrene	1.00	−0.80
m-Methylstyrene	0.91	−0.72
Methyl methacrylate	0.74	0.40
Acrylonitrile	0.60	1.20
Methyl acrylate	0.42	0.60
Vinylidene chloride	0.23	0.36
Vinyl chloride	0.044	0.20
Vinyl acetate	0.026	−0.22

and

$$r_2 = k_{22}/k_{21} = [Q_2/Q_1]e^{-e_2(e_2-e_1)} \tag{7.28}$$

Therefore,

$$r_1r_2 = e^{-(e_1-e_2)^2} \text{or } r_1r_2 = \exp\left[-(e_1-e_2)^2\right] \tag{7.29}$$

It is important that while the reactivity is related to resonance stability of the macroradical $M_1^{\bullet}$, the composition of the copolymer is related to the relative polarity of the two monomers M_1 and M_2.

7.3 COMMERCIAL COPOLYMERS

One of the first commercial copolymers, introduced in 1928, was made of VC (87%) and VAc (13%) (vinylite). As the presence of the VAc mers disrupted the regular structure of PVC, the copolymer was more flexible and more soluble than PVC itself.

Copolymers of VC and vinylidene chloride were introduced in the 1930s. The copolymer with very high VC content is used as a plastic film (Pliovic), and the copolymer with high vinylidene chloride content is used as a film and filament (Saran).

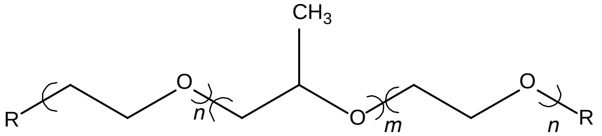
Polybutadiene, produced in emulsion polymerization, is not useful as an elastomer. However, the copolymers with styrene (SBR) and acrylonitrile (Buna-N) are widely used as elastomers.

EPMs, polyethylene-co-propylene, show good resistance to ozone, heat, and oxygen and are used in blends to make today's external automotive panels. Two general types of EPMs are commercially available. EPMs are saturated and require vulcanization if used as a rubber. They are used in a variety of automotive applications including as body and chassis parts, bumpers, radiator and heater hoses, seals, mats, and weather strips. EPMs are produced using ZNCs.

The second type of EPM is the EPDM, which is made by polymerizing ethylene, propylene, and a small amount (3–10 mol%) of nonconjugated diolefine employing ZNCs. The side chains allow vulcanization with sulfur. They are employed in the production of appliance parts, wire and cable insulation, coated fabrics, gaskets, hoses, seals, and high-impact PP.

7.4 BLOCK COPOLYMERS

Although block copolymers do not occur naturally, synthetic block copolymers have been prepared by all known classical polymerization techniques. The first commercial block copolymer was a surfactant (Pluronics) prepared by the addition of propylene oxide to polycarbanions of ethylene oxide. While neither water-soluble PEO nor water-insoluble poly(propylene oxide) exhibits surface activity, the ABA block copolymer consisting of hydrophilic and lyophilic segments, is an excellent surfactant. Each block has 20 plus repeat units of that variety.

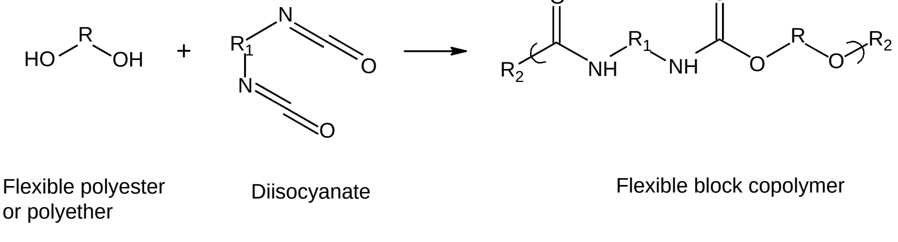


(7.30)

The ethylene oxide block is hydrophilic, whereas the propylene oxide block is (relatively) hydrophobic. The copolymer forms micelles in aqueous solutions with the hydrophilic portions pointing outward, interacting with the water, while the hydrophobic portions form the inner core, shielded from the water by the ethylene oxide-derived block. A micelle is also formed in organic liquids, but here the hydrophobic propylene oxide block "faces" outward, whereas the ethylene oxide block acts as the inner core.

Polymers that contain two reactive end groups are referred to as *telechelic polymers*. Joseph Shivers, a DuPont chemist, invented Spandex in 1959 after about a 10-year search. It was first named Fiber K, but DuPont chose the more appealing, smooth-sounding trade name of Lycra.

Elastomeric PU fibers consisting of at least 85% segmented PU are commercially available under the name Spandex. They are block copolymers and are among the first products specifically designed using the concept of soft and hard segments. The soft or flexible segment is composed of PEO chains that contain two hydroxyl end groups (one at each end of the PEO chain). The hard or stiff segment is derived from the reaction of the diisocyanate with the hydroxyl end groups forming polar urethane linkages that connect the PEO polymer segments through the urethane linkages. Such products are often referred to as segmented PU fibers. These products have found wide use in cloths, including bras. Similar products have also been formed using hydroxyl-terminated PE in place of the PEO.

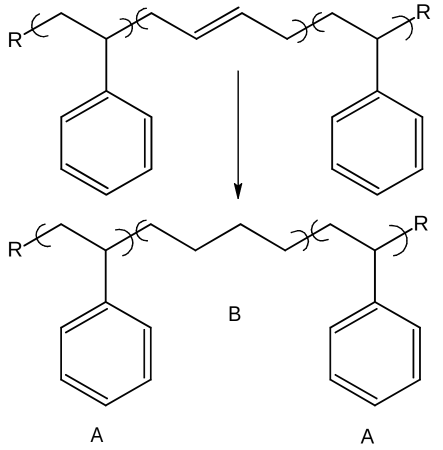


(7.31)

A related product is formed from the analogous reaction using hydroxyl-terminated PEO with aromatic diacids to form a segmented aromatic polyester block copolymer that is sold under the trade name Hytrel.

PEO is made from ethylene oxide through a base-catalyzed ROP. While the major use of PEO is in the manufacture of PU products, including foams, it can be synthesized giving viscous liquids to solids depending on the molecular weight. It is used as surfactants, functional fluids, thickeners, lubricants, and as plasticizers. Further, the circuit boards that hold the electronic components of computers are made from PEO.

The most widely used chain reaction block copolymers are those prepared by the addition of a new monomer to a macroanion. AB and ABA block copolymers called Soprene and Kraton, respectively, are produced by the addition of butadiene to styryl macroanions or macrocarbanions (Equation 7.32). This copolymer is normally hydrogenated (Equation 7.33).



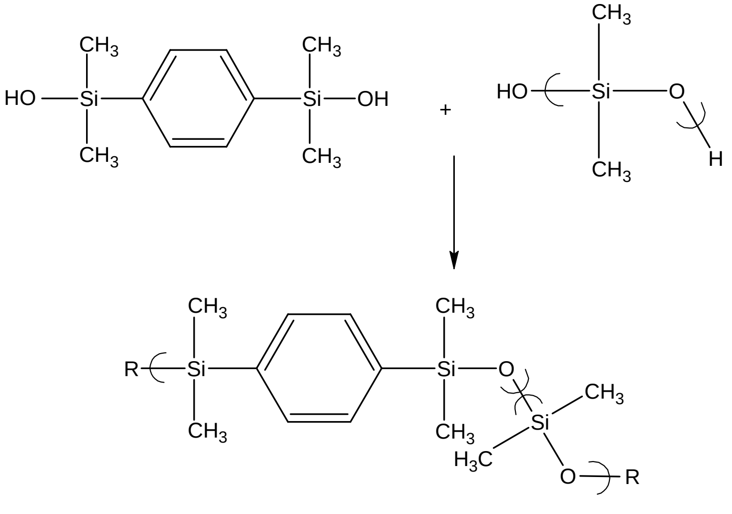
(7.32)

(7.33)

Today, new copolymers are making use of the hard–soft block strategy where the hard segment is a block portion as PE that readily crystallizes forming a physical cross-link. The soft segment consists of blocks formed from alpha-olefins, such as 1-butene, 1-hexene, and 1-octane, where the substituted alkane-arm discourages crystallization.

A number of siloxane ABA block polymers have been formed. Copolymers of dimethylsiloxane (A)-diphenylsiloxane (B)-dimethylsiloxane (A) have been synthesized by the sequential polymerization of reactants. The diphenylsiloxane block acts as a hard block and the more flexible dimethylsiloxane blocks act as soft blocks.

Hard segments have also been introduced using p-bis(dimethylhydroxysilyl)benzene with the soft block again being dimethylsiloxane.



(7.34)

Block copolymers, with segments or domains of random length, have been produced by the mechanical or ultrasonic degradation of a mixture of two or more polymers, such as hevea rubber and PMMA (Heveaplus).

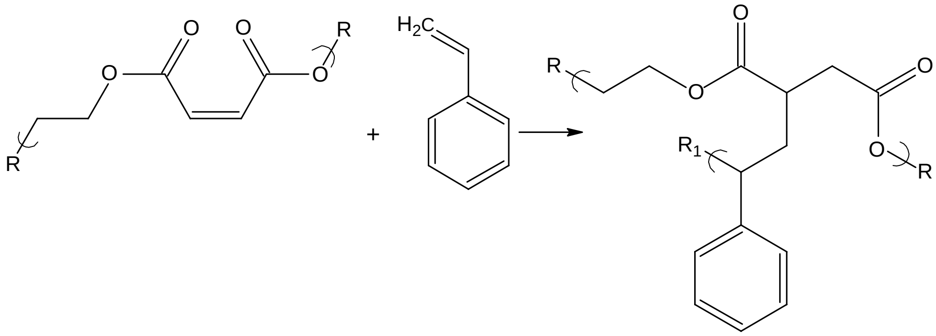
Thus, there have been prepared a number of different block copolymers including a number that utilize the hard–soft strategy.

7.5 GRAFT COPOLYMERS

The major difference between block and graft copolymers is the position of the second kind of unit. Thus, information that applies to block copolymers can often be applied to graft copolymers. So, domains where physical cross-linking occurs via crystallization can occur in either block components or within graft copolymers where the necessary symmetry occurs.

Graft copolymers of nylon, protein, cellulose, starch, copolymers, or vinyl alcohol have been prepared by the reaction of ethylene oxide with these polymers. Graft copolymers are also produced when styrene is polymerized by Lewis acids in the presence of poly-*p*-methoxystyrene. The Merrifield synthesis of polypeptides is also based on graft copolymers formed from chloromethaylated PS. Thus, the variety of graft copolymers is great.

The most widely used graft copolymer is the styrene–unsaturated polyester copolymer (Equation 7.35). This copolymer, which is usually reinforced by fibrous glass, is prepared by the free radical chain polymerization of a styrene solution of unsaturated polyester.



(7.35)

The graft copolymers of acrylamide, acrylic acid, and cellulose or starch are used as water absorbents and in enhanced oil recovery systems.

7.6 ELASTOMERS

Elastomers typically contain chemical and/or physical cross-links. Although there are thermoplastic elastomers (TPEs), such as SBS and block copolymers, most elastomers are thermosets. Elastomers are characterized by a disorganized (high-entropy) structure in the resting or nonstressed state. Application of stress is accompanied by a ready distortion requiring (relative to plastics and fibers) little stress to effect the distortion. This distortion brings about an alignment of the chains forming a structure with greater order. The driving force for such a material to return to its original shape is largely a return to the original less organized state. While entropy is the primary driving force for elastomers to return to the original resting state, the cross-links allow the material to return to its original shape giving the materials a type of memory. Materials that allow easy distortion generally have minimal interactions between the same or different chains. This qualification is fulfilled by materials that do not bond through the use of dipolar (or polar) or hydrogen bonding. Thus, the intermolecular and intramolecular forces of attraction are small relative to those present in fibers and plastics. Hydrocarbon-intense polymers are examples of materials that meet this qualification. Production generally requires the initial production of linear polymers, followed by the insertion of cross-links through a process called vulcanization or curing. Addition of fillers and other additives such as carbon black is also typical. Table 7.3 contains a listing of important elastomers.

The introduction of cross-links to inhibit chain slippage was discovered by Goodyear in 1839. He accomplished this through the addition of sulfur to NR. Shortly after this, an accelerator, zinc (II) oxide, was used to speed up the process. Other additives were discovered often through observation and trial-and-error so that today's elastomers have a number of important additives that allow them to perform demanding tasks.

TABLE 7.3
Common Elastomers and Their Uses

Common Name (Chemical Composition)	Abbreviation	Uses and Properties
Acrylonitrile–butadiene–styrene (terpolymer)	ABS	Oil hoses, fuel tanks, gaskets, pipe and fittings, appliance and automotive housings. Good resistance to oils and gas
Butadiene rubber	BR	Tire tread, hose, belts. Very low hysteresis; high rebound
Butyl rubber (from isobutene and 0.5%–3% isoprene)	IIR	Innertubes, cable sheathing, tank liners, roofing, Seals, coated fabrics. Very low rebound; high hysteresis
Chloroprene rubber (polychloroprene)	CR	Wire and cable insulation, hose footwear, mechanical automotive products. Good resistance to oil and fire, good weatherability
Epichlorohydrin (epoxy copolymers)		Seals, gaskets, wire, and cable insulation. Good resistance to chemicals
Ethylene–propylene rubbers (random copolymers with 60%–80% ethylene insulative properties)	EP or EPM	Cable insulation, window strips. Outstanding
Ethylene–propylene–diene (random terpolymers)	EPDM	Good resistance to weathering, resistant to ozone Attack
Fluoroelastomers (fluorine-containing copolymers)		Wire and cable insulation, aerospace applications
		Outstanding resistance to continuous exposure to high temperatures, chemicals, and fluids
Ionomers (largely copolymers of ethylene and acid-containing monomers with metal ions)		Golf ball covers, shoe soles, weather stripping
		Tough, flame-resistant, good clarity, good electrical properties, abrasion-resistant
Natural rubber (polyisoprene)	NR	General-purpose tires, bushings, and couplings, seals, footwear, belting. Good resilience
Nitrile rubber (random copolymer of butadiene and acrylonitrile)	NBR	Seals, automotive parts that are in contact with oils and gas, footwear, hose. Outstanding resistance to oils and gas, little swelling in organic liquids
Polysulfide		Adhesive, sealants, hose binders. Outstanding resistance to oil and organic solvents
Polyurethanes	PU	Sealing and joining, printing rollers, fibers, industrial tires, footwear, wire and cable coverings
Silicones (generally polydimethylsiloxane)		Medical applications, flexible molds, gaskets, seals. Extreme use temperature range
Styrene–butadiene rubber (random copolymer)	SBR	Tire tread, footwear, wire and cable covering, adhesives. High hysteresis

Around 1915, Mote found that a superior abrasion-resistant elastomer was produced through the use of carbon black. Today, it is recognized that factors such as surface area, structure, and aggregate size are important features in the production of superior elastomers. For instance, high surface areas (small particle size) increase the reinforcement and consequently the tensile strength and improve the resistance to tearing and abrasion. Large aggregates give elastomers that have improved strength before curing, high modulus, and an improved extrusion behavior.

Rubbers typically have low hysteresis. *Hysteresis* is a measure of the energy absorbed when the elastomer is deformed. A rubber that absorbs a great amount of energy as it is deformed (such as a tire hitting bumps on the roadway) is said to have a high hysteresis. The absorbed energy is equivalent to the reciprocal of resilience such that a material with a low hysteresis has a high resilience. Rubbers with a particularly high hysteresis are used where heat buildup is desirable such as in tires to give the tread a better grip on the road and the tire a smoother ride. Thus, tires with high hysteresis are often preferred in drag-race tires where heat buildup allows better grip of the track.

Typical thermosetting elastomers are difficult to recycle because cross-linking prevents them from being easily solubilized and reformed through application of pressure and heat. Recycling can be accomplished through the particalizing (grinding into small particles) of the elastomeric material followed by a softening-up by application of a suitable liquid and/or heat, and finally addition of a binder that physically or chemically allows the particles to bind together in the desired shape.

7.7 THERMOPLASTIC ELASTOMERS

A number of TPEs have been developed since the mid-1960s. The initial TPEs were derived from plasticized PVC and are called plastisols. *Plastisols* are formed from the fusing together of PVC with a compatible plasticizer through heating. The plasticizer acts to lower the T_g to below room temperature (RT). Conceptually, this can be thought of as the plasticizer acting to put additional distance between the PVC chains thus lowering the inter- and intrachain forces, as well as helping solubilize chain segments. The resulting materials are used in a number of areas including construction of boot soles.

The hard–soft segment scenario is utilized in the formation of a number of industrially important TPEs. Representative examples of such TPEs based on block copolymers are given in Table 7.4. TPEs contain two or more distinct phases and their properties depend on these phases being intimately mixed and small. These phases may be chemically or physically connected. For the material to be a TPE at least one phase must be soft or flexible under the operating conditions and at least one phase must be hard in the hard phase(s) becoming soft (or fluid) at higher temperatures. Often the hard segments or phases are crystalline thermoplastics, while the soft segments or phases are amorphous. In continuous chains containing blocks of hard and soft segments the molecular arrangement normally contains crystalline regions where there is sufficient length in the hard segment to form the crystalline regions or phases where the soft segments form amorphous regions.

Such hard–soft scenarios can also be achieved through employing grafts (Table 7.5) where the pendant group typically acts as the hard segment with the backbone acting as the soft segment. Equation 7.36 is a representation of a typical graft copolymer chain. In order for an effective network to be formed each "A" chain needs to have at least two "B" grafts to allow for formation of a continuous interlinked network. Although much research has been done with such graft materials they have not yet become very important commercially.

TABLE 7.4
Thermoplastic Elastomeric Block Copolymers

Hard Segment	Soft or Elastomeric Segment	General Type(s)
Polystyrene	Butadiene and polyisoprene[a]	Triblock, branched
Polystyrene	Poly(ethylene-co-butylene)[b]	Triblock
Polystyrene	Polyisobutylene	Triblock, branched
Poly(alpha-methylstyrene)	Polybutadiene	Triblock
Poly(alpha-methylstyrene)	Polyisoprene	Triblock
Poly(alpha-methylstyrene)	Poly(propylene sulfide)	Triblock
Polystyrene	Polydimethylsiloxane	Triblock, multiblock
i-Polypropylene	Poly(alpha-olefins)	Mixed
i-Propylene	a-Polypropylene	Mixed
Polyethylene	Poly(alpha-olefins)[c]	Multiblock
Polyethylene	Poly(ethylene-co-butylene)	Triblock
Polyethylene	Poly(ethylene-co-propylene)	Triblock
Polyurethane	Polydiacetylenes	Multiblock
Polyurethane	Polyester or Polyether[d]	Multiblock
Poly(methyl methacrylate)	Poly(alkyl acrylates)	Triblock, branched
Polysulfone	Polydimethylsiloxane	Multiblock
Polyetherimide	Polydimethylsiloxane	Multiblock
Polycarbonate	Polyether	Multiblock
Polycarbonate	Polydimethylsiloxane	Multiblock
Polyamide	Polyester or Polyether[e]	Multiblock
Polyester	Polyether[f]	Multiblock

Sample trade names of block copolymers:

[a] Kraton D, Cariflex TR, Taipol, Vector, Tufprene, Asaprene, Calprene, Europrene Sol T, Stearon, Flexprene, Quintac, Finaprene, Coperbo, Solprene, Stearon, and K-Resin. These products may be branched or linear with varying contents of the various components.

[b] Elexar, C-Flex, Tekron, Hercuprene, Kraton G, Septon, Dynaflex, and Multi-Flex.

[c] Flexomer, Exact, Affinity, and Engage.

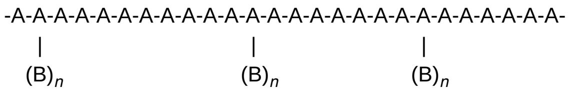
[d] Texin, Desmopan, Estane, Morthane, Elastollan, and Pellethane.

[e] Montac, Pebax, Orevac, Vestamide, Grilamid, and Grilon.

[f] Arnitel, Hytrel, Ecdel, Lomod, Riteflex, and Urafil.

TABLE 7.5
Thermoplastic Elastomers Based on Graft Copolymers

Hard Pendant Segment	Soft Backbone
Polystyrene	Poly(butyl acrylate)
Polystyrene	Poly(ethyl-co-butyl acrylate)
Poly(4-chlorostyrene)	Polyisobutylene
Polystyrene and poly(alpha-methylstyrene)	Polybutadiene
Polystyrene and poly(alpha-methylstyrene)	Polyisobutylene
Polystyrene and poly(alpha-methylstyrene)	Poly(ethylene-co-propylene)
Poly(methyl methacrylate)	Poly(butyl acrylate)
Polyindene	Polyisobutylene
Polyindene	Poly(ethylene-co-propylene)
Polyindene	Polybutadiene
Polyacenapthylene	Polyisobutylene



$$\begin{array}{l}\text{-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-}\\ \quad | \qquad\qquad\qquad\qquad | \qquad\qquad\quad | \\ \quad (B)_n \qquad\qquad\qquad (B)_n \qquad\qquad (B)_n\end{array} \qquad (7.36)$$

TPEs can also be achieved through physical mixing of hard and soft segments (Table 7.6). These are fine dispersions of a hard thermoplastic polymer and an elastomer. The two materials generally form interdispersed co-continuous phases. Often the physical combining is achieved through intense mechanical mixing but in some cases, such as with PP and EPMs the effect of blending is achieved through polymerizing the finely dispersed elastomer phase (EPM) phase simultaneously with the hard PP.

At times, the phases are cross-linked during mechanical mixing. This process is referred to as "dynamic vulcanization" and produces a finely dispersed discontinuous cross-linked elastomer phase. The products are referred to as thermoplastic vulcanizates or dynamic vulcanizates. The products of this process have an insoluble elastomer phase giving the material greater oil and solvent resistance. The cross-linking also reduces or eliminates the flow of this phase at high temperatures and/or under high stress. This gives the material better resistance to compression set.

SBS block copolymers differ structurally from the random copolymer of styrene and butadiene (SBR). Because styrene and butadiene blocks are incompatible, they form separate phases joined at the junctions where the various blocks are connected. This gives an elastomeric material where the butadiene blocks form the soft segments and the styrene blocks form hard blocks.

The block copolymer made from connecting blocks of PS with blocks of polybutadiene illustrates another use of soft and rigid or hard domains in TPEs. The PS blocks give rigidity to the polymer, while the polybutadiene blocks act as the soft or flexible portion. The PS

TABLE 7.6
Thermoplastic Elastomers Based on Hard–Soft Combinations

Hard Polymer	Soft or Elastomeric	Polymer Structure
Polypropylene	Ethylene–propylene copolymer[a]	Blend
Polypropylene	Natural rubber[b]	Dynamic vulcanizate
Polypropylene	Ethylene–propylene–diene monomer[c]	Dynamic vulcanizate
Polypropylene	Butyl rubber[d]	Dynamic vulcanizate
Polypropylene	Nitrile rubber[e]	Dynamic vulcanizate
Polypropylene	Poly(propylene-co-1-hexene)	Blend
Polypropylene	Poly(ethylene-co-vinyl acetate)	Blend
Polypropylene	Styrene–ethylene–butylene–styrene + oil	Blend
Polystyrene	Styrene–butadiene–styrene + oil	Blend
Nylon	Nitrile rubber	Dynamic vulcanizate
Poly(vinyl chloride)	Nitrile rubber + diluent[f]	Blend, dynamic vulcanizate
Chlorinated polyolefin	Ethylene interpolymer[g]	Blend

Sample tradenames

[a,c] Flexothene, Ferroflex, Hifax, Polytrope, Ren-Flex, Telcar.

[b] Geolast.

[c] Hifax MXL, Santoprene, Sarlink 3000 and 4000, Uniprene.

[d] Sarlink 2000, Trefsin.

[e] Geolast, Vyram.

[f] Apex N, Chemigum, Sarlink 1000.

[g] Alcryn.

portions also form semicrystalline domains that add to the strength of the copolymer and these domains also act as "physical cross-links" allowing the soft portions to respond in an "elastomeric" manner, while the semicrystalline domains give the material the "elastomeric" memory. The polybutadiene blocks act as the continuous phase, whereas the PS blocks act as the discontinuous phase. Heating the material above the T_m of the PS domains allows whole chain mobility allowing processability of the virgin material and subsequent reprocessability of used material. Upon cooling, the rigid domains reform. Block PS–polybutadiene copolymers are used in the soles of many of the athletic shoes.

Worldwide sales of TPEs are on the order of 1.5 million tons with a value of about $5 billion.

7.8 BLENDS

There is an ongoing search for new materials and materials that exhibit needed properties. Blends are one of the major avenues of achieving these new materials without actually synthesizing new polymers. *Polymer blends* are physical mixtures of two or more polymers though sometimes the various phases are chemically bonded together. These blended mixtures may offer distinct properties, one set of properties related to one member of the blend, and another set of properties related to the second member of the blend. The blended mixtures may also offer some averaging of properties. The property mix of polymeric blends is dependent on a number of factors, one of the major being the miscibility of the polymers in one another. This miscibility is in turn dependent on the nature of the polymers composing the blend and the amount of each component in the blend. Here polymer blends will be divided into miscible and immiscible polymer blends.

Extent of mixing is related to time since mixing requires sufficient time to allow the polymer chains to mix. Thus, for miscible blends particular structures can be "frozen-in" by rapid cooling when the desired mixing is achieved. Here, micelles of particular structures can cause the mixture to perform in one manner governed by the particular grouping that may not occur if more total mixing occurs.

Miscibility or immiscibility can be described in simple thermodynamic terms as follows, at constant temperature. Mixing occurs if the free energy of mixing is negative.

$$\Delta G_{\text{mixing}} = \Delta H_{\text{mixing}} - T\Delta S_{\text{mixing}} \tag{7.37}$$

Mixing is exactly analogous with polymer solubility. The driving force for mixing and solubility is the entropy or random-related term. The entropy-related term must overcome the opposing enthalpy energy term. In a more complete treatment, temperature and volume fraction must be considered.

7.8.1 IMMISCIBLE BLENDS

Immiscible combinations are all around us. Oil and water is an immiscible combination; as is the lava in the so-called lava lamps; and chicken broth in chicken soup. *Immiscible blends* are actually a misnaming at the molecular level since they are not truly mixed together. But at the macrolevel they appear mixed, so the name immiscible blends.

Immiscible blends are said to be phase separated, i.e., there are different phases mixed together. Both phases are solid in behavior.

Because PS is brittle with little impact resistance under normal operating conditions, early work was done to impart impact resistance. The best known material from this work is called HIPS, which is produced by dispersing small particles of BR in with the styrene monomer. Bulk or mass polymerization of the styrene is begun producing what is referred to as prepolymerization material. During the prepolymerization stage, styrene begins to polymerize with itself forming droplets of PS with phase separation. When nearly equal phase volumes of polybutadiene rubber particles and PS are obtained, phase inversion occurs and the droplets of PS act as the continuous phase within which the BR particles are dispersed. The completion of polymerization generally occurs employing either bulk or aqueous suspension conditions.

Most HIPS has about 4%–12% polybutadiene in it so that HIPS is mainly a PS-intense material. The polymerization process is unusual in that both a matrix composition of PS and polybutadienes is formed, as well as a graft between the growing PS onto the polybutadiene being formed. Grafting provides the needed compatibility between the matrix phase and the rubber phase. Grafting is also important in determining the structure and size of rubber particles that are formed. The grafting reaction occurs primarily by hydrogen abstraction from the polybutadiene backbone either by growing PS chains or alkoxy radicals if peroxide initiators are employed.

HIPS is an immiscible blend that is used in many applications and was employed as material for many of the automotive bumpers. The PS portion is strong and inflexible, whereas the polybutadiene particles are flexible allowing an impact to be distributed over a larger area. The polybutadiene rubbery portion allows the bumper to bend and indent and protects the PS from fracturing while the PS phase resists further deformation. This combination gives a strong flexible material.

In general, the morphology on a molecular level varies with the fraction of each component in the mixture. In general terms, we can talk about a continuous and discontinuous phase. For a combination of polymers A and B, such as PS and polybutadiene, at low amounts of A, polymer A will typically act as a discontinuous phase surrounded by B. Thus, at low amounts of PS, the PS congregates as small particles in a "sea" or continuous phase of B, the polybutadiene. As the fraction of polymer A increases, the spheres eventually become so large as to join together forming a continuous phase, and so two continuous phases are present. As the fraction of A continues to increase, polymer B becomes the discontinuous phase, being surrounded by the continuous phase, polymer A.

The discontinuous phase generally takes the rough shape of a sphere to minimize surface area exposure to the other phase. The size of the spheres influences the overall properties and varies with concentration. In general, because of the affinity of like polymer chains, spheres tend to grow. Larger sphere sizes are promoted because they give less relative contact area with the other phase.

As noted, immiscible blends can exhibit different properties. If the domains are of sufficient size, they may exhibit their own T_g and T_m values. Many commercially used immiscible blends have two separate T_g and/or T_m values.

Blends can also offer variable physical properties as already noted for HIPS. Consider a blend of polymer PS and butadiene where butadiene is the major component. PS is the stronger material with the blend weaker than PS itself. In some cases, the blend can be stronger than the individual polymers. Heat and pressure can result in the change of the discontinuous phase becoming flattened out when pressed against a mold. The spheres can also be caused to elongate forming rodlike structures with the resulting structure similar to composites where the rodlike structures strengthen the overall structure.

The strength can also be increased by using about the same amounts of the two polymers so that they form two continuous phases. Here, both phases can assist the blend to be strong. Another approach is to use compatibilizers. *Compatibilizers* are materials that help bind together the phases allowing stress or strain to be shared between the two phases. Many compatibilizers are block copolymers where one block is derived from polymers of one phase and the second block is composed of units derived from polymers of the second phase. The two blocks get "locked" into the structures of the like phases and thus serve to connect the two phases.

Graft copolymers are also used as compatibilizers to tie together different phases. HIPS contains PS grafted onto polybutadiene backbones. This allows stress or strain to be transferred from the PS to the polybutadiene phase transferring energy that might break the brittle PS to the more flexible polybutadiene phase. That is why HIPS is stronger than PS itself.

Compatibilizers also act to modify the tendency to form large spheres. The formation of large spheres is a result of the two polymer components trying to segregate. The compatibilizer causes the two phases to come together minimizing the tendency to form large spheres. For instance, for a mixture of 20:80 PS:polybutadiene the sphere size is about $5-10\ \mu m$, whereas addition of about 9% PS–PE (PE is enough like polybutadiene to be incorporated into the polybutadiene phases) block copolymer results in PS spheres of about $1\ \mu m$. This increases the interface between the two phases resulting in better mechanical properties because stress or strain can be more effectively transferred from one phase to the other.

7.8.2 MISCIBLE BLENDS

Miscible blends are not as easy to achieve as immiscible blends. As noted above, entropy is the major driving force in causing materials to mix. Because polymer chains are already in a state of relatively high order, increases in randomness are not easily achieved so that immiscible blends are often more easily formed. To make matters worse, for amorphous polymers the amount of disorder in the unmixed polymer is often higher than for blends that tend to arrange the polymer chains in a more ordered fashion.

Sometimes special attractions allow polymers to mix. This is true for the mixture of PS and PPO where the interaction between the phenyl groups allow the miscibility of the two polymers. For many combinations, such preferential associations are not present.

One approach is the use of copolymers. There are a number of variations to this. In some situations, polymer–copolymer combinations are used where the adage “the enemy of my enemy is my friend” comes into play. Thus, the random copolymer of styrene and acrylonitrile forms a miscible blend with PMMA. The copolymer is composed of nonpolar styrene units and polar acrylonitrile units that are incompatible with one another. These units will blend with PMMA in order to avoid one another.

Another approach is to use copolymers where the structures of the copolymer are similar to that of the other phase. This is what occurs for PE and copolymers of ethylene and propylene.

Generally, miscible blends will have properties somewhere between those of the unblended polymers. These properties will be dependent on the ratio of the two polymers and this ratio is often used to obtain a particular property. These properties include mechanical, chemical, thermal, weathering, etc. For instance, PPO is thermally stable with a high T_g, about 210°C. While this is good for some applications, it is considered too high for easy processing. Thus, PS, with a T_g of about 100°C, is added to allow a lower processing temperature. Noryl is PPO blended with a second polymer, which is generally PS or HIPS. Noryl is used in the construction of internal appliance components, brackets and structural components in office products, large computer and printer housings, automotive wheel covers, and high tolerance electrical switch boxes and connectors.

Industrial companies have long-term strategies. For example, Exxon (now ExxonMobil) is the third largest chemical company in the United States. Some time ago, they made the decision to emphasize the ethylene and propylene monomers that are obtained from the petrochemical interests of ExxonMobil. Thus, ExxonMobil has a research emphasis on the commercialization of products from these monomers. The major materials made from ethylene and propylene are polymeric, either homopolymers or copolymers. Efforts include developing catalysts that allow the formation of polymeric materials from the ethylene and propylene monomers and the use of these catalysts to synthesize polymeric materials that have varying properties allowing their application in different marketplaces in society.

A driving force for conversion of gasoline to polymeric materials is increased value in the products made from the polymers. The general trail is gasoline → ethylene, propylene monomers → raw polymers and copolymers → finished products.

One major use of HIPS was in automotive bumpers. These have been largely replaced by another blend, but here it is a miscible blend of PE and PP. HIPS bumpers have a more rubbery feel to them, whereas the PE–PP materials are more plastic in their behavior and feel. These PE and PP intense plastics are not only made into automotive bumpers but also as side and bottom panels. There are several processes employed to produce the raw materials used in the production of these automotive parts. One process developed by Exxon begins with the production of PP using a catalyst developed by Exxon. This catalyst system produces stereoregular iPP that is stronger and denser than nonstereoregular aPP. At some time during this polymerization, some of the liquid polyproplyene monomer is removed and ethylene monomer is added to the mix. Because of the continued presence of the catalyst that can also polymerize the ethylene monomer, copolymer containing ethylene and iPP units is produced. This product can be roughly pictured as being formed from iPP particles that have unreacted propylene monomer removed creating open-celled sponge-like particles. These iPP particles then become impregnated with ethylene monomer eventually resulting in the formation of a copolymer that contains both iPP and PE units with a iPP outer shell. This product is eventually mixed with an ethylene(60%)–iPP(40%) copolymer giving a blended material that has two continuous phases with a final iPP content of 70%. It is this material that is used in molding the automotive bumpers and panels. The iPP units contribute stiffness and the PE units contribute flexibility to the overall product. The inner PE units in the impregnated particles allow stress to be rapidly distributed to the stiffer outer iPP shell. The closeness of structure between the two components, the iPP impregnated particles, and the PE–iPP copolymer allows miscible mixing of the two phases.

The actual conditions and concentrations and ratios of monomer were developed by research scientists like Edward Kresge over a long period of time.

7.9 NETWORKS—GENERAL

Polymer networks are generally of one of two types. Thermoset elastomers have chemical cross-links where "un-linking" requires rupture of primary bonds. TPEs have physical cross-links that include chain entanglement and formation of crystalline or ordered domains that act as hard segments. Here "un-linking" can be accomplished without rupture of primary bonds. For both types stiffness and brittleness increase as the amount of cross-linking increases. Networks can also be divided according to flexibility. Highly cross-linked systems such as PF resins are network systems but they are very strong and brittle.

For elastomeric materials high flexibility and mobility are required so that flexible nonpolar chain units are generally required. Such materials typically have low T_g values that allow ready segmental mobility to occur. Some materials can be "tricked" into being flexible below their T_g through introduction of appropriate flexibilizing agents including plasticizers (diluents). Others can be made to become elastomeric through heating above the T_g of the crystalline areas.

Many of the copolymers are designed to act as elastomeric materials containing complex networks. In general, most elastomers undergo ready extension up to a point where there is an abrupt increase in the modulus. The cause of this limited extensibility was for many years believed to be due to the molecular extent of uncoiling of the polymer segments composing the elastomeric material. Today we know that while such ultimate chain elongations may contribute to this rapid increase in modulus, the primary reason for many elastomeric materials involves strain-induced crystallization. As a general observation, when the large increase in modulus is mainly due to limiting chain extension the limit will not be primarily dependent on temperature and presence/absence of a diluent. Conversely, when the abrupt increase in modulus is dependent on temperature and diluent, the limiting factor is probably stress-induced crystallization.

Ultimate properties of toughness (energy to rupture), tensile strength, and maximum extensibility are all affected by strain-induced crystallization. In general, the higher the temperature the lower the extent of crystallization and consequently the lower these stress/strain related properties. There is also a parallel result brought about by the presence of increased amounts of diluent since this also discourages stress-related crystallization.

There are some so-called noncrystallizable networks where stress/strain behavior is fairly independent of diluent and temperature. One such system is formed from reaction of hydroxyl terminated polydimethylsiloxane (PDMS), through reaction with tetraethyl orthosilicate. While these materials are not particularly important commercially, they allow a testing of various effects, in particular the "weakest-link" theory where it is believed that rupture is initiated by the shortest chains because of their limiting extensibility. From such studies it was found that at long extensions that short chains, that should be the "weakest-link" or more aptly put, the "shortest-link," was not the limiting factor but rather the system "shared" the distortion throughout the network distributing the strain. This redistributing continues until no further distributing is possible at which case stress-induced rupture occurs. Introduction of short or limiting chains has a positive effect on the modulus related properties because shorter chains are better at distributing induced strain.

We are now able to construct so-called bimodal network systems composed of short and long (average length between cross-links) chains and multimodel systems containing chains of predetermined differing lengths. It has been found that short chains are better at reapportioning applied stress/strain than longer chains so that greater elongation is required to bring about the "upturn" in modulus. In general, the stress/strain curve for short chains is steeper than that for long chain networks as expected. Interestingly, a combination of short and long chained networks gives a stress/strain curve that is between the one found for short chained networks and the one for long chained networks such that the area under the stress/strain curve, toughness, is much greater than for either of the monomodal systems. Products are being developed to take advantage of this finding.

Mismatching is important for some applications. Thus moderntly polar materials such as polyisoprene are ideal materials for hose construction where the liquid is nonpolar such as gasoline, flight fuel, lubricants, oils, etc., whereas nonpolar materials such as PE intense copolymers would be suitable for use with transport and containment of polar liquids, such as water.

Fillers are often added to polymeric networks. In particular, those elastomers that do not undergo strain-induced crystallization generally have some reenforcing filler added. The important cases involve carbon black that is added to many materials including NR, and silica that is added to siloxane elastomers. These fillers generally give the materials increased modulus, tear and abrasion resistance, extensibility, tensile strength, and resilience. Counter, they often create other effects such as giving the materials generally a higher hysteresis (heat build up when the material is exposed to repeated cycles of stress/strain) and compression set (permanent deformation).

7.10 POLYMER MIXTURES

Today there exist a number of polymer mixtures including blends noted in Section 7.8. Here we will briefly look at two more mixtures. A plastic or polymer *alloy* is a physical mixture of two or more polymers in a melt and is often structurally similar to blends, in fact the terms blends and

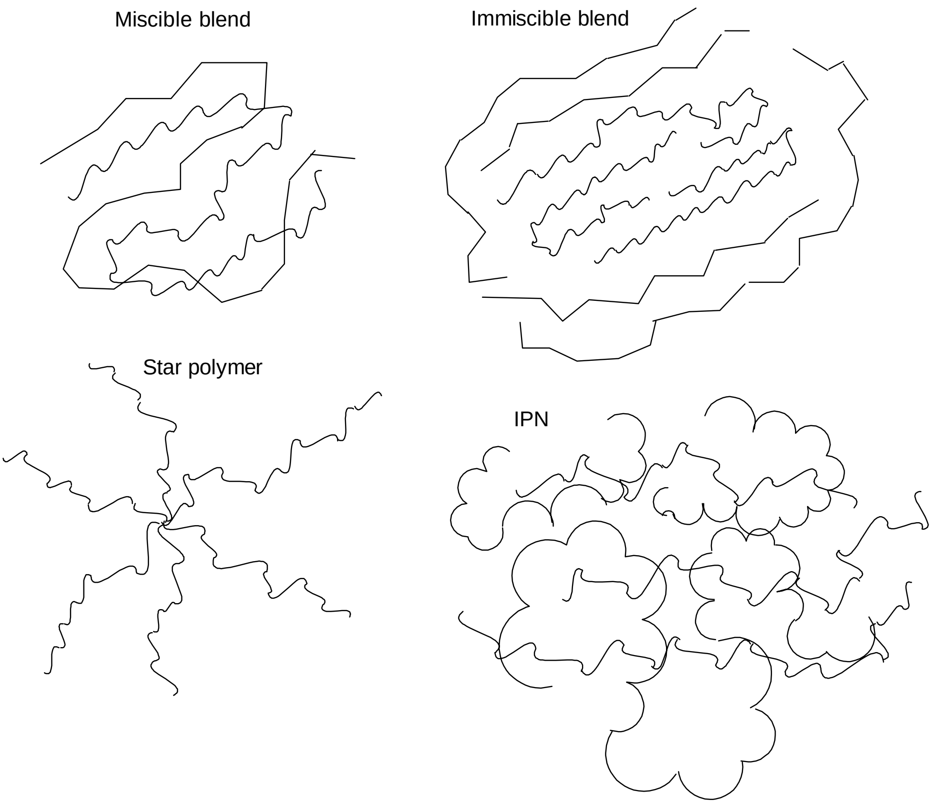


FIGURE 7.2 Polymer mixtures and special shapes.

alloys are sometimes used to describe the same materials. While some cross-linking may occur, such materials are generally not viewed as copolymers, though they are covered in this chapter along with blends and dendrites. Many alloys contain a matrix that is a mixture of polymer types with many of them containing ABS. ABS thermoplastics have a two-phase morphology consisting of elastic particles dispersed in a SAN copolymer matrix.

Interpenetrating polymer networks (IPNs) are described by Sperling to be an intimate combination of two polymers, both in network form, where at least one of the two polymers is synthesized and/or cross-linked in the immediate presence of the other. This is similar to taking a sponge cake; soaking in it warm ice-cream; and refreezing the ice-cream, resulting in a dessert (or mess) that has both spongy and stiff portions. Such IPNs, grafts, blocks, and blends can offer synergistic properties that are widely exploited. Some of these special polymer mixtures and special shapes are given in Figure 7.2.

7.11 DENDRITES

Along with the varying structures given in the previous sections, there exist other structurally complex molecules called dendrites developed by a number of scientists including Tomali and Frechet. These molecules can act as “spacers,” “ball-bearings,” and as building blocks for other structures. Usually, they are either wholly organic or may contain metal atoms. They may or may not be copolymers depending on the particular synthetic route employed in their synthesis.

Although some make a distinction between dendrimers and hyperbranched polymers, we will not do so here. In essence, hyperbranched polymers are formed under conditions that give a variety of related but different structures while dendrimers are formed one step at a time giving a fairly homogeneous product.

Dendrites are highly branched, usually curved, structures. The name comes from the Greek name ‘‘dendron,’’ meaning tree. Another term often associated with these structures is ‘‘dendrimers,’’ describing the oligomeric nature of many dendrites. Because of the structure, dendrites can contain many terminal functional groups for each molecule that can be further reacted. Also, most dendrites contain ‘‘lots’’ of unoccupied space that can be used to ‘‘carry’’ drugs, fragrances, adhesives, diagnostic molecules, cosmetics, catalysts, herbicides, and other molecules.

The dendrite structure is determined largely by the ‘‘functionality’’ of the reactants. The dendrite pictured in Figure 7.3a can be considered as being derived from a tetra-functional monomer formed from the reaction of 1,4-diaminobutane and acrylonitrile. The resulting polypropylenimine dendrimer has terminal nitrile groups that can be further reacted extending the dendrimer or terminating further dendrimer formation. The resulting molecule is circular with some three-dimensional structure. The dendrimer shown in Figure 7.3b is derived from difunctional reactants that are ‘‘bent’’ so as to encourage ‘‘fanlike’’ expansion rather than the typical linear growth.

Numerous approaches have been taken in the synthesis of dendrites or dendrimers. These approaches can be divided into two groupings. In divergent dendrimer growth, growth occurs outward from an inner core molecule. In convergent dendrimer growth, developed by Frechet and others, various parts of the ultimate dendrimer are separately synthesized and brought together to form the final dendrimer.

The somewhat spherical shape of dendimers gives them some different properties in comparison to more linear macromolecules. On a macroscopic level, dendimers act as ball bearings rather than strings. In solution, viscosity increases as molecular weight increases for linear polymers. With dendrimers, viscosity also increases with molecular weight up to a point after which viscosity decreases as molecular weight continues to increase.

Dendrimers are being used as host molecules, catalysts, self-assembling nanostructures; analogs of proteins, enzymes, and viruses; and in analytical applications including in ion-exchange displacement chromatography and electrokinetic chromatography.

We are continuing to recognize that polymer shape is important in determining material property. Another group of structurally complex shapes is referred to as stars. There are a

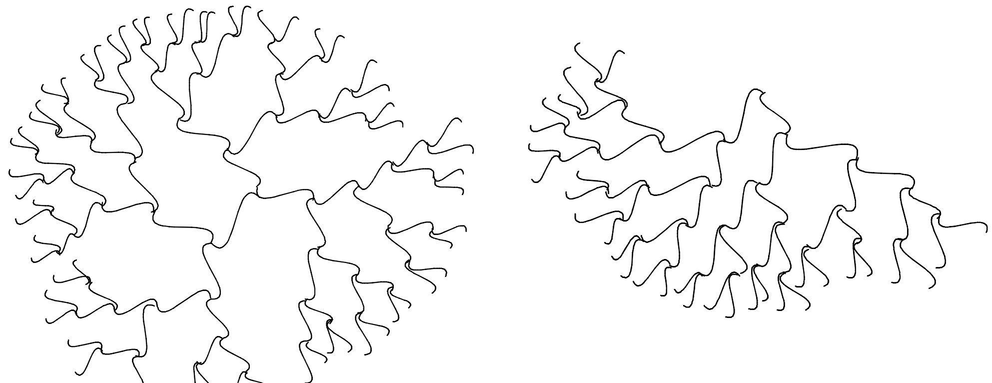


FIGURE 7.3 Dendrite structure derived from (a) the reaction of 1,4-diaminobutane and acrylonitrile and (b) ‘‘bent’’ difunctional reactants.

number of synthetic routes to star polymers. Fetters and coworkers developed a number of star polymers based on chlorosilanes. For instance 3-, 12-, and 18-arm star polymers can be formed. These arms are now reacted with other reactants such as living PS or polybutadiene giving now the star polymers with the silicon-containing inner core and polymer outer core. Through control of the length of the grafted PS or other reactant, the size of the "star" can be controlled.

For dendrimers made using flexible arms the core is mobile and, depending upon the situation, spends some time near the outer layer of the dendrimer sphere. Counter, stiff, and rigid arms produce a dendrimer that "holds" its core within the interior of the dendrimer.

The term "generation" describes the number of times "arms" have been extended. The nature of each generation can be varied so that mixtures of steric requirements and hydrophobic or hydrophilic character can be introduced offering materials with varying structures and properties. By varying the hydrophobic and hydrophilic interactions and steric nature of the arms secondary and tertiary structural preferences can be imposed on the dendrimer.

The dendrite structure can be used as a synthetic tool to craft a particular property into an overall structure. For instance, structures have been formed that are a combination of a conducting rigid rod backbone with dendritic structures radiating from the rigid rod. The backbone collects photons of visible light in the range of 300–450 nm. The dendritic envelope collects light in the UV region from 220 to 300 nm and transfers it to the backbone that then fluoresces blue light at 454 nm. Unprotected poly(phenyleneethynylene), the nondendritic backbone alone, does emit light but suffers from both being brittle and from collisional quenching. The dendrimer product allows both flexibility and discourages collisional quenching by forcing a separation between the backbone rods. This shielding increases with each successive generation of the dendritic wedge.

7.12 IONOMERS

Ionomers are ion-containing copolymers typically containing over 90% (by number) ethylene units with the remaining being ion-containing units, such as acrylic acid. These "ionic" sites are connected through metal atoms. Ionomers are often referred to as processable thermosets. They are thermosets because of the cross-linking introduced through the interaction of the ionic sites with metal ions. They are processable or exhibit thermoplastic behavior because they can be reformed through application of heat and pressure.

As with all polymers, the ultimate properties are dependant upon the various processing and synthetic procedures that the material is exposed to. This is especially true for ionomers where the location, amount, nature, and distribution of the metal sites strongly determines the properties. Many of the industrial ionomers are made where a significant fraction of the ionomer is un-ionized and where the metal-containing reactants are simply added to the preionomer followed by heating and agitation of the mixture. These products often offer superior properties to ionomers produced from fully dissolved preionomers (Figure 7.4).

For commercial ionomers bonding sites are believed to be of two different grouping densities. One of these groupings involves only a few or individual bonding between the acid groups and the metal atoms as shown in Figure 7.4. The second bonding type consists of large concentrations of acids groups with multiple metal atoms (clusters) as shown in Figure 7.5. This metal–acid group bonding (salt formation) constitutes sites of cross-linking. It is believed that the "processability" is a result of the combination of the movement of the ethylene units and the the metal atoms acting as "ball bearings." The "sliding" and "rolling" is believed to be a result of the metallic nature of of the acid–metal atom bonding. (Remember that most metallic salts are believed to have a high degree of ionic, nondirectional bonding as compared with typical organic bonds where there exists a high amount of covalent, directional bonding.) Recently,

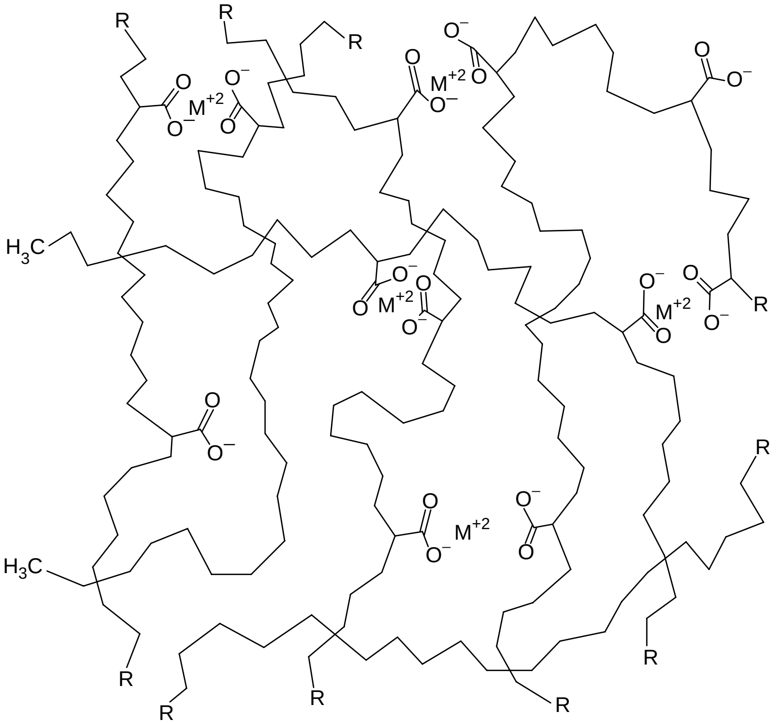


FIGURE 7.4 Ionomer structure showing individualized randomly dispersed bonding sites.

Carraher and coworkers have shown that the ethylene portions alone are sufficient to allow ionomers to be processed through application of heat and pressure.

Ionomers are generally tough and offer good stiffness and abrasion resistance. They offer good visual clarity, high melt viscosities, superior tensile properties, oil resistance, and are flame retarders. They are used in the automotive industry in the formation of exterior trim and bumper pads, in the sporting goods industry as bowling pin coatings, golf ball covers, in the manufacture of roller skate wheels, and ski boots. Surlyn (DuPont; poly(ethylene-co-methacrylic acid) is used in vacuum packaging for meats, in skin packaging for hardware and electronic items (such as seal layers and as foil coatings of multiwall bags), and in shoe soles.

Sulfonated EPDMs are formulated to form a number of rubbery products including adhesives for footwear, garden hoses, and in the formation of calendered sheets. Perfluorinated ionomers marketed as Nafion (DuPont) are used for membrane applications including chemical-processing separations, spent-acid regeneration, electrochemical fuel cells, ion-selective separations, electrodialysis, and in the production of chlorine. It is also employed as a ‘‘solid’’-state catalyst in chemical synthesis and processing. Ionomers are also used in blends with other polymers.

7.13 VISCOSITY MODIFIERS

Different mechanisms can be in operation to cause viscosity changes. As noted earlier, one general polymer property is that the addition of even small amounts of polymer to a solution can result in a relatively large increase in viscosity. This increased viscosity is related to the large size of the polymer chains causing them to be present in several flow planes resulting in

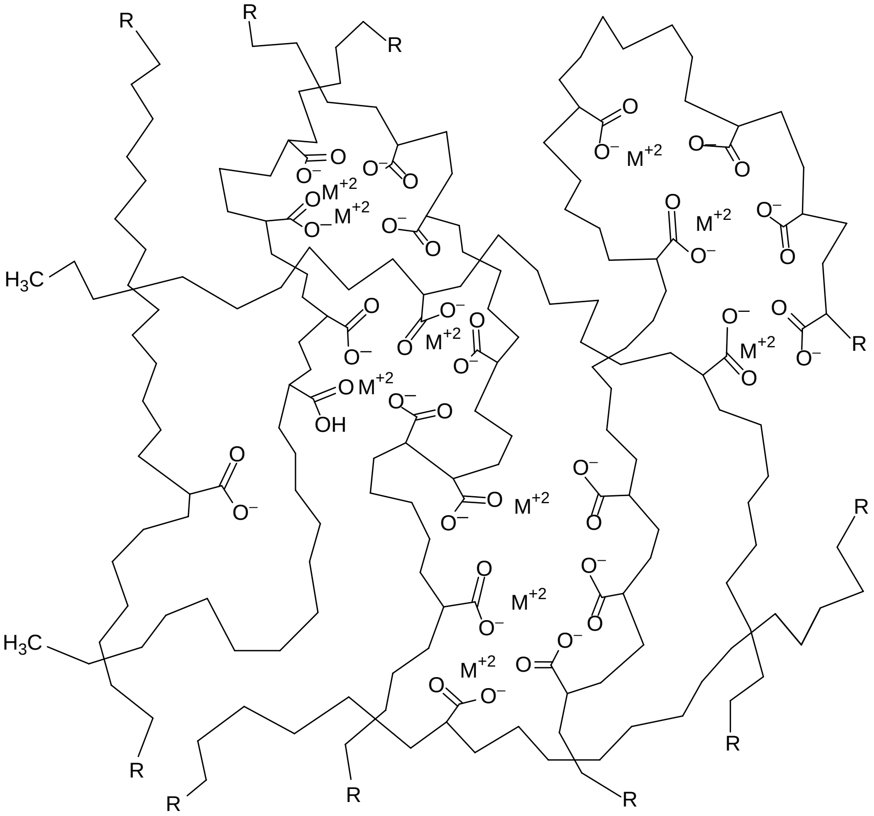


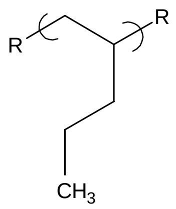
FIGURE 7.5 Ionomer bonding showing cluster bonding sites.

what is referred to as *viscous drag*. Factors that influence the apparent size of a polymer are reflected in their viscosity both in solution and bulk.

For many polymers, as one moves from a good solvent to poorer solvent, the extent of close coiling increases resulting in a decreased viscosity because the more tightly coiled polymer chains now reside in fewer flow planes (Figure 7.6). A similar phenomena can occur as the temperature is decreased (above T_g) since the available energy for chain extension becomes less. For some polymers additional specific mechanisms are in action.

Most commercial motor oils are composed of oligomeric, highly branched chains containing 12–20 carbons. These "oils" are derived from the usual fractionation of native oils with processing to remove the aromatic and other unwanted materials.

Synthetic motor oils also contain oligomeric materials containing 12–20 carbons formed from alpha-olefins generally containing 5, 6, and 7 carbon-containing units as shown in the following equation for a C_5 unit:



(7.38)

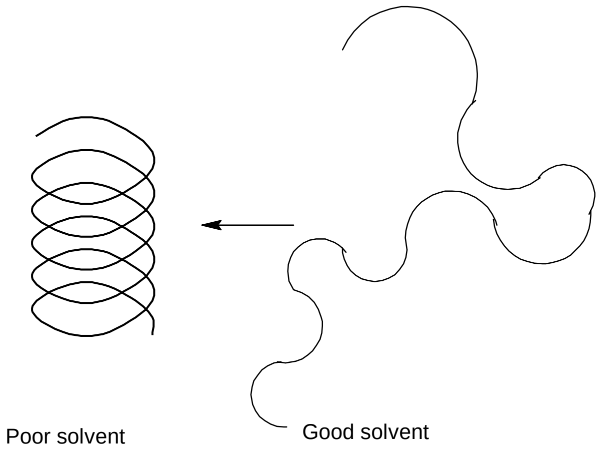


FIGURE 7.6 Polymer chain extensions in different solvents.

Synthetic motor oils outperform normal oils in offering better stability because of the lack of sites of unsaturation that are found in native motor oils and they offer a better wide temperature lubricity because of their designed lower T_g in comparison to native oils.

In general, for solutions and bulk polymeric materials, viscosity follows the general relationship shown in Figure 7.7 where viscosity is constant over much of the "fluid" range but sharply increases near T_g.

The purpose of a multiviscosity motor oil is to offer good engine protection over the operating range of the engine from a "cold start" to the normal operation temperature. Addition of a low T_g polymer allows for a wider range where viscosity is approximately constant.

Figure 7.8 is a plot similar to Figure 7.7 except where the influence of adding a low T_g material illustrates this phenomena. Here, the extreme left curve is the profile of a low molecular weight (low T_g) oil and extreme right curve is the profile of a high molecular

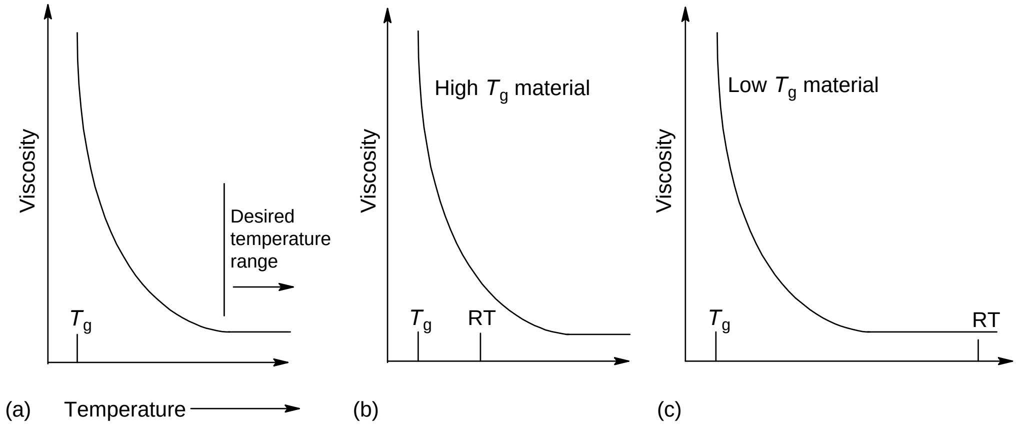


FIGURE 7.7 Plots of viscosity as a function of temperature from left to right. (a) General plot showing the desired temperature range where viscosity is approximately constant as temperature is varied, (b) plot for a high T_g material, and (c) plot for a low T_g material where RT = room temperature.

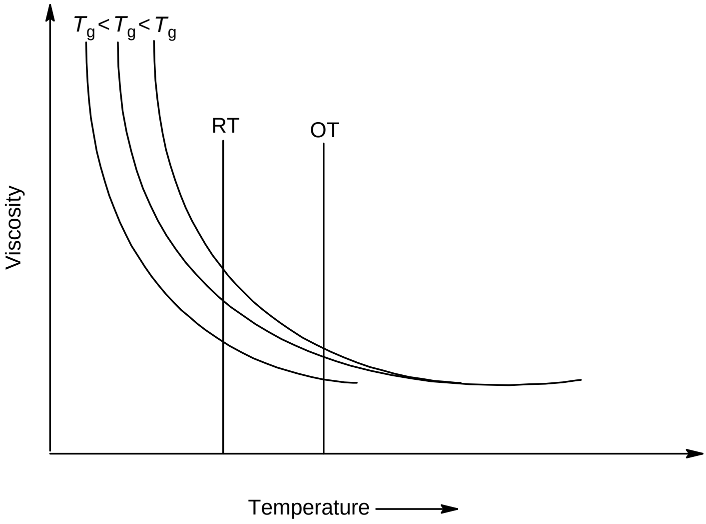


FIGURE 7.8 Viscosity as a function of molecular weight of a low molecular weight oil (extreme left), high molecular weight oil (extreme right), and of the low molecular weight oil to which an appropriate viscosity modifier has been added (middle).

weight (high T_g) oil. The high molecular weight oil offers the needed lubrication protection at the operating temperature (OT) but at RT it is too near its T_g so that the viscosity is high. The low molecular weight oil offers a good viscosity at RT but not at the OT. Addition of an appropriate viscosity modifier allows added lubrication protection and a somewhat constant viscosity over the needed temperature range. Today's motor oils are of the low molecular weight, low T_g variety with a polymer viscosity modifier added.

Addition of about 1% of an EPM is used today to achieve most of our multiviscosity oils. These copolymers were developed as part of Exxon's program that Ed Kresge and fellow researchers were involved with that also produced the miscible blends used to make automotive bumpers and panels (Section 7.8).

Exxon developed a single site soluble catalyst from the reaction of vanadium tetrachloride and $Et_3Al_2Cl_2$ in hexane. This catalyst has special properties that allowed a tailoring of the chain size and chain composition within each chain. Unlike many catalysts where individual chain formation is rapid, this catalyst system creates individual chains in about 4 min allowing growing chain composition to be controlled through varying the concentration of monomer feed as the chains are growing (see Section 7.1). They discovered that the chain extension could be varied by varying the amount of ethylene in the backbone. Figure 7.9 shows the average percentage of ethylene within each of the chains for today's multiviscosity modifiers. The polymer chains are all about 2800 units long. Each end is rich in propylene-derived units, while the middle is rich in ethylene-derived units. As the ethylene units move towards 65% there is an increased tendency to form crystalline micelles causing the polymer to collapse in size at lower temperatures, such as RT. As the temperature increases, the crystalline micelles melt allowing the chain length of the copolymer to increase increasing the viscosity compensating for the effect of the increased temperature on viscosity. Thus the polymer allows an approximately constant viscosity over the needed temperature range.

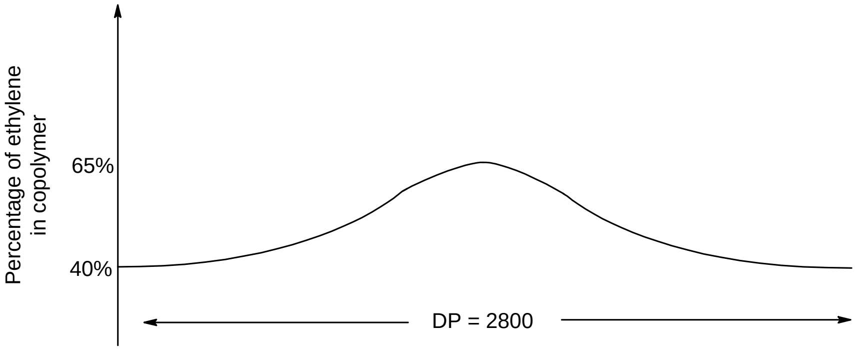


FIGURE 7.9 Polymer composition along a single polymer chain for the ethylene–propylene copolymer employed in most motor oils as the viscosity modifier.

7.14 SUMMARY

1. Unlike homopolymers, which consist of chains with identical repeating units, copolymers are macromolecules that contain two or more unlike units. These repeat units may be randomly arranged, or may alternate in the chain. Block copolymers are linear polymers that consist of long sequences of repeating units in the chain, and graft copolymers are branch polymers in which the branches consist of sequences of repeating units that differ from those present in the backbone. These different copolymers give materials with differing properties, even when synthesized using the same monomers.
2. The copolymerization between two different monomers can be described using only four reactions, two homo-polymerizations and two cross-polymerization additions. Through appropriate arrangements, equations that allow copolymer composition to be determined from the monomer feed ratio are developed.
3. The product of the reactivity ratios can be used to estimate the copolymer structure. When the product of the reactivity ratios is near 1, the copolymer arrangement is random; when the product is near zero, the arrangement is alternating; when one of the reactivity ratios is large, blocks corresponding to that monomer addition will occur.
4. Block and graft copolymers may differ from mixtures by having properties derived from each component. Block copolymers can be used as TPEs and graft copolymers with flexible backbones can be used for high-impact plastics. Block and graft copolymers can be produced by step and chain reaction polymerization. The principle block copolymers are TPEs and elastic fibers, such as ABS. Principal graft copolymers are grafted starch and cellulose.
5. Blends are physical mixtures of polymers. Depending on the extent and type of blend the properties may be characteristic of each blend member or may be some "blend" of properties. Immiscible blends are phase-separated with the phases sometimes chemically connected. They are generally composed of a continuous and discontinuous phase. HIPS is an example of an immiscible blend. Miscible blends occur when the two blended materials are compatible. Often the properties are a mixture of the two blended materials. The plastic automotive panels and bumpers are generally made from a miscible blend of PE and a copolymer of PE and PP.
6. Dendrites are complex molecules formed from building up of the dendrite by individual steps (divergent growth) or from bringing together the units already formed (convergent growth).

7. Ionomers are often referred to as processable thermosets. They are cross-linked through the use of metal ions such that application of heat and pressure allow them to be reformed.
8. There are a number of applications of copolymers. One of these is the important area of viscosity modifiers that recognizes the influence that small amounts of polymers generally have on increasing the viscosity of solutions to which they have been added. One of these applications is to allow the viscosity of motor oils to remain approximately constant over an engine's temperature operating range. Here, the polymer additive increases its effective chain distance as temperature increases compensating for the temperature decrease caused by increased temperature.

GLOSSARY

AB Block copolymer with two separate mers.

ABA Block copolymer with three sequences of mers in the order shown.

ABS Three-component copolymer of acrylonitrile, butadiene, and styrene.

alloy Rubber-toughened materials in which the matrix can be a mixture of polymer types.

alternation copolymer Ordered copolymer in which every other building is a different mer.

azeotropic copolymer Copolymer in which the feet and composition of the copolymer are the same.

blends Mixtures of different polymers on a molecular level; may exist in one or two phases.

block copolymer Copolymer that contains long sequences or runs of one mer or both mers.

Buna-N Elastomeric copolymer of butadiene and acrylonitrile.

Buna-S Elastomeric copolymer of butadiene and styrene.

butyl rubber Elastomeric copolymer of isobutylene and isoprene.

charge-transfer complex Complex consisting of an electron donor (D) and an electron acceptor (A) in which an electron has been transferred form D to A resulting in the charge-transfer agent D^+A^-.

composites Mixtures of different polymers, one forming a continuous phase (the matrix) and one the discontinuous phase (often a fiber).

compositional drift Change in composition of a copolymer that occurs as copolymerization takes place with monomers of different reactivities.

copolymer Macromolecule containing more than one type of mer in the backbone.

dendrites Complex molecules that are highly branched.

domains Sequences in a block copolymer or polymer.

graft copolymer Branched copolymer in which the backbone and the branches consist of different mers.

homopolymer Macromolecule consisting of only one type of mer.

Hytrel Trade name for a commercial TEP.

ideal copolymer Random copolymer.

interpenetrating polymer network (IPN) Intimate combination of two polymers, both in network form, where at least one of the two polymers is synthesized and or cross-linked in the immediate presence of the other.

ionomers Copolymers typically containing mostly ethylene units, with the remaining units being ion containing that are neutralized through reaction with metals.

Kraton Trade name for an ABA block copolymer of styrene and butadiene.

living polymers Macrocarbanions.

polyallomers Block copolymers of ethylene and propylene.

***Q–e* scheme** A semiempirical method for predicting reactivity ratios.

random copolymer Copolymer in which there is no definite order for the sequence of the different mers.

reactivity ratio Relative reactivity of one monomer compared to another monomer.

Saran Trade name for copolymer of VC and vinylidene chloride.

SBR Elastomer copolymer of styrene and butadiene.

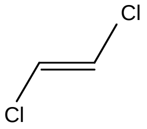
Spandex Elastic fiber consisting of a block copolymer of a PU, hard segment, and a polyester or polyether, soft segment.

viscosity modifier A polymer added to a solution that expands its effective length as temperature increases compensating for the effect that increased temperature has on decreasing the viscosity.

Wall equation Predecessor to the copolymer equation.

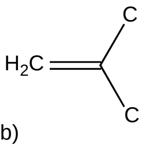
EXERCISES

1. Draw representative structures for (a) homopolymers, (b) alternation copolymers, (c) random copolymers, (d) AB block copolymers, and (e) graft copolymers of styrene and acrylonitrile.
2. If equimolar quantities of M_1 and M_2 are used in an azeotropic copolymerization, what is the composition of the feed after 50% of the copolymer has formed?
3. Define r_1 and r_2 in terms of rate constants.
4. Do the r_1 and r_2 values increase of decrease during copolymerization?
5. What is the effect of temperature on r_1 and r_2?
6. What will be the composition of copolymers produced in the first part of the polymerization of equimolar quantities of vinylidene chloride and vinyl chloride?
7. What monomer may be polymerized by anionic, cationic, and free radical chain techniques?
8. Which chain polymerization technique would you select to polymerize (a) isobutylene, (b) acrylonitrile, and (c) propylene?
9. If r_1r_2 is about zero, what type of copolymer would be formed?
10. Show a structure for an AB block copolymer.
11. What is the value of r_1r_2 for an ideal random copolymer?
12. Which would polymerize more readily?



(a)

or



(b)

13. Why are most elastomers difficult to recycle?
14. What is the composition of the first copolymer chains produced by the copolymerization of equimolar quantities of styrene and methyl methacrylate in (a) free radical, (b) cationic, and (c) anionic copolymerization?
15. What is the composition of the first copolymer butyl rubber chains produced form equimolar quantities of the two monomers?
16. What is the composition of the first copolymer butyl rubber chains produced from a feed containing 9 mol of isobutylene and 1 mol of isoprene?
17. How would you ensure that production of butyl rubber of uniform composition occurs in question 16?
18. For a graft copolymer with a backbone derived from monomer A and the graft B what often occurs when B is long?
19. What is the composition of the first polymer chains produced by the copolymerization of equimolar quantities of VC and VAc?
20. What are the advantages, if any, of the VC–VAc copolymer over PVC itself?
21. Why are ionomers superior to LDPE?
22. What is the difference among Buna-S, GRS, and SBR?
23. How can you connect two different phases in polymer blends?
24. Which sequence in the ABA block copolymer of ethylene oxide and propylene oxide is more lyophilic?
25. When will a blend exhibit two distinct properties?
26. Are dendrites really polymeric?
27. What product is obtained if 1.5 mol of styrene is copolymerized with 1 mol of maleic anhydride in benzene?
28. Why are ionomers referred to as processable thermosets?
29. What is the use of the copolymerization equation?
30. How could you use graft copolymerization techniques to reduce the water solubility of starch?
31. What is the end group when azobiscyanopentanoic acid is used as an initiator?
32. What are some advantages of ionomers?
33. In the synthesis of dendrites, why must some of the reactants have a functionality greater than two?

34. Why do companies often emphasize only selected materials and/or processes?
35. How would the properties of two polymers containing the same amounts of monomer A and B differ if one polymer is a simple random copolymer and the other polymer is a block copolymer?
36. Name one important property of an elastomer.
37. What are potential useful properties of dendrites?

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8 Composites and Fillers

One of the fastest growing areas today is composites. Composites offer good strength, corrosion resistance, and lightweight; so they are continually replacing metals. As the cost of fuel continues to increase, much of the replacement of metals is due to desired weight reductions. Composites are generally composed of two phases: the continuous or matrix phase, which surrounds the discontinuous or dispersed phase.

While many fillers are spherical, some are fiberlike. When the length of these fibrous materials approaches 100 times their thickness, many combinations offer great increases in the strength-related properties of the materials that contain them. If these fibers are contained within a continuous phase, they are generally described as traditional composites. Because of their importance, much of this chapter will deal with such traditional "long-fiber" composites.

8.1 FILLERS

According to the American Society for Testing and Materials (ASTM) standard D-883, a filler is a relatively inert material added to a plastic to modify its strength, permanence, working properties, or other qualities or to lower costs, whereas a reinforced plastic is one with some strength properties greatly superior to those of the base resin resulting from the presence of high-strength fillers embedded in the composition. The word extender is sometimes used for fillers. Moreover, the notion that fillers simply "fill" without adding some needed property is not always appropriate. Some fillers are more expensive than the polymer resin and do contribute positively to the overall properties.

Many materials tend to approach a spherical geometry to reduce the interface the materials have with its surroundings. Further, a spherical geometry is favored because of the old adage that "like likes like the best" and offers the best association of a material with itself.

The behavior of many fillers can be roughly treated as spheres. Current theories describing the action of these spherical-acting fillers in polymers are based on the Einstein equation (8.1). Einstein showed that the viscosity of a Newtonian fluid (η_o) was increased when small, rigid, noninteracting spheres were suspended in a liquid. According to the Einstein equation, the viscosity of the mixture (η) is related to the fractional volume (c) occupied by the spheres, and was independent of the size of the spheres or the polarity of the liquid.

$$\eta = \eta_o(1 + 2.5c) \quad \text{and} \quad \eta_{sp}/c = 2.5 \tag{8.1}$$

Providing that c is less than 0.1, good agreement with the Einstein equation is found when glass spheres are suspended in ethylene glycol. Equation 8.1 has been modified by including a hydrodynamics or crowding factor (β). The modified Mooney equation (8.2) resembles the Einstein equation when $\beta = 0$.

$$\eta = \eta_o(2.5c/(1 - \beta c)) \tag{8.2}$$

Many other empirical modifications of the Einstein equation have been made to predict actual viscosities. Since the modulus (M) is related to viscosity, these empirical equations, such as the Einstein–Guth–Gold (EGG) equation (8.3), have been used to predict changes in modulus when spherical fillers are added.

$$M = M_o(1 + 2.5c - 14.1c^2) \tag{8.3}$$

Since carbon black and amorphous silica tend to form clusters of spheres (grasping effect), an additional modification of the Einstein equation was made to account for the nonspherical shape or aspect ratio (L/D). This factor (f) is equal to the ratio of length (L) to diameter (D) of the nonspherical particles ($f = L/D$).

$$\eta = \eta_o(1 + 0.67fc + 1.62f^2c^2) \tag{8.4}$$

Both natural and synthetic fillers are used. Examples of such fillers are given in Table 8.1.

Among the naturally occurring filler materials are cellulosics such as wood flour, α-cellulose, shell flour, and starch, and proteinaceous fillers such as soybean residues. Approximately 40,000 t of cellulosic fillers are used annually by the U.S. polymer industry. Wood flour, which is produced by the attrition grinding of wood wastes, is used as filler for phenolic resins, urea resins, polyolefins, and PVC. Shell flour, which lacks the fibrous structure of wood flour, has been used as a replacement for wood flour for some applications.

α-Cellulose, which is more fibrous than wood flour, is used as filler for urea and melamine plastics. Melamine dishware is a laminated structure consisting of molded resin-impregnated paper. Presumably, the formaldehyde in these thermosetting resins reacts with the hydroxyl groups in cellulose producing a more compatible composite. Starch and soybean fillers have been used to make biodegradable composites and other materials.

Carbon black, which was produced by the smoke-impingement process by the Chinese over 1000 years ago, is now the most widely used filler for polymers. Much of the 1.5 million tons produced annually is used for the reinforcement of elastomers. Furnace carbon black is the most widely used carbon black.

Conductive composites are obtained when powered metal fillers, metal flakes, or metal-plated fillers are added to resins. These composites have been used to produce forming tools for the aircraft industry and to overcome electromagnetic interference in office machines.

Calcium carbonate is available as ground natural limestone and as synthetic chalk. It is widely used in paints, plastics, and elastomers. The volume relationship of calcium carbonate to resin or the pigment volume required to fill voids in the resin composite is called the pigment–volume concentration (PIVC).

8.2 TYPES OF COMPOSITES

There are a variety of polymer-intense composites that can be classified as shown in Figure 8.1. Many of these composite groups are used in combination with other materials including different types of composites.

Many naturally occurring materials such as wood are reinforced composites consisting of a resinous continuous phase and a discontinuous fibrous reinforcing phase.

Structural composites include laminas that can be sandwiched or laminated. At times there is confusion between which materials are sandwich or laminate laminas. Even so, here we will consider *laminate composites* as containing layers of material (generally considered the reinforcing agent) bound on one or both sides by an adhesive material. Generally, there are a number of layers of reinforcing material present within the distance between the layers, which are small compared with those present in *sandwich composites*. Plywood is an example of a sandwich

TABLE 8.1
Types of Fillers for Polymers

I. Organic Materials

A. Cellulosic products
  1. Wood products
    a. Kraft paper
    b. Chips
    c. Course flour
    d. Ground flour
  2. Comminuted cellulose products
    a. Chopped paper
    b. Diced resin board
    c. Crepe paper
    d. Pulp preforms
  3. Fibers
    a. α-cellulose
    b. Pulp preforms
    c. Cotton flock
    d. Textile byproducts
    e. Jute
    f. Sisal
    g. Rayon
B. Lignin-type products-processed lignin
C. Synthetic fibers
  1. Polyamides (nylons)
  2. Polyesters
  3. Polyacrylonitrile
D. Carbon
  1. Carbon black
    a. Channel black
    b. Furnace black
  2. Ground petroleum coke
  3. Graphite filaments
  4. Graphite whiskers

II. Inorganic Materials

A. Silica products
  1. Minerals
    a. Sand
    b. Quarts
    c. Tripoli
  2. Synthetic materials
    a. Wet-processed silica
    b. Pyrogenic silica
    c. Silica aerogel
B. Silicates
  1. Minerals
    a. Asbestos
    b. Karolinite (China clay)
    c. Mica
    d. Talc
    e. Wollastonite
  2. Synthetic products
    a. Calcium silicate
    b. Aluminum silicate
C. Glass
  1. Glass flakes
  2. Solid and hollow glass spheres
  3. Milled glass fibers
  4. Fibrous glass
    a. Filament
    b. Rovings and woven rovings
    c. Yarn
    d. Mat
    e. Fabric
D. Metals
E. Boron fibers
F. Metallic oxides
  1. Ground material
    a. Zinc oxide
    b. Alumina
    c. Magnesia
    d. Titania
  2. Whiskers (including nonoxide)
    a. Aluminum oxide
    b. Beryllium oxide
    c. Zirconium oxide
    d. Aluminum nitride
    e. Boron carbide
    f. Silicon carbide and nitride
    g. Tungsten carbide
    h. Beryllium carbide
G. Calcium carbonate
  1. Chalk
  2. Limestone
  3. Precipitated calcium carbonate
H. Polyfluorocarbons
I. Barium ferrite and sulfate

lamina where layers or plies of wood are bound together using an adhesive, such as one of the formaldehyde-related resins. Formica is an example of a laminate where paper, cloth, or other material is impregnated with the continuous phase material. Sandwich laminas are widely used in the textile industry where foam, plastic, and fabric are bound together into new textiles. Many electronic boards are laminas. Examples of laminates include surfaces for countertops and wall paneling.

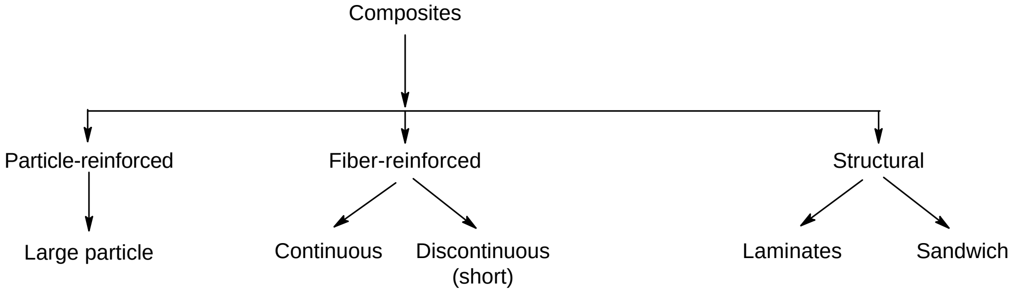

FIGURE 8.1 Classification of polymer-intense composites.

Particulate composites consist of the reinforcing materials being dispersed throughout the resin. Unlike fibrous composites, the reinforcing material is more bulky and not fibrous in nature.

Some materials to which fillers have been added can be considered as composites. These include a number of "cements" including concrete (Section 10.2). As long as the added particles are relatively small, of roughly the same size, and evenly distributed throughout the mixture, there can be a reinforcing effect. The major materials in Portland cement concrete are Portland cement, a fine aggregate (sand), course aggregate (gravel and small rocks), and water. The aggregate particles act as inexpensive fillers. Water is also inexpensive. The relatively expensive material is the Portland cement. Good strength is gained by having a mixture of these such that there is a dense packing of the aggregates and good interfacial contact, both achieved by having a mixture of aggregate sizes—thus the use of large gravel and small sand. The sand helps fill the voids between the various larger gravel particles. Mixing and contact is achieved with the correct amount of water. Sufficient water must be present to allow a wetting of the surfaces along with providing some of the reactants for the setting of the cement. Too much water creates large voids and weakens the concrete.

At times the difference between fillers and particulate composites is small. For particulate composites, the emphasis is on the added strength due to the presence of particulates within the resin. Particle board is often used as an example of particulate composites where the particulates are pieces of wood, woodlike, or derived material. Unlike plywood, particle board generally uses flakes or chips of wood rather than layers.

8.3 LONG FIBER COMPOSITES—THEORY

Because of the use of new fibers and technology, most of the composites discussed here are referred to as "space-age" and "advanced materials" composites.

According to the ASTM definition, fillers are relatively inert, while reinforcements improve the properties of the materials to which they are added. Actually, few fillers that do not improve properties are used, but reinforcing fibers produce dramatic improvements to the physical properties of the material to which it is added, generally to form composites.

The transverse modulus (M_T) and many other properties of a long fiber–resin composite may be estimated from the law of mixtures. The longitudinal modulus (M_L) may be estimated from the Kelly–Tyson equation (8.5), where the longitudinal modulus is proportional to the sum of the fiber modulus (M_F) and the resin matrix modulus (M_M). Each modulus is based on a fractional volume (c). The constant k is equal to 1 for parallel continuous filaments and decreases for more randomly arranged shorter filaments.

$$M_L = kM_F c_F + M_M c_M \tag{8.5}$$

Since the contribution of the resin matrix is small in a strong composite, the second term in the Kelly–Tyson equation can be disregarded. Thus, the longitudinal modulus is dependent on the reinforcement modulus, which is independent of the diameter of the reinforcing fiber.

As noted earlier, for the most part, the resulting materials from the use of reinforcements are composites, which are materials that contain strong fibers embedded in a continuous phase. The fibers are called ‘‘reinforcement’’ and the continuous phase is called the matrix. While the continuous phase can be a metallic alloy or inorganic material, it is typically an organic polymer that is termed a ‘‘resin.’’ Composites can be fabricated into almost any shape and after hardening, they can be machined, painted, etc., as desired.

Although there is a lot of science and ‘‘space-age technology’’ involved in the construction of composites, many composites have been initially formulated through a combination of this science and ‘‘trial-and-error,’’ giving ‘‘recipes’’ that contain the nature and form of the fiber and matrix materials, amounts, additives, and processing conditions.

Composites have high tensile strengths (on the order of thousands of megapascals—MPa), high Young’s modulus (on the order of hundreds of gigapascals—GPa), and good resistance to weathering exceeding the bulk properties of most metals. The resinous matrix, by itself, is not particularly strong relative to the composite. Further, the overall strength of a single fiber is low. In combination, the matrix–fiber composite becomes strong. The resin acts as a transfer agent, transferring and distributing applied stresses to the fibers. Generally, the fibers should have aspect ratios (ratio of length to diameter) exceeding 100, often much larger. Most fibers are thin (less than 20 μm thick, about a tenth the thickness of a human hair). Fibers should have a high tensile strength and most have a high stiffness, i.e., low strain for high stress or little elongation as high forces are applied.

There exists a relationship between the ‘‘ideal’’ length of a fiber and the amount of adhesion between the matrix and the fiber. For instance, assume that only the tip, one end, of a fiber is placed in a resin (Figure 8.2, left). When the fiber is pulled, the adhesion is

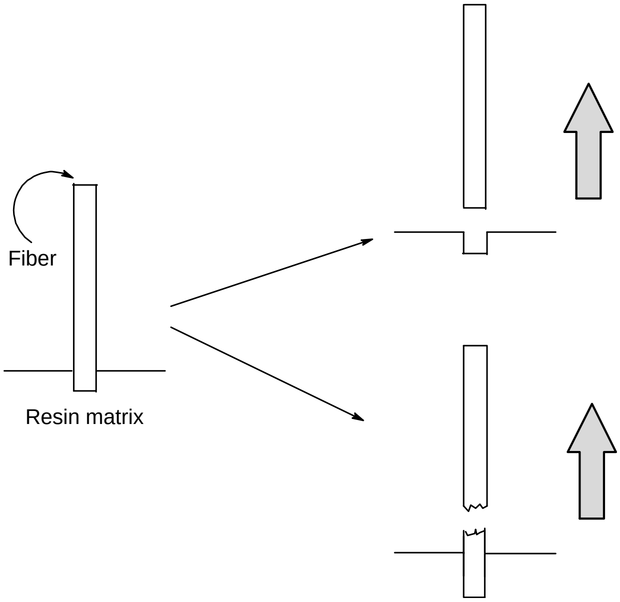

FIGURE 8.2 Tensile loading experiments performed on single fibers embedded in a matrix. The illustration on the left is preapplication of the tensile loading and those on the right are postapplication of the tensile loading.

insufficient to "hold" the fiber and is pulled from the resin (Figure 8.2, top right). The experiment is repeated until the fiber is broken (outside the matrix) rather than being pulled (without breaking) from the resin (Figure 8.2, right bottom). Somewhere between the two extremes, there is a length where there exists a balance between the strength of the fiber and the adhesion between the fiber and matrix. Most modern composites utilize fiber–matrix combinations that exploit this "balance."

Mathematically the critical fiber length necessary for effective strengthening and stiffening can be described as follows:

Critical fiber length = [Ultimate or tensile strength times fiber diameter/2] times the fiber–matrix bond strength or the shear yield strength of the matrix—whichever is smaller

Fibers that have a length greater than this critical length are called *continuous fibers*, while those that are less are called *discontinuous* or *short fibers*. Little transference of stress and thus little reinforcement is achieved for short fibers. Thus, fibers whose lengths exceed the critical fiber length are used.

Fibers can be divided according to their diameters. Whiskers are very thin single crystals that have large length/diameter ratios. They have a high degree of crystalline perfection and are essentially flawless. They are some of the strongest materials known. Whisker materials include graphite, silicon carbide, aluminum oxide, and silicon nitride. Fine wires of tungsten, steel, and molybdenum are also used but here, even though they are relatively fine than other metal wires, they have large diameters. The most used fibers are those that are either crystalline, amorphous, or semicrystalline with small diameters.

Fiber failure is usually of the "catastrophic" type where the failure is sudden. This is typical in polymeric materials where the material is broken at the "weak-link" and where the strength-related property is related to a combination of individual links (chains).

8.4 FIBERS AND RESINS

Tables 8.2 and 8.3 contain a partial listing of the main materials employed in the fabrication of composites. It is important to note that many of the entries given in Tables 8.1 and 8.2 represent whole families of materials. Thus, there are a large number of possible combinations, but not all combinations perform in a satisfactory manner. Generally good adhesion between the matrix and fiber is needed. Table 8.4 contains a listing of some of the more utilized combinations.

About 98% of the fibers employed in composites are glass (Sections 12.5 and 12.6), carbon (graphite, carbon fibers, etc.; Section 12.16), and aromatic nylons (often referred to as aramids; Section 4.8). New composites are emerging that employ carbon nanotubes and the fibers (Section 12.17). Asbestos (Section 12.13), a major fiber choice years ago, holds less than 1% of the market today because of medical concerns linked to it.

TABLE 8.2
Frequently Employed Fibers in Composites

Alumina (aluminum oxide: Al_2O_3)
Aromatic nylons
Boron
Carbon and graphite
Glass
Polyolefin
Silicon nitride (Si_3N_4)
Titanium carbide (TiC)
Tungsten carbide (WC)
Zirconia (ZrO_2)

TABLE 8.3
Polymer Resins Employed in the Fabrication of Composites

Thermosets	Thermoplastics
Epoxys	Nylons
Melamine–Formaldehyde	Polycarbonates
Phenol–formaldehyde	Poly(ether ether ketone)
Polybenzimidazoles	Poly(ether ketone)
Polyimides	Poly(ether sulfones)
Polyesters	Poly(phenylene sulfide)
Silicones	Polyethylene
	Acetal
	Polyolefins

Glass fibers are described using several terms including fiberglass, glass fibers, and fibrous glass. Glass fibers are mainly composed of silicon dioxide glass. They are "pulled" from the glass melt forming fibers that range from 2 to 25 μm in diameter. The pulling action helps orientate the overall three-dimensional structure giving a material with greater strength and stiffness along the axis of the pull. The ability to pull fibers from molten glass was known for centuries, but fibrous glass was not produced commercially until the 1930s. Table 8.5 contains a brief description of the most important glass fiber types.

As with many polymers, the limits of strength are due to the presence of voids. For glass fibers, these voids generally occur on the surface, thus care is taken to protect these surfaces through surface treatments with methacrylatochromic chloride, vinyl trichlorosilanes, and other silanes. These surface agents chemically react with the fiber surface acting to repel and protect the surface from harmful agents such as moisture.

Different kinds of carbon-intense fibers are used, the most common being carbon and graphite fibers, and carbon black. As is the case with fibrous glass, surface voids are present. Carbon-intense fibers are often surface-treated with agents such as low molecular weight epoxy resins. Such surface treatments also aim at increasing the fiber–matrix adhesion.

Two general varieties of aromatic nylons are often employed. A less stiff variety is employed when some flexibility is important, whereas a stiffer variety is used for applications where greater strength is required. While good adhesion with the resin is often desired, poor adhesion is sometimes an advantage such as in the construction of body armor where "delamination" is a useful mode for absorbing an impact.

As we understand materials better, we are able to utilize them for additional applications. It is known that elongational flow through orifices can result in the stretching and reorientation

TABLE 8.4
Typically Employed Fiber–Resin Pairs

Alumina–epoxy
Alumina–polyimide
Boron–carbon–epoxy
Boron–epoxy
Boron–polyimide
Boron–carbon–epoxy
Carbon–acrylic
Carbon–epoxy
Carbon–nylon–epoxy
Carbon–polyimides
Glass–epoxy
Glass–carbon–polyester
Glass–polyester
Glass–polyimide
Glass–silicon
Nylon–epoxy

TABLE 8.5
Types of Glass Fibers

Designation	General Properties
C-Glass	Chemical resistant
E-Glass	"Typical" glass fiber
R-Glass and S-Glass	Stiffer and stronger than E-Glass

of polymer chains giving a stronger fiber in the direction of pull. Some polymers are entangled and the flow gives additional orientation. Finally, polymer solutions may be stable at rest, but under high rates of extrusion they may be removed from solution, forming a gel phase. These observations have allowed the production of a number of new polyolefin fibers including ultrahigh-modulus PE fibers that have low density but relatively high tensile strength with an elongation at break over two times greater than glass and aromatic nylon fibers.

Both thermoset and thermoplastic resin systems are employed in the construction of composites (Table 8.3). The most common thermoset resins are polyimides, unsaturated polyesters, epoxys, PFs, and amino-formaldehydes. A wide variety of thermoplastic resins have been developed.

8.5 LONG FIBER COMPOSITES—APPLICATIONS

Many of the applications for composite materials involve their (relative) lightweight, resistance to weathering and chemicals, and their ability to be easily fabricated and machined. Bulk applications employ composites that are relatively inexpensive. Combinations of rigorous specifications, low volume, specific machining and fabrication specifications, and comparative price to alternative materials and solutions allow more expensive specialized composites to be developed and utilized.

Applications are ever increasing. Following is a brief description of some of these. One of the largest and oldest applications of composites is the construction of small vessels like rowboats, sailboats, racing boats, and motor craft to large ships. The use of freshwater and saltwater-resistant composites allowed the boating industry to grow and today includes a range from individually operated backyard construction to the use of large boatyards producing craft on an assembly line. Most of these crafts are composed of fiberglass and fiberglass–carbon combination composites.

Compositions are also important in the construction of objects to both propel material into outer space and exist there. Because of the large amount of fuel required to propel spacecraft into outer space, weight reduction, offered by composites, is essential. The polymeric nature of composites also makes it an ideal material to resist degradation caused by the vacuum of outer space.

Many biomaterials are composites. Bone and skin are relatively light compared to metals. Composite structures can approach the densities of bone and skin and offer the necessary inertness and strength to act as body-part substitutes.

Power-assisted arms have been made by placing hot-form strips of closed-cell PE foam over the cast of an arm. Grooves are cut into these strips prior to application and carbon or resin added to the grooves. The resulting product is strong, light and the cushioned PE strips soften the attachment site of the arm to the living body. Artificial legs can be fashioned in glass or polyester and filled with PU foam adding strength to the thin-shelled glass or polyester shell. Artificial legs are also made from carbon–epoxy composite materials. Some of these contain a strong interior core with a soft, flexible "skin."

Carbon–epoxy “plates” are now used in bone surgery replacing the titanium plates that had been employed. Usually a layer of connective tissue forms around the composite plate.

Rejection of composite materials typically does not occur, but as is the case of all biomaterials, compatibility is a major criterion. Often, lack of biocompatibility has been found to be the result of impurities (often additives) found in the materials. Removal of these impurities allows the use of purified materials.

Carbon and carbon–glass composites are being used to make “advanced-material” fishing rods, bicycle frames, golf clubs, baseball bats, racquets, skis and ski poles, basketball backboards, etc. These come in one color—black—because the carbon fibers are black. Even so, they can be coated with about any color desired.

Composites are being employed in a number of automotive applications. These include racing car bodies as well as “regular” automobiles. Most automobiles have the lower exterior panels composed of rubbery, plastic blends, and/or composite materials. Corvettes have composite bodies that allow a lightweight vehicle with decent fuel economy and they do not rust. Other parts such as drive shafts and leaf springs in private cars and heavy trucks, antennas, and bumpers are being made from composite materials.

Industrial storage vessels, pipes, reaction vessels, and pumps are now made from composite materials. They offer necessary resistance to corrosion, acids and bases, oils and gases, salt solutions, and the necessary strength and ease of fabrication to allow their continued adoption as a major industrial “building” material.

The Gulf War spotlighted the use of composite materials in the new-age aircraft. The bodies of both the Stealth fighter and bomber are mainly carbon composites. The versatility is apparent when one realizes that the Gossamer Albatross, the first plane to cross the English Channel with human power, was largely made up of composite materials including a carbon–epoxy and aromatic nylon composite body, propeller containing a carbon composite core, etc.

The growth of composite materials in the aerospace industry is generally due to their outstanding strength and resistance to weathering and friction, and their lightweight allowing fuel reduction savings. Its growth in commercial aircraft is seen in the increased use of fiberglass composite material in succeeding families of Boeing aircraft from about 20 sq. yd. for the 707, to 200 sq. yd. for the 727, to 300 sq. yd. for the 737, and over 1000 sq. yd. for the 747. This amount is increased in the Boeing 767 and includes other structural applications of other space-age composites. Thus, the Boeing 767 uses carbon–aromatic nylon–epoxy landing gear doors and wing-to-body fairings.

Until the late 1960s almost all tactical aircraft were largely titanium. Although titanium is relatively light, it is costly and has demanding production requirements so that its use was limited to moderate temperature aircraft applications. Today, most tactical aircraft have a sizable component that is polymeric, mainly composite. The Boeing F/A 18E/F and Lockheed F/A-22 have about 25%, by weight, composite material. It is projected that future military aircraft will have more than 35% composite materials.

Composites have displaced more conventional materials because they are lighter with greater strength and stiffness allowing them to carry a greater payload further. Composites are also relatively insensitive to flaws. In comparison to metals, fatigue-testing of composites shows that they have a high resistance to cracking and fracture propagation. They are stable and not subject to corrosion. However, in the design process, particular care must be taken with respect to the metal–composite interface because galvanic action of some metals will corrode when in contact with certain composites such as the carbon graphite–resin laminates.

The Stealth Bomber, more accurately known as the Northrop Grumman B-2 Spirit Stealth Bomber, is cited as the largest composite structure produced with over 30% of the weight being carbon–graphite–epoxy composites. The Stealth Bomber was originally slated to hunt Russian mobile missiles that were built in the 1980s. It was deployed in 1993 and has a wingspan of over 52 m, a 21 m length, and is over 5 m high. The reported cost of a single B-2 is varied ranging from about $2.4 billion to a low of $500 million. In any case, it is expensive and only about 21 bombers have been produced with no plans to build more. The technology associated with the B-2 has been continuously upgraded allowing it to perform tasks with even greater accuracy and stealthiness.

The word stealth comes for ancient roots meaning "to steal." There are a number of stealth aircraft in operation today with others coming on line. To be "stealthy," a plane should:

1. Be difficult to see with the eye
2. Make little or no noise (achieved by muffling the engines)
3. Display little heat from engines and other moving parts
4. Minimize a production of contrails and other signs
5. Absorb and scatter radar beams

The most common mode of aircraft detection is radar. Essentially, radar is the detection of radio waves that have been "thrown out" and which bounce off objects returning to the site of origin. Today's radar, if properly used, can help identify the location, speed, and identity of the aircraft. The radar cross-section (RCS) of an aircraft is how much echo the plane sends from radar. Birds have an RCS of about 0.01 m^2. The Stealth Bomber has an RCS of 0.75 m^2. The Stealth Bomber and many stealth aircraft gain their stealth character from both the shape of the aircraft and the presence of radar absorbing material (RAM), which is made to absorb and eliminate radio waves rather than reflect them. Most of the RAM materials are polymeric.

The Stealth Bomber has a covering of RAM skin. The basic elements of the composite cover consist of graphite carbon fibers embedded in an epoxy resin. The carbon fibers dissipate some of the absorbed radiation by ohmic heating. The material also contains ferrite particles that are important because they are good "lossy" radar absorbers. The good absorbency of radar signals is dependent on a low dielectric constant. In principle, the thicker the coating the greater the absorption of signals. Thick coatings increase cost and weight and decrease the aerodynamics of the aircraft. (In fact, the flying wing is aerodynamically unstable and is flown with a quadruple-redundant fly-by-wire [FBW] system.) The thickness of the layers needed to provide the necessary radar signature can be reduced by use of materials with intermediate absorption behavior, ferrite particles, to smooth the interference between the aircraft and the surrounding air since extreme differences cause strong radar reflections.

The graphite resin layers are laid in a manner similar to that employed in making the hull of a fiberglass boat. This layering, over a frame or mold, is accomplished using computer-guided assistance. Thin layers of gold foil are also applied to the canopy to give radar-reflecting characteristics similar to the rest of the aircraft.

The Stealth Bomber is shaped like a wafer-thin Batman boomerang with smooth, knife-like curved surfaces that lack right angles. The reflective nature of the design can be understood by looking straight at a mirror. Your image will be reflected back at you. Tilt the mirror 45° and it will reflect your image upward. The bomber design is a large system of triangles with flat surfaces angled to deflect radar waves away from the emitter. It scrambles the radar all around but not back to the receiver. This shape is also intended to offer minimum disruption to the air, i.e., the shape brings about a minimum amount of air resistance resulting in a minimization of radar difference between the aircraft and its surroundings.

The use of composites allows few seams thus reducing radar reflections. For years, seams were believed to be essential for a large aircraft. For instance, the wings of the large bombers actually "flap" in the wind contributing to the ability of the aircraft to remain in the air for long periods. Without seams and some flexibility these large metal-based aircraft would literally snap apart. Composite assemblies have minimum flexibility. To discourage reflections in unwanted directions, the electrical continuity is maintained over the entire surface of the bomber. Thus, all moving and major body parts are tight-fitting. The composite nature of the outer skin allows this to be achieved closely.

The engines are buried deep within the aircraft's interior reducing noise and "heat signature." The heat signature is further reduced by mixing the jet's exhaust with cool air and exiting it through slit-like vents.

Stealth aircraft are often painted a medium gray or bluish gray that matches the sky so that it does not stand out. Coatings are composed of RAM that penetrates cracks reducing the number of minor repairs and use of special tape for repair. Every screw, panel, seam, and gap is covered with a special tape or the RAM coating adding to the bomber's stealthiness.

Because most traditional polymers have low dielectric constants, they can be used as RAMs and many have been used in various applications in military and civil applications. While the B-2 largely depends on a graphite–carbon impregnated composite for its integrity and stealthiness, many other polymers are used as RAMs. Many of these are various elastomeric materials. Neoprene is widely used in naval applications as a RAM because of its good weather resistance. Nitrile is used for fuel and oil resistance and fluoro-elastomers are used where wide temperature ranges are encountered. Often, thin flexible sheets or layers of the elastomer are adhered to a metal substrate. Although the polysiloxanes offer good RAM behavior, they are difficult to adhere to many metal structures and thus are not as widely employed in comparison to neoprene and nitrile rubbers. Products are also made using various molding methods. To improve weather resistance, the absorber is often painted with another RAM, an epoxy or urethane-based coating.

The modern ski is a good example of the use of composites to make a product with unique properties (Figure 8.3). The top and sides are composed of ABS polymer that has a low T_g allowing it to remain flexible even at low temperatures. It is employed for cosmetic and containment purposes. PU forms the core and a damping layer that acts as filler and to

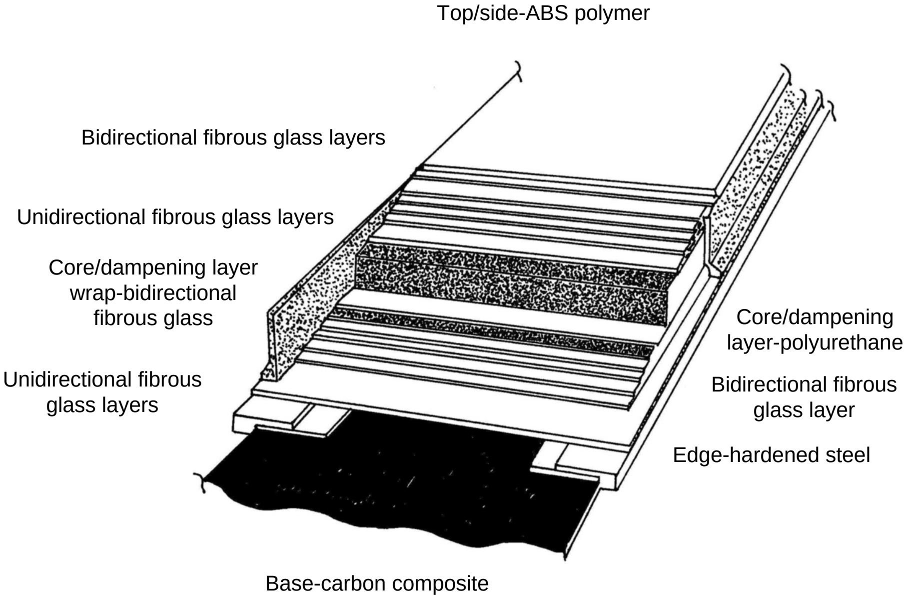

FIGURE 8.3 Cut-away illustration of a modern ski.

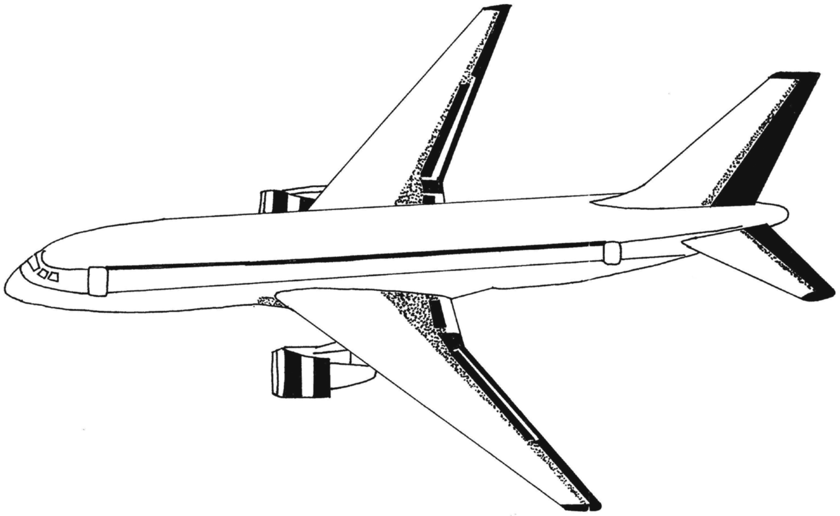

FIGURE 8.4 Use of graphite (solid) and graphite/Kevlar (TM) (dotted) composites in the exterior of the Boeing 767 passenger jet. Sites include wing tips, fixed trailing edge panels, inboard and outboard spoilers, and inboard and outboard ailerons for the large wings and for the tail wings the fin tip, rudder, elevators, stabilizer tips, and fin fixed trailing edge panels.

improve chatter resistance. The base is a carbon-impregnated matrix composite that is hard, strong, and with good abrasion resistance. There are numerous layers of fibrous glass that are a mixture of bidirectional layers to provide torsional stiffness, unidirectional layers that provide longitudinal stiffness with bidirectional layers of fiberglass acting as outer layers to the PU layers composing a torsional box. The only major noncomposite material is the hardened steel edge that assists in turning by cutting into the ice. This combination works together to give a light, flexible, shock-absorbing, tough ski.

Composites are also used extensively where light, but very strong materials are needed, such as in the construction of the new Boeing 767, where composites play a critical role in the construction of the exterior (Figure 8.4).

8.6 NANOCOMPOSITES

Nature has employed nanomaterials since the beginning of time. Much of the inorganic part of our soil is a nanomaterial with the ability to filter out particles often on a molecular or nanolevel. The driving force towards many of the nanomaterials is that they can offer new properties or enhanced properties unobtainable with "traditional" bulk materials. Along with lightweight, high strength to weight features, and small size, new properties may emerge because of the very high surface area to mass where surface atomic and molecular interactions become critical. The nanoworld is often defined for materials where some dimension is on the order of 1–100 nm. In reality, single linear polymers are nanomaterials since the diameter of the single chain is within this range. The carbon–carbon bond length is on the order of 0.15 nm or the average zigzag bond length is about 0.13 nm. While some short to moderate-length vinyl polymers have contour lengths less than 100 nm, higher molecular weight polymers have contour lengths that far exceed this. Even so, individual polymer chains fall within the realm of nanomaterials when they act independently. Since the cumulative attractive forces between chains are large, polymer chains generally act in concert with other polymer chains leading to properties that are dependent on the bulk material. Chain folding, inexact coupling, and chain branching are some of the reasons that bulk properties fall short of in theoretical properties, but with the ability to work with chains individually, strength and related properties are approaching theoretical values. Much of the nanorevolution with materials involves how to synthesize and treat materials on an individual basis as well as visualizing uses for these materials.

The ultimate strength and properties of many materials are dependent upon the intimate contact between the various members. Thus, for ceramics, nano-sized particles allow a more homogeneous structure resulting in stronger ceramic materials.

As noted earlier, nanocomposites have also been with us since almost the beginning of time. Our bones are examples of nanocomposites. The reinforcement materials are platelike crystals of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, with a continuous phase of collagen fibers. The shell of a mollusk is microlaminated containing as the reinforcement material, aragonite (a crystalline form of calcium carbonate), and the matrix is a rubbery material. Allowing nature to be a source of ideas is a continuing theme in synthetic polymer science, including modification of natural polymers. Much of the renewed interest in nanocomposite materials is the direct result of the availability of new nano-building blocks.

Within a composite material, much of the ultimate strength comes from the intimate contact the fiber has with the matrix material. Nanofibers allow more contact between the fiber (on a weight basis) and the matrix resulting is a stronger composite because of an increased fiber surface–matrix interface.

A number of inorganic or organic nanocomposites have been made. These include nanoinorganics including nanofibers from silicon nitride, titanium (IV) oxide, zirconia, alumina, titanium carbide (TiC), and tungsten carbide. It also includes the use of special clays (layered silicates) mixed with nylons to form nanocomposites. The clay layers are separated giving platelets about 1 nm thick. These nylon–clay microcomposites are used to make the air intake cover of some of the Toyota automobiles. These individual clay platelets have also been used to form nearly single layer polymer chain sheets similar to lignin. The interaction with the silicate surface encourages the polymer chains to take different arrangements. To be effective, the hydrophilic silicate surface is generally modified to accommodate the more hydrophobic common monomers and polymers.

While carbon fiber (thickness on the order of 1000 nm) composites offer very strong materials, carbon nanotubes make even stronger composites. These carbon nanotubes have aspect ratios of over 1000 (ratio of length to diameter). Further, because some carbon nanotubes are electrically conductive, composites containing them can be made to be conductive. A number of carbon nanotube matrixes have been made including using a number of engineering resins, such as polyesters, nylons, polycarbonates, and PPE.

Individual polymer chains can be more flexible than groups of chains (bulk) even when the polymer is generally considered to be rigid. This is presumably because single chains have less torsional strain imparted by near neighbors and various chain entanglements and associations are not present. Compared with carbon fibers, carbon nanotubes imbedded within a polymer matrix can withstand much greater deformations before they break. Further, nanomaterials are generally more efficient in transferring applied load from the nanomaterial to the matrix. These factors contribute to the greater strength of carbon nanotube composites.

Adhesion between the reinforcing agent and matrix is important. Some matrix materials do not adhere well with certain fibers. This is partially overcome through introduction of defects or functional groups onto the nanomaterials that act as hooks to anchor them to the matrix material.

Research with tires continues to be active with the end goals of reducing tire weight and increasing tire lifetime. For example, truck tires are now capable of running 750,000 miles with the carcass married to four tire threads. The truck tire liners weigh about 9 lb.

A decrease in weight of 50% would translate into a significant increase in mileage of 3–5 mpg. Solutions should be inexpensive employing readily available and abundant materials.

Nanocomposites are being used in tires, in particular, tire inner liners. Here, less permeable inner layers are achieved by the introduction of "clad" layers, which allow the use of a thinner inner liner, resulting in an overall lighter tire. Tire inner layers are typically derived from butyl rubber, often halogenated butyl rubber.

Exfoliate means to open, such as to open the pages of a book. New sheetlike nanocomposites are being investigated in the production of tire inner layers. These approaches focus on the use of two different materials, silicates and graphite. Most silicates and graphite exist in layered groupings.

Layered clay silicates, generally from the intermediate-grained montmorillonite kaolin clay, are often used as filler in plastics and in the production of pottery and other ceramic items. These silicates consist of the silicate sheets held together mostly by the sodium cation with lesser amounts of other metal ions, such as iron, copper, nickel, etc. There are several approaches to open these silicate layers.

The layers of kaolin clay open up when treated with water. The water acts to remove the cations that hold together the clay matrix. The resulting sheets are negatively charged, since the positively charged sodium ion is removed. These negatively charged sheets repel one another resulting in the formation of nano-sheets as shown in Figure 8.5.

Toyota works with karolin clay that has about a distance of 10 nm between the sheets. The clay is treated with caprolactam monomer that impregnates the clay sheets increasing the distance between sheets to 30–50 nm. The caprolactam monomer impregnating the silicate sheets is then polymerized giving nylon–silicate sheets. This sequence is illustrated in Figure 8.6.

Another approach utilizes highly oriented pyrolytic graphite that is separated into individual graphite sheets as the inner layer material. In each case, the nano-clay or graphite material is present in about 2% by weight in the tire inner liner.

As the inner liner is processed, the sheets align forming a clad that reduces the ability of air to flow from the tire.

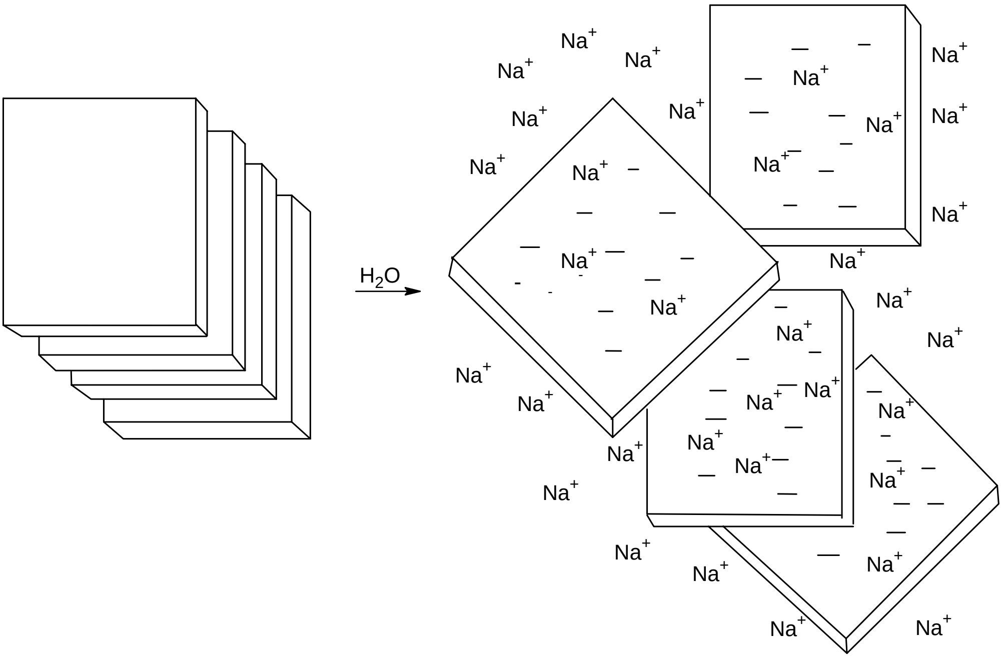

FIGURE 8.5 Formation of individual silicate sheets from exposure to water.

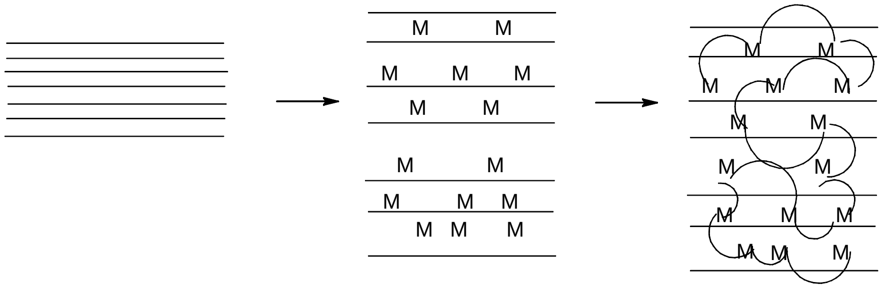

FIGURE 8.6 Silicate sheets impregnated with caprolactam monomer (M) that are eventually polymerized.

8.7 FABRICATION

Fabrication of composites can be divided into three general approaches: fibrous, structural materials including laminates, and particulates. Following is a brief description of each.

8.7.1 Processing of Fiber-Reinforced Composites

These composites exist in a wide variety of particular operations but can be briefly described in terms of filament winding, preimpregnation of the fiber with the partially cured resin, and pultrusion. Pultrusion is used to produce rods, tubes, and beams employing continuous fibers that have a constant cross-sectional shape. The fiber (as a continuous fiber bundle, weave or tow) is impregnated with a thermosetting resin and pulled through a die that shapes and establishes the fiber/resin ratio. This stock is then pulled though a curing die that can machine or cut producing the final shape, such as filled and hollow tubes, and sheets.

Continuous fiber-reinforcement preimpregnation with a polymer resin that is only partially cured is called "prepreg," which is generally delivered to the customer in the form of a tape. The customer then molds and forms the tape material into the desired shape finally curing the material without having to add any additional resin. Preparation of the prepreg can be carried out using a calendaring process. Briefly, fibers from many spools are sandwiched and pressed between sheets of resin, which is heated enough to allow impregnation but not so high as to be a fluid.

Thus, the fiber is impregnated in the partially cured resin. Depending upon the assembly the fiber is usually unidirectional, but they can also be made bidirectional or some other combination. The process of fitting the prepreg into, generally onto, the mold is called "lay-up." Generally a number of layers of prepreg are used. The lay-up may be done by hand, called hand lay-up, or done automatically, or by a combination of automatic and hand lay-up. As expected, hand lay-up is more costly but is essential where one-of-a-kind products are produced.

In *filament winding* the fiber is wound to form a desired pattern, usually but not necessarily hollow and cylindrical. The fiber is passed through the resin and then spun onto a mandrel. After the desired number of layers of fiber is added, it is cured. Prepregs can be filament wound. With the advent of new machinery, complex shapes and designs of the filament can be readily wound.

8.7.2 Structural Composites

Structural composites can be combinations of homogeneous and composite materials. Laminar composites are composed of two-dimensional sheets that generally have a preferred high-strength direction. The layers are stacked so that the preferred high-strength directions are different, generally at right angles to one another. The composition is held together by a resin. This resin can either be applied simply as an adhesive to the various surfaces of the individual sheets or the sheet can be soaked in the resin prior to laying the sheets together. In either case, the bonding is usually of a physical type. Plywood is an example of a laminar composite. Laminar fibrous glass sheets are included as part of the modern ski construction. These fibrous glass sheets are fiber-reinforced composites used together as laminar composites.

Laminar materials are produced by a variety of techniques. Coextrusion blow-molding produces a number of common food containers that consist of multilayers such as layers consisting of PP–adhesive–PVA–adhesive–adhesive–PP.

Sandwich composites are combinations where a central core(s) is generally surrounded by stronger outer layers. These composites are present in the modern ski and as high temperature stable materials used in space program. Some cores are very light, acting more or less like a filler with respect to high strength, with the strength provided by the outer panels. Simple corrugated cardboard is an example of a honeycomb core sandwich structure except that the outer paper-intense layers are not particularly strong. Even in the case of similar PE and polypropylene corrugated structures, the outer layers are not appreciatively stronger than the inner layer. In these cases the combination acts to give a lightweight but strong combination, moreover, they are not truly composites but simply exploit a common construction.

8.7.3 LAMINATING

Laminating is a simple binding together of different layers of materials. The binding materials are often thermosetting plastics and resins. The materials to be bound together can be paper, cloth, wood, or fibrous glass. These are often referred to as the reinforcing materials. Typically sheets, impregnated by a binding material, are stacked between highly polished metal plates, subjected to high pressure and heat in a hydraulic press producing a bonded product, which may be subsequently treated, depending on its final use. The end product may be flat, rod-shaped, tubular, rounded, or some other formed shape.

Reinforced plastics differ from high-pressure laminates in that little or no pressure is employed. For instance, in making formed shapes, impregnated reinforcing material is cut to a desired shape, the various layers are added to a mold, which is then heated. This process is favored over the high-pressure process because of the use of a simpler, lower cost mold and production of strain-free products.

8.7.4 PARTICULATE

Particulate composites consist of the reinforcing materials being dispersed throughout the resin. Unlike fibrous composites, the reinforcing material in particulate composites is more bulky and is not fibrous in nature. These particulates can be of many shapes and relative sizes. One of the shapes employed is that of flat rounded rectangular “disklike” particulates, which form overlapping layers, thus reinforcing one another (Figure 8.7). Particle board is an example of particulate composites. At times, there is little to differentiate between fillers and reinforcing agents. The emphasis on reinforcing agents is one where increased strength results from the presence of the reinforcing agent, whereas fillers fulfill the role of simply increasing the bulk of the material. Further, fillers are generally smaller than reinforcing agents.

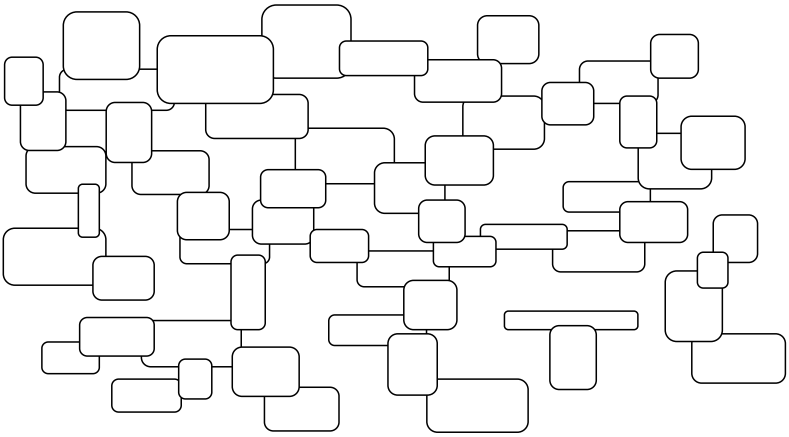

FIGURE 8.7 Composite formed from the reinforcing material being present as disklike rounded rectangular particles.

8.8 METAL–MATRIX COMPOSITES

There were driving forces for the development of composites in the 1950s and 1960s. These included the need for materials that offered greater strength/density ratios. Another driving force was the promise that the marriage between two materials would produce materials with especially high strength and elastic moduli. There was also the need for new materials to meet the demands of the aerospace industries that were rapidly developing. Applications for these materials rapidly spilled over from the aerospace and military into the general public with advancements made in one sector fueling advances in another sector. Many of the earlier advanced materials were of the clad or laminate type of composite. We will not be concerned with clad or laminate type of composites in this chapter, but rather those where the two phases are mixed together.

Space-age or advanced composites were front stage in the early 1960s with the development of high modulus whiskers and filaments. Whiskers were easily made but at the same time the science and engineering for the development of good composites had not been established. Even so, high modulus fibers from boron were successfully impregnated into epoxy forming high strength and modulus composites.

Often there is a borrowing of terms between metal-intense materials science and polymer-intense materials science where there is actually little relationship between the two. This is not the case with metal–matrix composites (MMCs). Although the materials are often different, there are a number of similarities. For polymer-intense composites, the matrix materials are organic polymers. For MMCs, the matrix materials are typically a metal or less likely an alloy. Popular metals include aluminum, copper, copper-alloys, magnesium, titanium, and “superalloys.”

In polymer–matrix composites the noncontinuous phase or reinforcement material is a fiber such as glass, carbon fibers (graphite), aromatic nylons, and a number of inorganic fibers including tungsten carbide (WC), TiC, zirconia (ZrO_2), and alumina (Al_2O_3). For the MMCs, the discontinuous phase generally exists as fibers, wires, whiskers, and particulates (Figure 8.8). A few of the discontinuous phase materials overlap with the listing given for polymer-intense composites including tungsten carbide, TiC, alumina, and graphite, but there are a number of other materials whose fibers and whiskers are employed including silicon carbide, boron carbide, coated boron, and wire materials such as niobium–titanium and

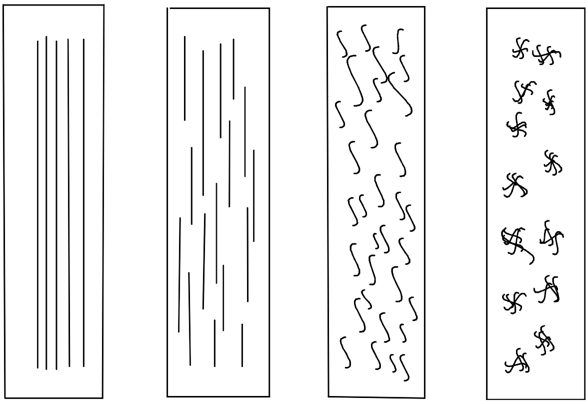

FIGURE 8.8 General forms for discontinuous phase materials, from left, are continuous or long fibers, short fibers, whiskers, and particulates.

niobium–tin, and tungsten. By volume, the amount of whiskers, wires, and particulates is greater for the MMCs.

As in the case with polymer-intense composites, the matrix and fiber must be matched for decent properties. Table 8.6 contains a listing of typical matrix–fiber mixes.

In some cases, alloy formation is possible. The term MMC is restricted to materials where such alloy formation does not occur so that there is a phase separation between the matrix and reinforcing material.

TABLE 8.6
Typical Metal Composite Matches

	Discontinuous Phase	
Matrix Material	**Form**	**Material**
Aluminum	Fibers	Boron
		Alumina
		Graphite
		Alumina–silica
		Silicon carbide
	Whiskers	Silicon carbide
	Particulates	Silicon carbide
		Boron carbide
Titanium	Fibers	Boron (coated)
		Silicon carbide
	Particulates	Titanium carbide
Copper	Fibers	Graphite
		Silicon carbide
	Particulates	Boron carbide
		Silicon carbide
		Titanium carbide
	Wires	Niobium–titanium
		Niobium–tin
Magnesium	Fibers	Alumina
		Graphite
	Particulates	Boron carbide
		Silicon carbide
	Whiskers	Silicon carbide
Superalloys	Wires	Tungsten

In comparison to single metal materials, such as aluminum, copper, and iron, MMCs generally have:

- Higher strength/density ratio
- Better fatigue and wear resistance
- Better high temperature strength
- Lower creep related to lower coefficients of thermal expansion and they are stiffer

In comparison to polymer-intense composites, MMCs offer:

No moisture absorption
Greater fire resistance
Higher use temperatures
Greater radiation resistance
Greater stiffness and strength
Higher thermal and electrical conductivities

MMCs also have some disadvantages in comparison to polymer–matrix composites. These include:

Higher cost
Newer and less developed technology and scientific understanding
Less known long-term information
Generally more complex fabrication
Greater weight

As noted above, the range of fibers employed does not precisely overlap with those employed for organic composites. Because the formation of the MMCs generally requires melting of the metal–matrix, the fibers need to have some stability to relatively high temperatures. Such fibers include graphite, silicon carbide, boron, alumina–silica, and alumina fibers. Most of these are available as continuous and discontinuous fibers. It also includes a number of thin metal wires made from tungsten, titanium, molybdenum, and beryllium.

As with organic–matrix composites, the orientation of the reinforcing material determines whether the properties will be isotropic or oriented in a preferential direction so that the strength and stiffness are greater in the direction of the fiber orientation.

There are a number of differences between organic and MMCs. These include the following. First, the MMCs can also have considerable strength themselves so their contribution to the overall strength is more important than for organic–matrix composites. Second is a greater difference between the coefficient of expansions between the reinforcing material and metal–matrix. Because of the greater use temperature differences often required for MMCs, these differences become more important. Such differences can result in large residual stresses in MMCs that may result in yielding. Third is related to the relative lower flexibility of MMCs. This leads to a greater need to be concerned with the marrying or joining of such composite parts. Many methods of joining these composite parts have been developed. Fourth is the possible greater reactivity between the matrix and fiber for MMCs. This limits combinations but has been overcome in many situations. One major approach is to place a barrier coating onto the reinforcement. For example, boron carbide is applied as a barrier coating to boron fibers allowing their use to reinforce titanium. Because these coatings can be "rubbed" away from usage, composites made from these coated reinforcements should be monitored more closely and more often.

Some effort has gone into working with copper wire containing niobium and tin looking for how to make niobium–tin alloys, which is one of the better low-temperature superconductors. Such alloys are brittle, so copper was added in the hope of creating a less brittle material. It was noticed that the copper–niobium–tin, and also simply copper–niobium combination gave a material with greater than expected strength. Because copper and niobium are not miscible, at low niobium concentrations it formed dendrites within the copper matrix allowing strong, ductile wires and rods to be drawn. As the size of the rods became smaller, niobium filaments, about only 10 nm and 30 atoms wide, across formed. If cast, the thickness is 5 μm thick, much thicker than the niobium filaments formed from the drawing down of the copper–niobium rod. This is, therefore, not only an MMC, but a metal–metal composite.

As with organic–matrix composites, advances with MMCs are continually being made to answer the call for better materials meet ever increasingly restrictive requirements and ever-broadening applications.

8.9 SUMMARY

1. Fillers are relatively inert materials that usually add bulk but when well chosen, they can enhance physical and chemical properties. Many natural and synthetic materials are used as fillers today. These include polysaccharides (cellulosics), lignin, carbon-based materials, glass, and other inorganic materials.
2. The most important reinforced materials are composites. They contain a continuous phase and a discontinuous phase. There are a variety of composites. These include particulate, structural, and fiber composites.
3. Fiber-reinforced composites contain strong fibers embedded in a continuous phase. They form the basis of many of the advanced and space-age products. They are important because they offer strength without weight and good resistance to weathering. Typical fibers are fiberous glass, carbon-based, aromatic nylons, and polyolefins. Typical resins are polyimides, polyesters, epoxys, PF, and many synthetic polymers. Applications include biomedical, boating, aerospace and outer space, sports, automotive, and industry.
4. Nanocomposites employ nanofibers that allow for much greater fiber–resin surface contact per mass of fiber and consequently they generally offer greater strength in comparison to similar non-nanocomposites.
5. Concrete and particle board are examples of particulate composites. Plywood and Formica are laminate composites.
6. MMCs offer a number of possible advantages over classical organic composites including greater radiation resistance, greater strength, greater fire resistance, greater stiffness, and higher thermal and electrical conductivities.

GLOSSARY

aspect radio Ratio of length to diameter.
comminuted Finely divided.
composites Materials that often contain strong fibers embedded in a continuous phase called a matrix or resin.
diatomaceous earth Siliceous skeletons of diatoms.
discontinuous phase Discrete filler additive, such as fibers, in a composite.
extender Term sometimes applied to inexpensive filler.
Fiberglass Trade name for fibrous glass.
fibrous filler Fiber with an aspect ratio of at least 150:1.
fibrous glass Filaments made from molten glass.

filament winding Process in which resin-impregnated continuous filaments are sound on a mandrel and the composite is cured.

filler Usually a relatively inert material used as the discontinuous additive; generally inexpensive.

Fuller's earth Diatomaceous earth.

graphite fibers Fibers made by the pyrolysis of polyacrylonitrile fibers.

lamellar Sheetlike.

laminate Composite consisting of layers adhered by a resin.

pultrusion Process in which bundles of resin-impregnated filaments are passed through an orifice and cured.

reinforced plastic Composite whose additional strength is dependent on a fibrous additive.

roving Bundle of untwisted strands.

sheet molding compound (SMC) Resin-impregnated mat.

strand Bundle of filaments.

syntactic foam Composite of resin and hollow spheres.

whiskers Single crystals used as reinforcement; extremely strong.

wood flour Attrition-ground, slightly fibrous wood particles.

EXERCISES

1. Name three unfilled polymers.
2. What is the continuous phase in wood?
3. What filler is used in Bakelite?
4. Name three laminated plastics.
5. How would you change a glass sphere from an extender to a reinforcing filler?
6. If one stirs a 5 mL volume of glass beads in 1 L of glycerol, which will have the higher viscosity, small or large beads?
7. When used in equal volume, which will have the higher viscosity: (a) a suspension of loosely packed spheres, or (b) a suspension of tightly packed spheres?
8. Why is the segmental mobility of a polymer reduced by the presence of filler?
9. What effect does filler have on the T_g?
10. Which would yield the stronger composite: (a) peanut shell flour, or (b) wood flour?
11. What is the advantage and disadvantage, if any, of α-cellulose over wood flour?
12. What filler is used in decorative laminates such as Formica table tops?
13. What are potential advantages of natural fillers?
14. What is a disadvantageous to using chipped glass as a filler in comparison to glass spheres?
15. What is the advantage of using BMC and SMC over hand lay-up techniques such as those used to make boat hulls?
16. Was carbon black always used as a reinforcing filler for tires?
17. Why does a tire filled with oxygen lose pressure faster than a tire filled with nitrogen gas?
18. You discovered a new fiber and want to see if it might make a good composite. How might you do this rapidly to a first approximation?
19. What are some natural sources of fibers?
20. Why is phase separation an important consideration in the formation of composite materials?
21. What would you expect with respect to the density of metal-composites and regular organic composites?
22. List some advantages of MMCs in comparison to classical organic composites.

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9 Naturally Occurring Polymers: Plants

There may be many ways to divide nature. One way is to divide it according to being alive, that is, self-replicating and the ability to be dead, and nonliving such as rocks and sand. Again, we have two further main divisions—plants and animals. In this, and the following chapter, we will deal with materials that are alive or were once alive. With the exception of lignin, the chemical groups that constitute animals and plants are the same on the macrolevel. Both base their ability to replicate on nucleic acids that form genes containing the blueprint for their life. But, the two classifications do differ on the major building material. Animals have proteins as their basic building material, while plants have polysaccharides as their basic building material. All of the basic building and genetic materials are polymeric.

Industrially, we are undergoing a reemergence of the use of natural polymers as feedstocks and materials in many old and new areas. Since natural polymers are typically regeneratable or renewable resources, nature continues to synthesize them as we harvest them. Many natural polymers are available in large quantities. For instance, cellulose makes up about one-third of the bulk of the entire vegetable kingdom, being present in corn stocks, tree leaves, grass, and so on. With the realization that we must conserve and regulate our chemical resources comes the awareness that we must find substitutes for resources that are not self-renewing, thus, the reason for the increased emphasis in polymer chemistry towards the use and modification of natural, renewable polymers by industry.

Natural feedstocks must serve many human purposes. Carbohydrates are valuable raw materials due to their actual or potential value. For example, protein plants are already utilizing rapidly reproducing reengineered bacteria that metabolize cellulose wastes converting it to more protein-rich bacteria that are harvested and then used as a protein source feedmeal for animals. Further, natural materials can be used in applications now largely reserved only for synthetic polymers. Sufficient natural materials are available for the supply of both food and polymer needs.

When plant or animal tissues are extracted with nonpolar solvents, a portion of the material dissolves. The components of this soluble fraction are called lipids and include fatty acids, triacylglycerols, waxes, terpenes, postagladins, and steroids. The insoluble portion contains the more polar plant components including carbohydrates, lignin, proteins, and nucleic acids.

Many renewable feedstocks are currently summarily destroyed (through leaving them to rot or burning) or utilized in a noneconomical manner. Thus, leaves are ‘‘ritualistically’’ burned each fall. A number of these seemingly useless natural materials have already been utilized as feedstock sources for industrial products with more becoming available.

Just to bring natural polymers a little closer to home, the following might be our breakfast from the viewpoint of natural polymers. This breakfast includes polymers derived from both the animal and plant kingdoms.

- *Milk*
  - Proteins
- *Fruit*
  - Starches
  - Cellulose
  - Pectin
- *Meat*
  - Bacon
- *Coffee cake*
  - Gluten
  - Starches
  - Dextrins
- *Scrambled eggs*
  - Ovalbumin
  - Conalbumin
  - Ovomucoid
  - Mucins
  - Globins

9.1 POLYSACCHARIDES

Carbohydrates are the most abundant organic compounds, constituting three-fourths of the dry weight of the plant world. They represent a great storehouse of energy as food for humans and animals. About 400 billion tons of sugars are produced annually through photosynthesis, dwarfing the production of other natural polymers, with the exception of lignin. Much of this synthesis occurs in the oceans, pointing to the importance of harnessing this untapped food, energy, and renewable feedstocks storehouse.

The potential complexity of even the simple aldohexose monosaccharides, two of which are glucose and mannose, is indicated by the presence of five different chiral centers, giving rise to 2^5 or 32 possible stereoisomeric forms of the basic structure. Although these sugars differ in specific biological activity, their gross chemical reactivities are almost identical, permitting one to often employ mixtures within chemical reactions without regard to actual structure. Their physical properties are also almost the same, again allowing for the mixing of these structures with little loss in physical behavior.

Carbohydrates are diverse with respect to occurrence and size. Familiar mono and disaccharides include glucose, fructose, sucrose (table sugar), cellobiose, and mannose. Familiar polysaccharides are listed in Table 9.1 along with their source, purity, and molecular weight range.

TABLE 9.1
Naturally Occurring Polysaccharides

Polysaccharide	Source	Monomeric Sugar Unit(s)	Structure	Mol Wt.
Amylopectin	Corn, potatoes	D-glucose	Branched	10^6–10^7
Amylose	Plants	D-glucose	Linear	10–10^6
Chitin	Animals	2-Acetamidoglucose		
Glucogen	Animals(muscles)	D-glucose	Branched	$> 10^8$
Inulin	Arichokes	D-fructose	(Largely) linear	10^3–10^6
Mannan	Yeast	D-mannose	Linear	—
Cellulose	Plants	D-glucose	Linear (2D)	10^6
Xylan	Plants	D-xylose	(Largely) linear	—
Lichenan	Iceland moss	D-glucose	Linear	10^5
Galactan	Plants	D-galactose	Branched	10^4
Arabinoxylan	Cereal grains	L-arabinofuranose linked to xylose chain	Branched	$>10^4$
Galactomannans	Seed mucilages	D-mannopyranose chains with D-galactose side chains	(Largely) linear	10^5
Arabinogalactan	Lupin, soybean, coffee beans	D-galactopyranose chain, side chain galactose, arabinose	Branched	10^5
Carrageenan	Seaweeds	Complex	Linear	10^5–10^6
Agar	Red seaweeds	Complex	Linear	—
Alginic	Brown seaweeds	β-D-mannuronic acid and α-L-guluronic acid	Linear	—

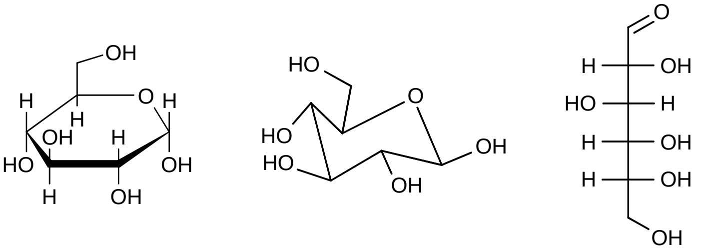


FIGURE 9.1 Beta-D-glucose using the Boeseken–Haworth, chair, and linear (from left to right) representations.

The most important polysaccharides are cellulose and starch. These can be hydrolyzed to lower molecular weight carbohydrates (oligosaccharides) and finally to D-glucose. Glucose is the building block for many carbohydrate polymers. It is called a monosaccharide as it cannot be further hydrolyzed while retaining the ring. Three major types of representations are used to reflect saccharide structures. These are given in Figure 9.1. Here, we will mainly use the Boeseken–Haworth planer hexagonal rings to represent polysaccharide structures.

Kobayashi and others have pioneered in the synthesis of polysaccharides, which is particularly difficult because of the need to control the stereochemistry of the anomeric carbon and regioselectivity of the many hydroxyl groups with similar reactivities. This problem was initially solved by employing enzymatic polymerizations with the synthesis of cellulose in 1991 when the cellobiosyl fluoride monomer was subjected to polycondensation catalyzed by cellulase, a hydrolysis enzyme of cellulose. Prior to this, cellulose was formed only in living cells as a high-order material with parallel-chain alignment. The synthesis of other natural polysaccharides followed. Chitin, the most abundant animal-derived polysaccharide, was synthesized using a ring-opening polyaddition of an oxazoline monomer catalyzed by the chitinase enzyme. Chondroitin and hyaluronan, both glycosaminoglycan heteropolysaccharides, have been synthesized using hyaluronidase enzymes. In these reactions, the hydrolase acted to catalyze bond formation producing polymers but not the hydrolysis to break the bonds.

Such enzymatic catalyzed polycondensations have allowed the synthesis of a number of "natural" polysaccharides, but has also allowed the production of "nonnatural" polysaccharides such as cellulose–xylan hybrids and functionalized hyaluronan, chondroitin sulfate, and chondroitin. Such work illustrates the ever-narrowing bridge between natural and synthetic polymers and polymer syntheses.

9.2 CELLULOSE

Cellulose was originally "discovered" by Payen in 1838. For thousands of years impure cellulose formed the basis of much of our fuel and construction systems in the form of wood, lumber (cut wood), and dried plant material; served as the vehicle for the retention and conveying of knowledge and information in the form of paper; and clothing in the form of cotton, ramie, and flax. Much of the earliest research was aimed at developing stronger materials with greater resistance to natural elements (including cleaning) and to improve dyeability so that the color of choice by common people for their clothing material could be other than a drab white. In fact, the dyeing of textile materials, mainly cotton, was a major driving force in the expansion of the chemical industry in the latter part of the 19th century.

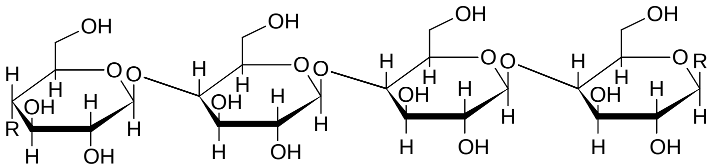
Cellulose is a polydisperse polymer with an average DP in the general range of 3,500–36,000. Native cellulose is widely distributed in nature and is the principle constituent of cotton, kapok, flax, hemp, jute, ramie, and wood. Cellulose comprises more than one-third of all vegetable matter and is the world's largest renewable resource. Approximately 50 billion tons are produced annually by land plants, which absorb 4×10^{20} cal of solar energy. Natural cotton fibers, which are the seed hairs from *Gossypium*, are about 1–2 cm in length and about 5–20 μm in diameter. The molecules in native cellulose are present in threadlike strands or bundles called fibrils. Cellulose is not found in a pure form, but is rather associated with other materials such as lignin and hemicelluloses. Cotton contains the purest form of cellulose. Wood, in its dry state, contains 40%–55% cellulose, 15%–35% lignin, and 25%–40% hemicelluose. Plant pulp is the major source of commercial cellulose. The extraction of cellulose from plants is called pulping, which is achieved using thermomechanical, chemical, or mechanical approaches. Plant pulp, from wood, is the major source of nontextile fibers, whereas cotton is the major source of textile fibers.

Cellulose is used in the textile industry in cloths, cartons, carpets, blankets, and sheets. Paper is made from cellulose. Cellulosic fibers are also used as filter materials in artificial kidneys and reverse osmosis though today most kidney dialysis units use cuprammonium tubular films derived from cellulose rather than cellulose itself.

While the celluloses are often largely linear, they are not soluble in water because of the presence of strong intermolecular hydrogen bonding and sometimes the presence of a small amount of cross-linking. Highly ordered crystalline cellulose has a density as high as 1.63 g/cm^3, while amorphous cellulose has a density as low as 1.47 g/cm^3. High molecular weight native cellulose, which is insoluble in 17.5% aqueous sodium hydroxide, is called α-cellulose. The fraction that is soluble in 17.5% sodium hydroxide but insoluble in 8% solution is called β-cellulose, and that which is soluble in 8% sodium hydroxide is called γ-cellulose.

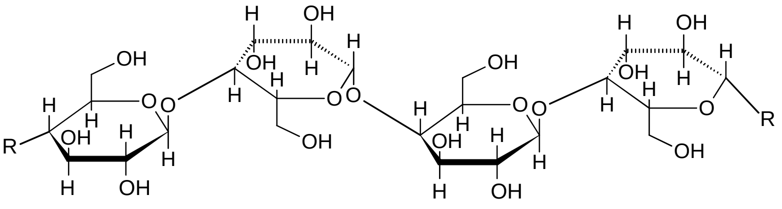
Strong basic solutions, such as sodium hydroxide, penetrate the crystalline lattice of α-cellulose producing an alkoxide called alkali or soda cellulose. Mercerized cotton is produced by aqueous extraction of the sodium hydroxide.

Most linear celluloses may be dissolved in solvents capable of breaking the strong hydrogen bonds. These solutions include aqueous solutions of inorganic acids, calcium thiocyanate, zinc chloride, lithium chloride, ammonium hydroxide, iron sodium tartrate, and cadmium or copper ammonium hydroxide (Schweitzer's reagent). The product precipitated by the addition of a nonsolvent to these solutions is a highly amorphous, regenerated cellulose.



(9.1)

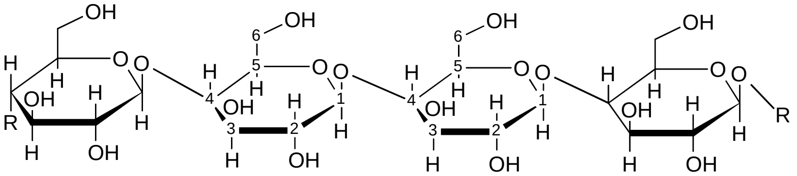
Cellulose



(9.2)

Cellulose 3D structure

Structure 9.1 is most commonly employed as a description of the repeat unit of cellulose but structure 9.2 more nearly represents the actual three-dimensional structure with each D-glucosyl unit rotated 180°. We will employ a combination of these two structural representations. Numbering is shown in structure 9.3 and the type of linkage is written as 1 → 4 since the units are connected through oxygen atoms contained in carbon 1 and 4 as shown in structure 9.3.



(9.3)

We also call the linkage, by agreement with the anomeric nature of the particular carbons involved in linking together the glucosyl units, a beta or β-linkage. Thus, this linkage is a β 1 → 4 linkage. The other similar 1 → 4 linkage found in starch is called an alpha or α-linkage. The geometric consequence of this difference is great. The linear arrangement of cellulose with the β-linkage gives an arrangement where the hydroxyl groups reside somewhat uniformly on the outside of the chain allowing close contact and ready hydrogen-bond formation between chains. This arrangement results in a tough, insoluble, rigid, and fibrous material that is well suited as cell wall material for plants. By comparison, the α-linkage of starch (namely amylose) results in a helical structure where the hydrogen bonding is both interior and exterior to the chain allowing better wettability. This difference in bonding also results in one material being a "meal" for humans (the α-linkage), whereas the other is a meal for termites. The reason for this is the difference in the composition of enzymes present in the two species—humans with the enzyme capability to lyse or break α-linkages, and for cows, termites, and other species that contain symbiotic bacteria in their digestive systems, which furnish the enzymes capable to digest or break the β-glucoside linkages.

While the stomach acid in humans and most animals can degrade polysaccharides to the energy-giving monomeric units, this is not efficient unless a specific enzyme, which is normally present in the gut, allows the ready and rapid degradation of polysaccharide. Since these enzymes are somewhat specific, their ability to degrade is polysaccharide-specific.

The various crystalline modifications have different physical properties and chemical reactivities. These variations are a consequence of the properties varying according to plant source, location in the plant, plant age, season, seasonal conditions, treatment, etc. Thus, in general, bulk properties of polysaccharides are generally measured with average values and tendencies given. These variations are not important for most applications but possibly are important for specific biological applications where the polysaccharide is employed as a drug, within a drug delivery system, or as a biomaterial within the body.

9.2.1 Paper

It is believed that paper was invented by Ts'ai in China around the 2nd century AD. The original paper was a mixture of bark and hemp. Paper was first produced in the United States by William Rittenhouse in Germantown, Pennsylvania, in 1690 and was made from rags. Paper was named after the papyrus plant, *Cyperus papyrus*.

Paper comes in many forms with many uses. The book you are reading is made from paper, we have paper plates, paper napkins, newspapers and magazines, cardboard boxes, in fact the amount of paper items is probably over twice, by weight, that of all the synthetic polymers combined. About 30% of the paper is used for writing and printing. The rest is mainly used for tissues, toweling, and packaging. If you rip a piece of ordinary paper you will see that it consists of small fibers. Most of these cellulosic fibers are randomly oriented, but a small percentage are preferentially oriented in one direction because the paper is made from a cellulose-derived watery slurry with the water largely removed through use of heated rollers that somewhat orient the fibers.

Modern paper is made from wood pulp, largely cellulose, which is obtained by the removal of lignin from debarked wood chips by use of chemical treatments with sodium hydroxide, sodium sulfite, or sodium sulfate. Newsprint and paperboard, which is thicker than paper, often contains a greater amount of residual lignin.

Wood is almost entirely composed of cellulose and lignin. In the simplest paper-making scheme, the wood is chopped, actually torn, into smaller fibrous particles as it is pressed against a rapidly moving pulpstone. A stream of water washes the fibers away dissolving much of the water-soluble lignin. The insoluble cellulosic fibers are concentrated into a paste called pulp. The pulp is layered into thin sheets and rollers are used to both squeeze out much of the water and assist in achieving paper of uniform thickness. The paper obtained is not very white. It is also not very strong. The remaining lignin is somewhat acidic (lignin contains acidic phenolic groups that hydrolyze to give a weakly acidic aqueous solution) that causes the hydrolytic breakdown of the cellulose. Most of the newsprint is of this type or it is a regenerated, reused paper.

Pulping processes are designed to remove the nonsaccharide lignin portion of wood, which constitutes about 25% of the dry weight. The remaining is mostly cellulose with about 25% hemicellulose (noncellulose cell wall polysaccharides that are easily extracted by dilute aqueous base solutions). Pulping procedures can be generally classified as semichemical, chemical, and semimechanical. In semimechanical pulping, the wood is treated with water or sulfate, bisulfite, or bicarbonate solution that softens the lignin. The pulp is then ground or shredded to remove much of the lignin giving purified or enriched cellulose content. The semichemical process is similar but the time taken for digestion is longer and digesting solutions are more concentrated giving a product with less lignin, and the overall yield of cellulose-intense material is lowered by 70%–80%. Further, some degradation of cellulose occurs.

Most paper is produced by the chemical process where chemicals are employed to solubilize and remove most of the lignin. Although overall yields are lower than the other two main processes, the product gives good quality writing and printing paper. Three main chemical processes are used for this purpose: (1) in the soda process extracting solutions containing about 25% sodium hydroxide and 2.4% sodium carbonate are used; (2) in the sulfite process the extracting solution contains a mixture of calcium dihydrogen sulfite and sulfur dioxide; (3) the sulfide process utilizes sodium hydroxide, sodium monosulfide, and sodium carbonate in the extracting solution.

After the chemical treatment, the pulped wood is removed, washed, and screened. Unbleached, brown-colored paper is made directly for this material. Most whitened or bleached paper is made by the treatment of the pulp with chlorine, chlorine dioxide, hypochlorite, and/or alkaline extraction. In general, sulfate-pulped paper is darker and requires more bleaching and alkaline extraction to give a "white" pulp.

The *sulfide process*, also called the kraft process (the term "kraft" comes from the Swedish word for strong since stronger paper is produced), is more commonly used. The kraft process is favored over the sulfite treatment because of environmental considerations. On the other hand, the sulfite process employs more chemicals that must be disposed of—particularly mercaptans (RSHs) that are quite odorous. Research on reclaiming and recycling pulping chemicals still continues.

If pure cellulose was solely used to make paper, the fiber mat would be water soluble with only particle surface polar groups and internal hydrogen bonding acting to hold the fibers together. White pigments such as clay and titanium dioxide are added to help "cement" the fibers together and fill voids producing a firm, white writing surface. This often occurs as part of an overall coating process.

Most paper is coated to provide added strength and smoothness. The coating is basically an inexpensive paint that contains a pigment and a small amount of polymeric binder. Unlike most painted surfaces, most paper products are manufactured with a short lifetime in mind with moderate performance requirements. Typical pigments are inexpensive, low-refractive index materials such as platelike clay and ground natural calcium carbonate. Titanium dioxide is used only when high opacity is required. The binder may be a starch or latex or a combination of these. The latexes are usually copolymers of styrene, butadiene, acrylic, and vinyl acetate. Other additives and coloring agents may also be added for special performance papers. Resins in the form of surface-coating agents and other special surface treatments (such as coating with polypropylene and PE) are used for paper products intended for special uses such as milk cartons, ice-cream cartons, light building materials, and drinking cups. The cellulose supplies the majority of the weight (typically about 90%) and strength with the special additives and coatings providing special properties needed for the intended use.

A better understanding of the nature of paper and films made from synthetic polymers such as PE can be seen when considering why authorities worry about anthrax escaping from a paper envelope yet confining it in a plastic container with no fear of it escaping. When you hold good paper up to the light or tear it you will observe the tiny fibers that compose paper. Even when these fibers appear tiny, they are very large in comparison to individual polymer chains, be they cellulose or PE. The web of chains for cellulose eventually composes the cellulose fibers that are put together physically forming paper with lots of "unoccupied" spaces between the fibers, which are of sufficient size to allow the escape of the anthrax. In contrast, PE film has little unoccupied spaces between the individual chains with the entire film composed of these individual chains and no large spaces so that the anthrax cannot escape.

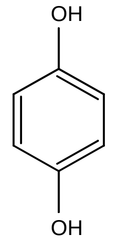
Recycling of paper continues. Today, up to about one-half of our paper products are recycled and this fraction is increasing as we do a better job of collecting and recycling paper products.

9.3 CELLULOSE-REGENERATING PROCESSES

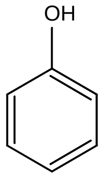
Cellulose is sometimes used in its original or native form as fibers for textile and paper, but is often modified through dissolving and reprecipitation or through chemical reaction. The *xanthate viscose process*, which is used for the production of rayon and cellophane, is the most widely used regeneration process. The cellulose obtained by the removal of lignin from wood pulp is converted to alkali cellulose. The addition of carbon disulfide to the latter produces cellulose xanthate.

Although terminal hydroxyl and aldehyde groups, such as those present in cellobiose, are also present in cellulose, they are not significant because they are only present at the ends of very long chains.

The hydroxyl groups are not equivalent. For instance, the pK_a values of the two ring hydroxyl groups are about 10 and 12, which are approximately the same as the hydroxyl groups on hydroquinone and the first value about the same as the hydroxyl group on phenol. The pK_a value of the nonring or methylene hydroxyl group is about 14, the same as found for typical aliphatic hydroxyl groups 9.

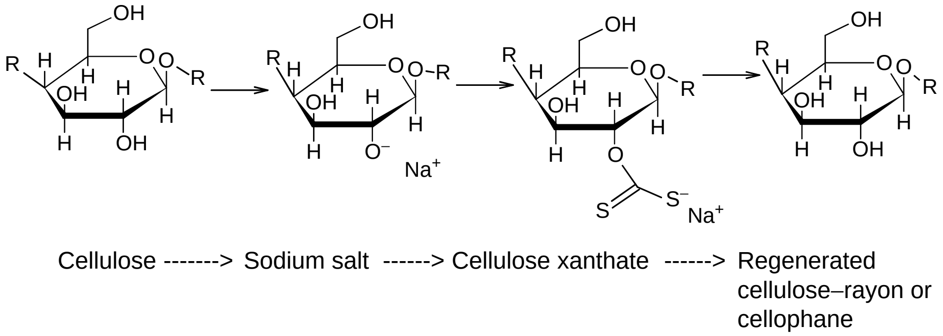


Hydroquinone (9.4)



Phenol (9.5)

In the cellulose-regenerating process, sodium hydroxide is initially added such that approximately one hydrogen, believed to be predominately a mixture of the hydroxyl groups on carbons 2 and 3, is replaced by the sodium ion. This is followed by treatment with carbon disulfide forming cellulose xanthate, which is eventually rechanged back again, regenerated, to cellulose. This sequence is depicted in structure 9.6.



(9.6)

The orange-colored xanthate solution, or viscose, is allowed to age and then extruded as a filament through holes in a spinneret. The filament is converted to cellulose when it is immersed in a solution of sodium bisulfite, zinc II sulfate, and dilute sulfuric acid. The tenacity, or tensile strength, of this regenerated cellulose is increased by a stretching process that reorients the molecules so that the amorphous polymer becomes more crystalline. Cellophane is produced by passing the viscose solution through a slit into an acid bath. Important noncellulosic textile fibers are given in Table 9.2 and a listing of important cellulosic textile fibers is given in Table 9.3.

Since an average of only one hydroxyl group in each repeating glucose unit in cellulose reacts with carbon disulfide, the xanthate product is said to have a degree of substitution (DS) of one out of a potential DS of three.

Partially degraded cellulose is called hydrocellulose or oxycellulose, depending on the agent used for degradation. The term holocellulose is used to describe the residue after lignin has been removed from wood pulp.

Control of the regeneration conditions, together with a wide variety of modification, allows the production of a wide variety of products including high-wet modulus fibers, hollow fibers, crimped fibers, and flame-resistant fibers. While almost all rayon is produced using the

TABLE 9.2
Noncellulosic Textile Fibers

Fiber Name	Definition	Properties	Typical Uses	Patent Names (Sample)
Acrylic	Acrylonitrile units, 85% or more	Warm, lightweight, shape-retentive, resilient, quick-drying, resistant to sunlight	Carpeting, sweaters, skirts, baby cloths, socks, slacks, blankets, draperies	Orlon
Modacrylic	Acrylonitrile units, 35%–85%	Resilient, softenable at low temps., easy to dye, abrasion-resistant, quick drying, shape-retentive, resistant to acids, bases	Simulated fur, scatter rugs, stuffed toys, paint rollers, carpets, hairpieces, wigs fleece fabrics	Verel, Dynel
Polyester	Dihydric acid–terephthalic acid ester, 85% or more	Strong, resistant to stretching and shrinking, easy to dye, quick drying, resistant to most chemicals, easily washed, abrasion-resistant; retains heat-set (permanent press)	Permanent press ware, skirts, slacks, underwear, blouses, rope, fish nets, tire cord, sails, thread	Vycron, Kodel, Fortrel, Chemstrand Dacron
Spandex	Segmented polyurethane, 85% or more	Light, soft, smooth, resistant to body oils, can be stretched often, retain original form, abrasion-resistant	Girdles, bras, slacks bathing suits, pillows	Lycra
Nylon	Reoccurring amide groups	Very strong, elastic, lustrous, easy to wash, abrasion-resistant, smooth, resilient, low moisture absorbency, recovers quickly from extensions	Carpeting, upholstery, blouses, tents, sails, hosiery, suits, tire cord, fabrics, rope, nets	Caprolan, Astroturf, Celanese polyester

TABLE 9.3
Cellulosic Textile Fibers

Fiber Name	Definition	Properties	Typical Uses	Patent Names (Sample)
Rayon	Regenerated cellulose with less than 15% OH substituted	Highly absorbent, soft, comfortable, easy to dye, good drapability	Dresses, suits, slacks, blouses, coats, tire cord, ties, curtains, blankets	Avril, Cuprel, Zantel
Acetate	Not less than 92% OH groups acetylated	Fast-drying, supple, wide range of dyeability, shrink-resistant	Dresses, shirts, slacks, draperies, upholstery, cigarette filters	Estron, Celanese acetate
Triacetate	Derived from cellulose by combining with acetic acid and/or acetic anhydride	Resistant to shrinking, wrinkling, and fading; easily washed	Skirts, dresses, sportswear	Arnel

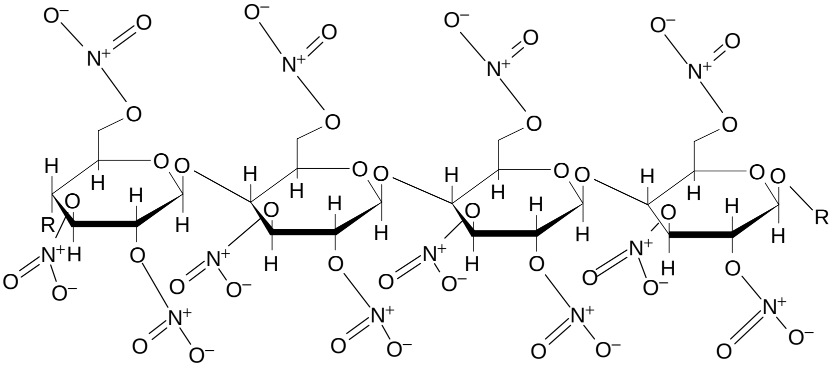
viscose process, some fibers are still produced using the cuprammionium process whereby cellulose is dissolved in an ammonium–copper II–alkaline solution.

9.4 ESTERS AND ETHERS OF CELLULOSE

It must be remembered that the three hydroxyl groups on the individual cellulose rings are not equivalent. The two ring hydroxyls are acidic with pK_a similar to hydroquinone while the third nonring hydroxyl group is similar to an aliphatic hydroxyl in acidity. Thus, in an aqueous sodium hydroxide solution the two ring hydroxyls will be deprotonated at high pHs. In theory, all three hydroxyl groups can undergo reaction, but in reality less than three hydroxyl groups undergo reaction either because of reactivity restrictions and/or steric limitations. With many of the electrophilic and/or nucleophilic reactions, it is the ring hydroxyls that are favored to react initially. The average number of hydroxyl groups that are reacted is often given as the DS.

9.4.1 INORGANIC ESTERS

The most widely used "inorganic ester" of cellulose is cellulose nitrate (CN), also called nitrocellulose or gun cotton. Celluloid is produced from a mixture of CN and camphor. It was first made in 1833 when cellulose-containing linen, paper, or sawdust was reacted with concentrated nitric acid. It was the first "synthetic" cellulose product that was recognized. Initially, CN was used as a military explosive and improvements allowed the manufacture of smokeless powder. A representation of CN is given in structure 9.7.



(9.7)

Cellulose nitrate

The development of solvents and plastizing agents for CN led to the production of many new and useful nonexplosive products. Celluloid was produced in 1870 from a mixture of CN and camphor. Films were cast from solution and served as the basis for the original still and motion pictures. After World War I the development of stable CN solutions allowed the production of fast-drying lacquer coatings.

Although CN played an important role in the development of technology, its importance today is greatly diminished. It is still used as a protective and decorative lacquer coating, in gravure inks, in water-based emulsions as coatings, and to a lesser extent in plastics and films.

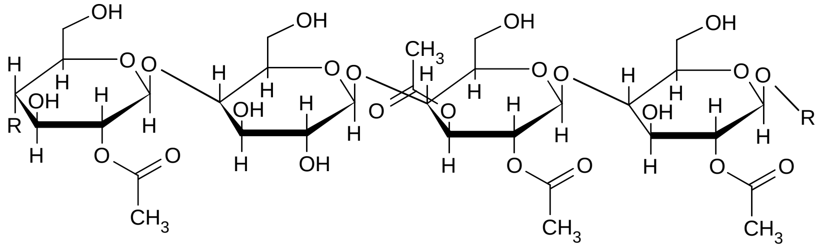
Cellulose phosphate esters are produced from reaction with phosphoric acid and urea. The products are used to treat hypercalciuria because of its ability to bind calcium. It has also been used for the treatment of kidney stones.

9.4.2 ORGANIC ESTERS

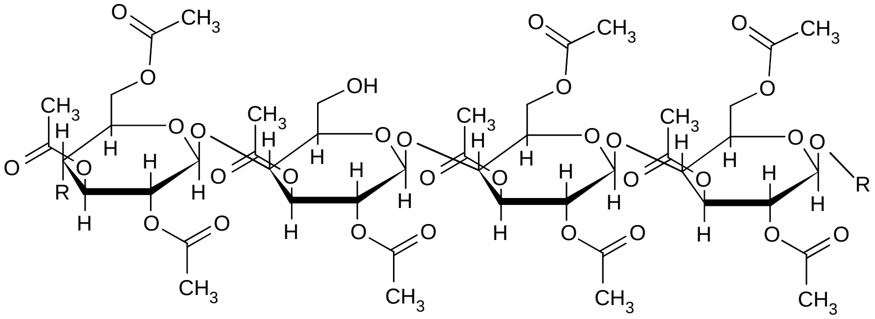
The most important cellulose ester is cellulose acetate because of its use in fibers and plastics. They were first made in 1865 by heating cotton with acetic anhydride. During World War I, cellulose acetate replaced the highly flammable CN coating on airplane wings and fuselage fabrics.

Varying properties are achieved by varying the amount of substitution. The melting point generally decreases with decreasing acetylation. Lower acetylation gives products with greater solubility in polar solvents and corresponding decreased moisture resistance. Cellulose acetate is made using heterogeneous solutions containing the cellulose, sulfuric acid as the catalyst, and acetic anhydride in acetic acid. Reaction occurs beginning with the surface or outermost layer and continues on layer by layer as new areas are exposed. When more homogeneous modification is desired, preswelling of the cellulose in water, aqueous acetic acid solutions, or in glacial acetic acid is carried out.

Reaction occurs differently since there are two "types" of hydroxyl groups (as noted earlier), the two ring hydroxyls and the methylene hydroxyl. In the typical formation of esters, such as cellulose acetate, the ring hydroxyl groups are acetylated initially (structure 9.8) prior to the C-6 exocyclic hydroxyl. Under appropriate reaction conditions, reaction continues to almost completion with the esterification of all three hydroxyl groups (structure 9.9). In triacetate products, only small amounts (on the order of 1%) of the hydroxyls remain free, and of these generally about 80% are C-6 hydroxyl.



(9.8)



(9.9)

The most common commercial products are the triacetate (DS approaching 3) and the secondary acetate (DS about 2.45).

While other organic esters are commercially available, namely cellulose butyrate and cellulose propionate, by far the most widely used is cellulose acetate, which is available as plastics, in films, sheets, fibers, and lacquers. Cellulose acetate is used in the manufacture of display packaging and as extruded film for decorative signs, and to coat a variety of fibers. Injected molded products include toothbrush handles, combs, and brushes. It is also used in lacquers and protective coatings for metal, glass, and paper. Cellulose acetate films are used in reverse osmosis to purify blood, fruit juices, and brackish water. Some eyeglass frames are made of cellulose acetate. Biodegradable films, sponges, and microencapsulation of drugs for controlled release also utilize cellulose acetate. Cellulose triacetate is used for photographic film bases. Numerous continuous filament yarns, tows, staples, and fibers are made from cellulose acetate. The precise form of filament produced is controlled by a number of factors including the shape of the die.

As in all large-scale industrial processes, the formation of the cellulose esters involves recovery of materials. Acetic anhydride is generally employed. After reaction, acetic acid and solvent are recovered. The recovered acetic acid is employed in the production of additional acetic anhydride. The recovered solvent is also reintroduced after treatment.

Cellulose esters are used as plastics for the formation by extrusion of films and sheets and by injection molding of parts. They are thermoplastics and can be fabricated employing most of the usual techniques of (largely compression and injection) molding, extrusion, and casting. Cellulose ester plastics are noted for their toughness, smoothness, clarity, and surface gloss.

Acetate fiber is the generic name of a fiber that is partially acetylated cellulose. They are also known as cellulose acetate and triacetate fibers. They are nontoxic and generally nonallergic, and so are ideal from this aspect as clothing material.

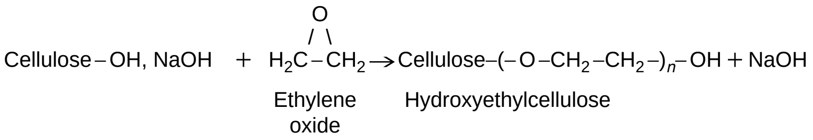
Although acetate and triacetate differ only moderately in the degree of acetylation, this small difference accounts for differences in the physical and chemical behavior for these two fiber materials. Triacetate fiber is hydrophobic and application of heat can bring about a high degree of crystallinity that is employed to "lock-in" desired shapes (such as permanent press). Cellulose acetate fibers have a low degree of crystallinity and orientation even after heat treatment. Both readily develop static charge and thus antistatic surfaces are typically employed to clothing made from them.

For clothing application there are a number of important performance properties that depend on the form of the textile. These properties include wrinkle resistance, drape, strength, and flexibility. These properties are determined using ASTM tests that often involve stress–strain behavior. Thus, the ability of a textile to resist deformation under an applied tensile stress is measured in terms of its modulus of elasticity or Young's modulus. As with any area of materials, specialty tests are developed to measure certain properties. Some of these are standard tests like the aforementioned Young's modulus while others are specific to the desired property measured for a specific application. For instance, resistance to slightly acidic and basic conditions is important for textiles that are to be laundered. Again, these are tested employing standard test procedures. In general, triacetate materials are more resistant than acetate textiles to basic conditions. Both are resistant to mild acid solutions but degrade when exposed to strong mineral acids. Further, behavior to various dry-cleaning agents is important. As the nature of dry-cleaning agents changes, additional testing and modification in the fabric treatments are undertaken to offer a textile that stands up well to the currently employed cleaning procedures. Again, both are stable to perchloroethylene dry-cleaning solvents but can soften when exposed to trichloroethylene for extended treatment. Their stability to light is dependent upon the wavelength, humidity present, etc. In general, they offer a comparable stability to light as that offered by cotton and rayon.

Although cellulose acetates are the most important cellulose ester, they suffer by their relatively poor moisture sensitivity, limited compatibility with other synthetic resins, and a relatively high processing temperature.

9.4.3 ORGANIC ETHERS

Reaction with an epoxide such as ethylene oxide under alkaline conditions gives hydroxyethylcellulose (HEC).



$$\text{Cellulose–OH, NaOH} + \underset{\substack{\text{Ethylene}\\ \text{oxide}}}{\overset{\overset{\text{O}}{/\ \backslash}}{\text{H}_2\text{C–CH}_2}} \rightarrow \underset{\text{Hydroxyethylcellulose}}{\text{Cellulose–(–O–CH}_2\text{–CH}_2\text{–)}_n\text{–OH}} + \text{NaOH} \qquad (9.10)$$

This is an S_N2 reaction, which is proportional to the concentration of the epoxide and alkali cellulose, but since the base is regenerated, it is first order in epoxide.

$$\text{Rate} = k[\text{epoxide}] \qquad (9.11)$$

Industrially, HECs with DS values below 2 are used. Low DS materials (to about 0.5) are soluble only in basic solutions while those with DS values of about 1.5 are water soluble. Concentrated solutions of HEC are pseudoplastic with their apparent viscosities decreasing with increased rates of shear. Dilute solutions approach being Newtonian in their flow properties, even under a wide range of shear rates.

HEC is used as a protective colloid in latex coatings, and pharmaceutical emulsions; a film former for fabric finishes, fiberous glass, and in aerosol starches; thickener for adhesives, latex coatings, toothpaste, shampoos and hair dressings, cosmetic creams and lotions, inks and joint cements; lubricant for wallpaper adhesives and in pharmaceutical gels; and a water binding for cements, plastics, texture coatings, ceramic glazes, and in printing inks.

Sodium carboxymethylcellulose is formed by the reaction of sodium chloroacetate with basic cellulose solutions. The sodium form of carboxymethylcellulose is known as CMC or as a food grade product as cellulose gum. It is soluble in both hot and cold water.

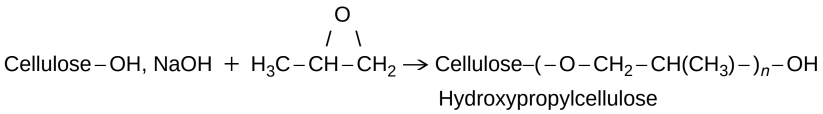
$$\text{Cellulose–OH, NaOH} + \text{Cl–CH}_2\text{COONa} \rightarrow \underset{\text{Sodium carboxymethylcellulose}}{\text{Cellulose–O–CH}_2\text{–COONa}} \qquad (9.12)$$

The most widely used cellulose gums have DS values of about 0.65–1.0. CMCs are used as thickening, binding, stabilizing, and film-forming agents.

Carboxymethylhydroxyethylcellulose (CMHEC) is synthesized from the reaction of hydroxethylcellulose with sodium chloroacetate. The product is a mixed ether. It has properties similar to both CMC and HEC. Like CMC it exhibits a high water-binding ability and good flocculating action on suspended solids but it is more compatible than CMC with salts. It forms ionic cross-links in the presence of salt solutions containing multivalent cations allowing its viscosity to be greatly increased by the presence of such cations. Solutions can be gelled by addition of solutions of aluminum and iron. It is a water-soluble material used in oil recovery and hydraulic fracturing fluids.

Methyl and hydroxyalkylmethylcelluloses are nonionic polymers soluble in cool water. Methylcellulose (MC), hydroxyethylmethylcellulose (HEMC), and hydroxypropylmethylcellulose (HPMC) do not interact with cations forming insoluble salts, but electrolytes that compete with MC for water can cause precipitation.

Hydroxypropylcellulose (HPC) is a thermoplastic nonionic cellulose ester that is soluble in both water and a number of organic liquids. It is synthesized through reaction of the basic cellulose slurried with propylene oxide.



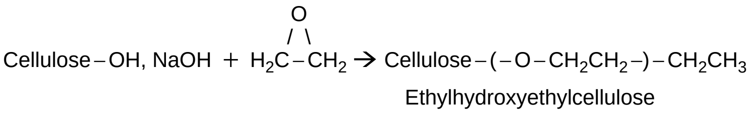
$$\text{Cellulose–OH, NaOH} + \text{H}_3\text{C–}\overset{\overset{\text{O}}{/\ \ \backslash}}{\text{CH–CH}_2} \rightarrow \underset{\text{Hydroxypropylcellulose}}{\text{Cellulose–(–O–CH}_2\text{–CH(CH}_3\text{)–)}_n\text{–OH}} \qquad (9.13)$$

MC is formed from the reaction of basic cellulose with chloromethane.

$$\text{Cellulose}-\text{OH, NaOH}+\text{CH}_3\text{Cl}\rightarrow\underset{\text{Methylcellulose}}{\text{Cellulose}-\text{O}-\text{CH}_3}\qquad(9.14)$$

MC is used as an adhesive; in ceramics to provide water retention and lubricity; in cosmetics to control rheological properties and in the stabilization of foams; in foods as a binder, emulsifier, stabilizer, thickener, and suspending agent; in paints, paper products, plywood as a rheology control for the adhesive; in inks, and in textiles as a binder, and for coatings.

Ethylhydroxyethylcellulose (EHEC) is a nonionic mixed ether available in a wide variety of substitutions with corresponding variations in aqueous and organic liquid solubilities. It is compatible with many oils, resins, and plasticizers along with other polymers such as nitrocellulose. EHEC is synthesized through a two-step process beginning with the formation of the HEC-like product through reaction between the basic cellulose and ethylene oxide. The second step involves further reaction with ethyl chloride.



$$\text{Cellulose}-\text{OH, NaOH}+\text{H}_2\overset{\text{O}}{\text{C}-\text{C}}\text{H}_2\rightarrow\underset{\text{Ethylhydroxyethylcellulose}}{\text{Cellulose}-(-\text{O}-\text{CH}_2\text{CH}_2-)-\text{CH}_2\text{CH}_3}\qquad(9.15)$$

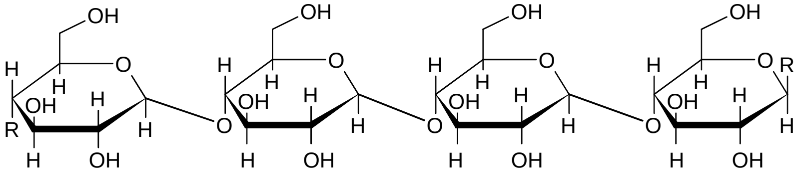
The water-soluble EHEC is used in water-borne paints, pastes, polymer dispersions, ceramics and cosmetics, and pharmaceuticals,whereas organic soluble EHEC is used in inks, lacquers, and as coatings.

Cellulose undergoes reaction with activated ethylenic compounds such as acrylonitrile giving cyanoethylcellulose via a Michael addition.

$$\text{Cellulose}-\text{OH}+\text{H}_2\text{C}=\text{CHCN}\rightarrow\text{Cellulose}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CN}\qquad(9.16)$$

9.5 STARCH

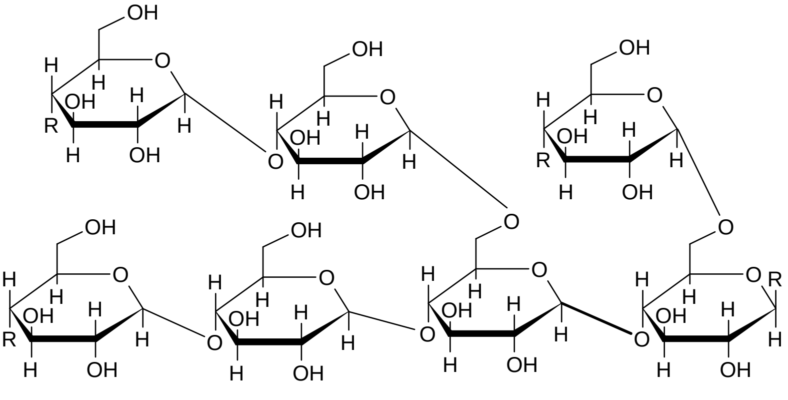
While starch is the major structural polysaccharide, plant energy storage and regulation utilize a combination of similar polysaccharides that are referred to as starch. Starch can be divided into two general structures, largely linear amylose (structure 9.17) and largely branched amylopectin (structure 9.18).



(9.17)

Linear amylose

Most starches contain about 20%–30% amylose and 70%–80% amylopectin though the ratio can vary greatly. Although cellulose can be considered a highly regular polymer of D-glucose with units linked through a β-1,4 linkage, amylose is a linear polysaccharide with glucose units linked in an α-1,4-fashion, amylopectin contains glucose units with chains of α-1,4 glucopyranosyl units but with branching occurring every 25–30 units, with the chain-branch occurring from the sixth position. While this difference in orientation is how the connected glucose units appear small, it causes great differences in the physical and biological properties of cellulose and starch. As noted earlier, humans contain enzymes that degrade the α-glucose units but are unable to digest β units. Thus, starch is a source of food for us, but cellulose is not. Also, the individual units of cellulose can exist in the chair conformation with all of the substituents equatorial, yet amylose must either have the glycosyl substituent at the first position in an axial orientation or exist in a nonchair conformation.



(9.18)

Branched amylopectin

Amylose typically consists of over 1000 D-glucopyranoside units. Amylopectin is a larger molecule containing about 6,000–1,000,000 hexose rings essentially connected with branching occurring at intervals of 20–30 glucose units. Branches also occur on these branches giving amylopectin a fan- or treelike structure similar to that of glycogen. Thus, amylopectin is a highly structurally complex material. Unlike nucleic acids and proteins where specificity and being identical are trademarks, most complex polysaccharides can boast of having the ‘‘mold broken’’ once a particular chain was made so that the chances of finding two exact molecules is very low.

Commercially, starch is prepared from corn, white potatoes, wheat, rice, barely, millet, cassava, tapioca, and sorghum. The fraction of amylose and amylopectin varies between plant species and even within the same plant varies depending on location, weather, age, and soil conditions. Amylose serves as a protective colloid. Mixtures of amylose and amylopectin, found combined in nature, form suspensions when placed in cold water. Starch granules are insoluble in cold water but swell in hot water, first reversibly until gelationization occurs at which point the swelling is irreversible. At this point the starch loses its birefringence, the granules burst, and some starch material is leached into solution. As the water temperature continues to increase to near 100°C, a starch dispersion is obtained. Oxygen must be avoided during heating or oxidative degradation occurs. Both amylose and amylopectin are then water soluble at elevated temperatures. Amylose chains tend to assume a helical arrangement giving it a compact structure. Each turn contains six glucose units.

The flexibility of amylose and its ability to take on different conformations are responsible for the ‘‘retrogradation’’ and gelation of dispersions of starch. Slow cooling allows the chains to align to take advantage of inter- and intrachain hydrogen bonding squeezing out the water molecules, leading to precipitation of the starch. This process gives retrograded

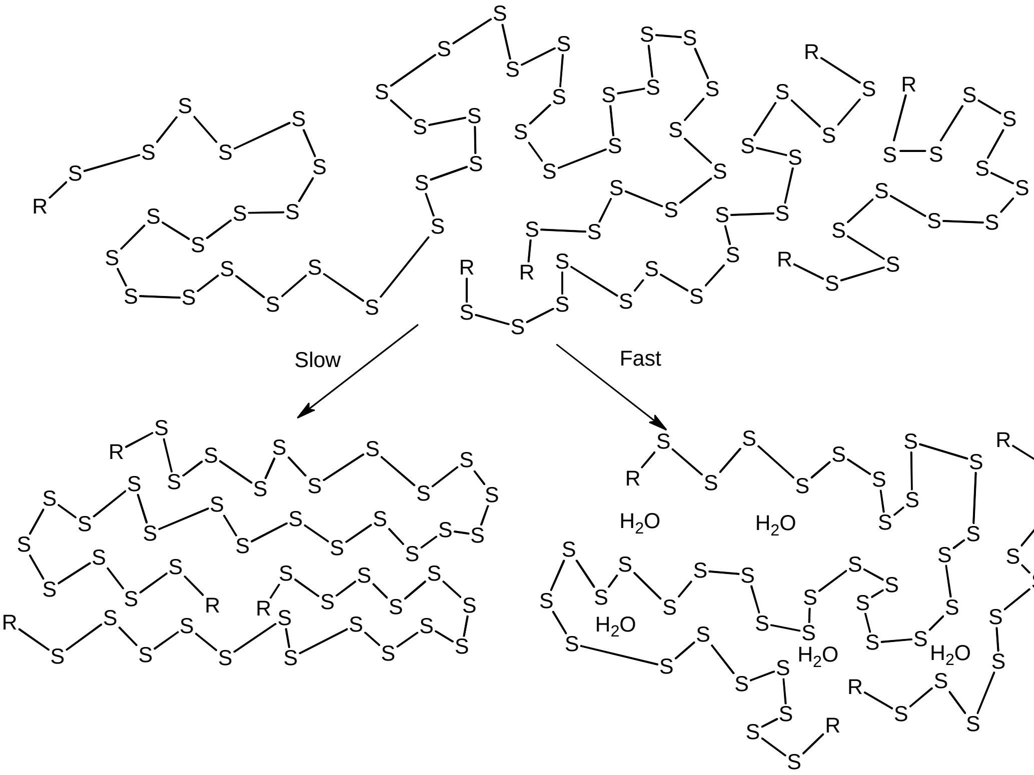


FIGURE 9.2 Behavior of amylose in a concentrated aqueous solution as a function of cooling rate.

starch, either in the presence of amylose alone or combined in native starch, which is more difficult to redisperse. Rapid cooling of starch allows some inter- and intrachain hydrogen bonding, but also allows water molecules to be captured within the precipitating starch allowing it to be more easily redispersed (Figure 9.2).

Most uses of starch make use of the high viscosity of its solutions and its gelling characteristics. Modification of starch through reaction with the hydroxyl groups lowers the gelation tendencies decreasing the tendency for retrogradation. Starch is the major source of corn syrup and corn sugar (dextrose or glucose). In addition to its use as a food, starch is used as an adhesive for paper and as a textile-sizing agent.

Oligomeric materials called cyclodextrins are formed when starch is treated with *Bacillus macerans*. These oligomeric derivatives generally consist of six, seven, eight, and greater numbers of glucose units joined through 1,4-α-linkages to form rings. These rings are doughnutlike with the hydroxyl groups pointing upward and downward along the rim. Like crown ethers used in phase transfer reactions, cyclodextrins can act as "host" to "guest" molecules. In contrast to most phase transfer agents, cyclodextrins have a polar exterior and nonpolar interior. The polar exterior allows guest molecules to be water soluble. The nonpolar interior allows nonpolar molecules to also be guest molecules. Cyclodextrins are being used as enzyme models since they can first bind a substrate through substituent groups and act on the guest molecule—similar to the sequence carried out by enzymes.

A major commercial effort is the free radical grafting of various styrenic, vinylic, and acrylic monomers onto cellulose, starch, dextran, and chitosan. Grafting has been achieved using a wide variety of approaches including ionizing and UV/visible radiation, charge-transfer agents, and various redox systems. Much of this effort is aimed at modifying the native properties such as tensile-related (abrasion resistance and strength) and care-related (crease resistance and increased soil and stain release) properties, increased flame resistance, and modified water absorption. One area of emphasis has been the modification of cotton and starch in the production of super-absorbent material through grafting. These materials are competing with all synthetic cross-linked acrylate materials that are finding use in diapers, feminine hygiene products, wound dressings, and sanitary undergarments.

9.6 HOMOPOLYSACCHARIDES

The best known homopolysaccharides are derived from D-glucose and known as glucans. Glucose has a number of reactive sites and a wide variety of polymers formed utilizing combinations of these reactive sites are found in nature. We have already visited the two most well-known members of this group—cellulose and starch containing amylose and amylopectin. Here we will visit some other important members.

Glycogen is a very highly branched glucan or polysaccharide formed from glucose. It is structurally similar to amylopectin though more highly branched. This greater branching gives glycogen a greater water solubility. Glycogens are the principle carbohydrate food reserve materials in animals. They are found in both invertebrates and vertebrates and are likely found in all animal cells. The highest concentration of glycogen is found in muscle with the greatest amount found in our liver, the tissue from which it is often isolated.

Glycogen is an amorphous polymer of high molecular weight, generally 10^6–10^9 Da. In spite of its high molecular weight, it has good water solubility because of its highly, but loosely branched character. It is polydisperse with respect to molecular weight as are other polysaccharides. The particular molecular weight and MWD vary within and between cells and metabolic need. It stores D-glucose units until needed as an energy source. It also serves as a buffering agent and helps in controlling the amount of glucose in the blood. It is stored in tissues as spherical particles called β particles.

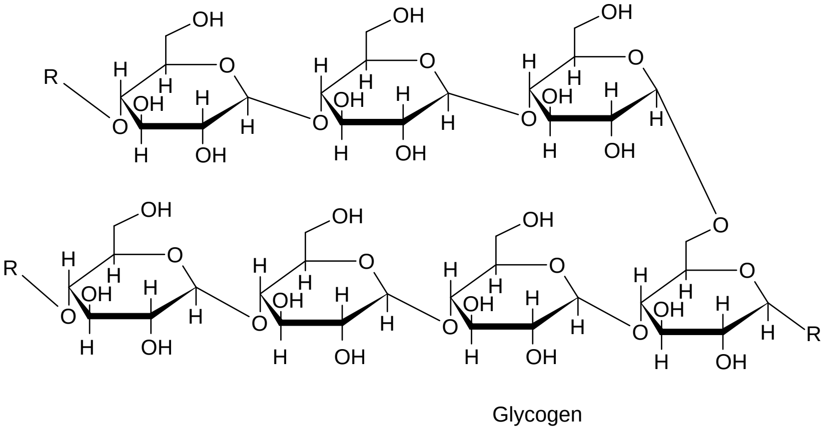
The average distance between branch points is only about 10–15 in comparison to amylopectin with about 20–30 units between branch points. Many glycogen particles contain small amounts of protein to which the polysaccharide chains are covalently bonded. Glycogen reacts weakly with iodine giving a yellow–orange color. It is believed that about 50 linear glucose units are required to form the blue complex found for amylose and because of the high degree of branching, few "runs" near 50 linear glucose units are found in glycogen.

Starch and glycogen are produced when the amount of glucose is high and are readily degraded to glucose when energy is needed. In plants, this degradation occurs mainly through the action of two enzymes known as alpha- and beta-amylase. Interestingly, while the alpha-amylase can degrade starch and glycogen completely to glucose, beta-amylase is not able to degrade the branch points.

In animals, glycogen degradation to give the glucose needed as an energy source or to increase the blood sugar concentration begins with the action of phosphorylase, which occurs in active "a" and inactive "b" forms. Phosphorylase "b" is converted into phosphorylase "a" by phosphorylation that occurs at the end of a series of events initiated by an increased intercellular concentration of cAMP and activation of the protein kinase (Figure 10.8). This is reversed by a phosphoprotein phosphatase whose activity is hormonally regulated. Thus, phosphorylation initiated by increased intracellular concentrations of cAMP inactivates glycogen synthetase and activates phosphorylase. This is an example of the complex steps that are carried out in our bodies every moment. Here, enzymes that are responsible for the glycogen metabolism do not act directly on glycogen but regulate the activity of other enzymes.

Skeletal muscle glycogen delivers glucose primarily as a response to contractile stress. Regulation occurs through both modification of the enzyme phosphorylase, primarily by the action of epinephrine–adrenaline and allosteric regulation of phosphorylase related to a demand for ATP.

Glycogen found in the liver is seldom utilized as a source of energy but is rather employed to regulate blood sugar levels. Some tissues, such as nerve and brain tissue, rely solely on glucose as their energy source so that a steady supply of sugar is essential for their well-being. It is also found in some fungi and yeasts. Some plants such as sweet corn synthesize a polysaccharide that is similar to glycogen.



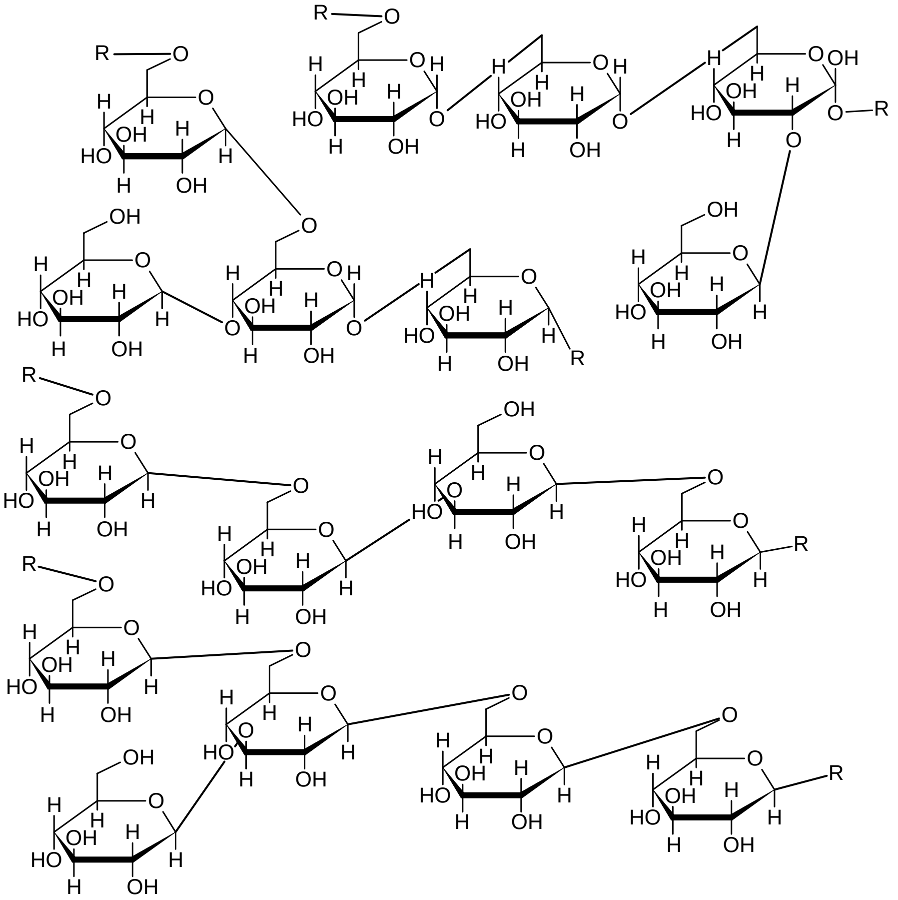
(9.19)

Dextrans are a high molecular weight branched extracellular polysaccharide synthesized by bacteria. These bacteria are found in many places including the human mouth where they flourish on sucrose-containing food, which are trapped between our teeth. The generated dextrans become part of the dental plaque and are thus involved in tooth decay. Dextran-causing bacteria can also infect sugarcane and sugar beet after harvest and act to not only decrease the yield of sucrose but also interfere with sugar-refining by clogging filters and pipelines. These bacteria can also contaminate fruit juices and wines, in fact any ready source of glucose or sucrose.

On the positive side, dextran itself has been refined and employed as a therapeutic agent in restoring blood volume for mass casualties. Natural dextrans have very high molecular weight (on the order of 10^8–10^9 Da) and are found to be unsuitable as a blood-plasma substitute. Lower molecular weight (about 10^6 Da) dextran is suitable and often referred to as clinical dextran.

Dextran gels are commercially used. The gel formed from reaction with epichlorohydrin gives a cross-linked material used as a molecular sieve. Commercial cross-linked dextran is known as Sephadex™. Sephadex is obtained in the form of a bead by dissolving dextran in sodium hydroxide solution followed by dispersion in an immiscible organic liquid such as toluene containing PVAc and finally added to epichlorohydrin. Different series of Sephadex are used industrially and for research purposes. Ionic groups are often incorporated to give anionic and cationic dextrans and ion-exchange molecular sieves. Sulfate esters of dextran are also used in separations.

Structure 9.20 illustrates some typical units that compose dextrans.

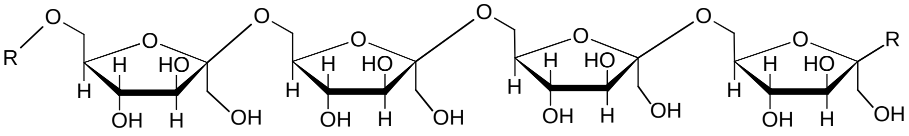


(9.20)

Representative dextran structures appear in 9.20, top left, 1→6 linked glucose units with a 1→4 branch; top right, linear 1→6 linked glucose units with a 1→2 branch; middle, linear chain with both 1→6 and 1→3 linkages; bottom, linear chain of 1→6 linked glucose units with a 1→3 branch. All links are α-linkages.

9.6.1 FRUCTANS

Fructans are polysaccharides composed of D-fructofuranose units. They are important in short-term energy reserves for grasses and some plants. Inulin, found in dahlias, and levans from grasses are examples of fructans. Levans are short linear polysaccharides composed of β 2→1 linked fructose units as illustrated in structure 9.21.

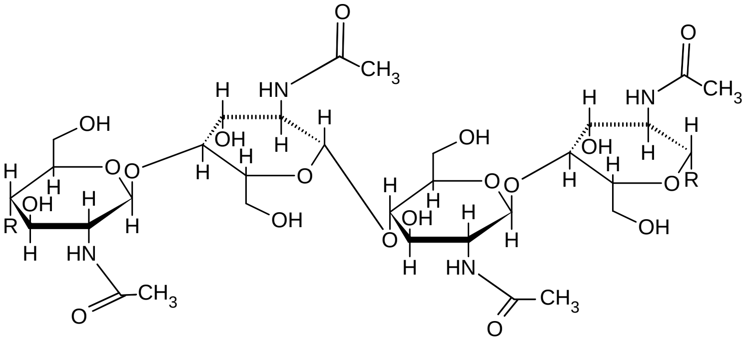


(9.21)

Levan

9.6.2 CHITIN AND CHITOSAN

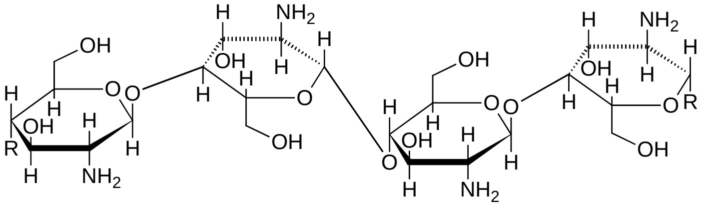
Chitin is generally a homopolymer of 2-acetamido-2-deoxy-D-glucose (*N*-acetylglucosamine) 1→4 linked in a β configuration; it is thus an amino sugar analog of cellulose. While it is widely distributed in bacteria and fungi, the major source is crustaceans. In fact, chitin is the most abundant organic skeletal component of invertebrates. It is believed to be the most widely distributed polysaccharide with the Copepoda alone synthesizing on the order of 10^9 t each year. It is an important structural material often replacing cellulose in cell walls of lower plants. It is generally found covalently bonded to protein. Invertebrate exoskeletons often contain chitin that provides strength with some flexibility along with inorganic salts such as calcium carbonate. In a real sense, this is a composite where chitin holds together the calcium carbonate domains.



Chitin

(9.22)

Chitosan is produced from the deacetylation of chitin. Chitosan is employed in the food industry. It is a hemostatic from which blood anticoagulants and antithrombogenic have been formed. It is often sold as a body fat-reducing agent or to be taken along with food to encapsulate fat particles.

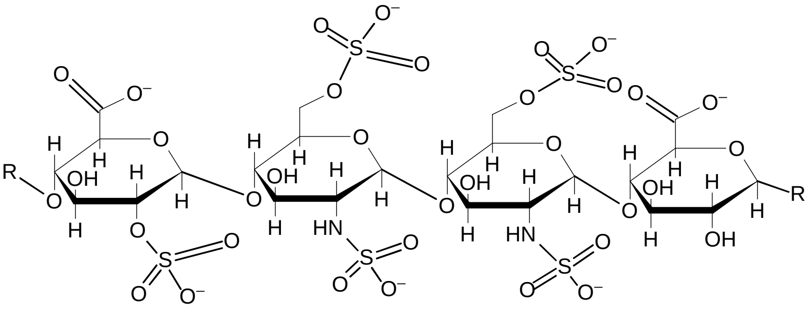


Chitosan

(9.23)

Both chitosan and chitin are greatly underused, readily available abundant materials that deserve additional study as commercial materials and feedstocks. Chitin itself is not antigenic to human tissue and can be inserted under the skin or in contact with bodily fluids generally without harm. In the body, chitin is slowly hydrolyzed by lysozyme and absorbed. Chitin and chitosan can be safely ingested by humans and are often consumed in the form of mushrooms, crabs, shrimp, many breads, and beer. Chitin and chitosan are believed to accelerate wound healing. Chitosan is also reported to exhibit bacteriacidal and fungicidal properties. Chitosan solutions are reported to be effective against topical fungal infections such as athlete's foot.

A constant problem related to the introduction of bioengineering materials into our bodies is their incompatibility with blood. Many materials cause blood to clot (thrombosis) on the surfaces of the introduced material. Heparin (structure 9.24) is an anticoagulant, nontoxic material that prevents clot formation when coated on vascular implants. Although chitosan is a hemostatic material (stops bleeding by enhancing clotting), chitosan sulfate has the same anticoagulant behavior as heparin.



(9.24)

Representative structure of heparin

Next to cancer, cardiovascular disease is the second leading cause of death in America. A contribution factor to cardiovascular disease is serum cholesterol. When ingested, chitosan exhibits hypocholestereolemic activity. Chitosan dissolves in the low pH found in the stomach and reprecipitates in the more alkaline intestinal fluid entrapping cholic acid as an ionic salt preventing its absorption by the liver. The cholic acid is then digested by bacteria in the large intestine. Chitosan may also act to increase the ratio of high density lipoprotein to total cholesterol. Chitosan has been studied in the formation of films including membrane–gels that immobilize enzymes and other materials because of the mild conditions under which they form. Chitosan has been used as a flocculate in wastewater treatment. The presence of the amine gives coacervation with negatively charged materials such as negatively charged proteins allowing removal of unwanted protein waste. The amine groups also capture metal ions, in particular polyvalent and heavy metal ions such as iron, lead, mercury, and uranium. Carraher, Francis, and Louda have also used chitosan to chelate with platinum salts to form materials with structures similar to the anticancer drug *cis*-dichlorodiamineplatinum II chloride. The amine and hydroxyl groups can be modified through the use of a wide range of reactions including formation of amides and esters.

Thus, there exist sufficient reasons to consider these abundant materials in dietary, biomedical, cosmetic, etc., applications.

9.6.3 OTHERS

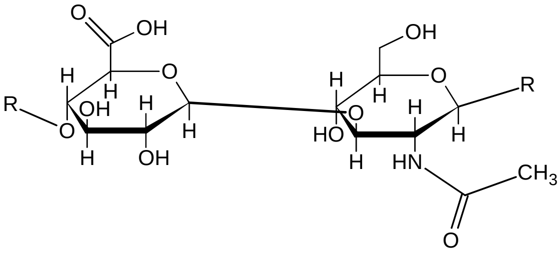
Mannans are found in plants, particularly some seeds, and in some microorganisms such as algae and yeasts. Xylans are an important component of "hemicellulose," the base soluble materials, closely associated with cellulose that is present in the secondary cell walls of higher plants. They are generally composed of β 1→4 linked D-xylopyranose units, thus the name. Arabinans are also plant material being present as a component of cell walls. Most arabinose-containing polysaccharides are actually combinations containing various saccharide units though there are some that contain largely only arabinose units.

9.7 HETEROPOLYSACCHARIDES

Heteropolysaccharides contain two or more different monosaccharides. Glycosaminoglycans are polysaccharides that contain aminosugar units. Most of them are of animal origin.

The representative structure of heparin (structure 9.24) is a complex containing D-glucuronic acid, L-iduronic acid, and D-glucosamine units. The glucosamine units may be *N*-acetylated or *N*-sulfonated. It is found in the lung, liver, and arterial walls of mammals. It is also found in intracellular granules of mast cells that line arterial walls and are released through injury. The glucuronic acid and iduronic acid units are not randomly present but occur in blocks. Heparin is found as the free polysaccharide and bonded to protein. Heparin acts as an anticoagulant, an inhibitor of blood clotting, and is widely used for this in medicine. In nature, its purpose appears to be to prevent uncontrolled clotting.

Hyaluronic acid is found in connective tissues, umbilical cord, skin, and it is the synovial fluid of joints. It can have very large molecular weights, up to 10^7 Da, making solutions of hyaluronic acid quite viscous. They can also form gels. As a synovial fluid in joints it acts as a lubricant and in the cartilage may also act, along with chondroitin sulfates, as a shock absorber. In some diseases such as osteoarthritis the hyaluronic acid of the joints is partially degraded resulting in a loss of elasticity of the area. The molecules can also adopt a helical structure.

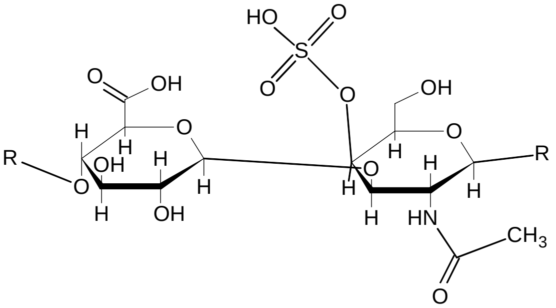


(9.25)

Hyaluronic acid

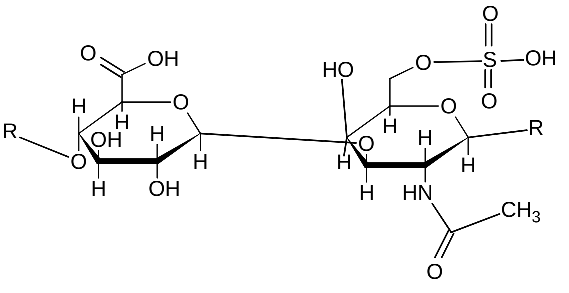
Chondroitin sulfates are found in bone, skin, and cartilage but not as a free polysaccharide. Rather it exists as proteoglycan complexes where the polysaccharide is covalently bonded to a protein. The proteoglycan of cartilage contains about 10% protein, keratan sulfate (structure 9.26), and chondroitin sulfate, mainly the 4-sulfate in humans. The chondroitin sulfate chains have an average molecular weight of about 50,000 Da, but the complex has a molecular weight of several million. Again, chondroitin sulfates can adopt a helical conformation. The function of proteoglycan in cartilage is similar to that of noncellulosic polysaccharides and protein in plant cell walls. In cartilage, collagen fibers provide the necessary strength that is provided in plants by cellulose fibers. Thus, cartilage proteoglycan is an important part of the matrix that surrounds the collagen fibers giving it rigidity and incompressibility. This network can also act as a shock absorber since on compression the water is squeezed out to a near by uncompressed region acting to "share the load" by distributing a shock, stress, or strain.

Chondroitin sulfate is sold as a health aid to "maintain healthy mobile joints and cartilage."



(9.26)

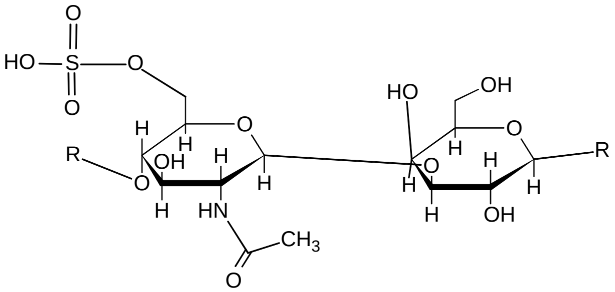
Chondroitin 4-sulfate



(9.27)

Chondroitin 6-sulfate

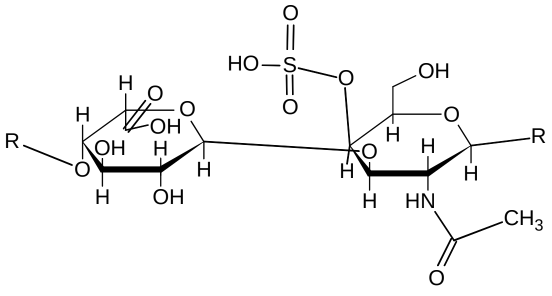
The second polysaccharide present in cartilage proteogylcan is keratan sulfate. It is generally found in shorter chains than chondroitin sulfate with an average molecular weight of about 20,000 Da. It is also found in the cornea of the eye.



(9.28)

Keratan sulfate

Dermatan sulfate is found in the skin, arterial walls, and tendon where it is a part of another proteoglycan complex. It is about the same size as chondroitin sulfate and is also able to form helical conformations.



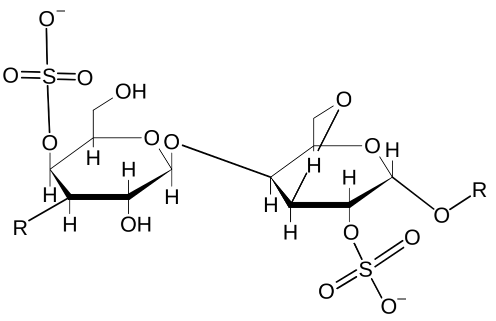
(9.29)

Dermatan sulfate

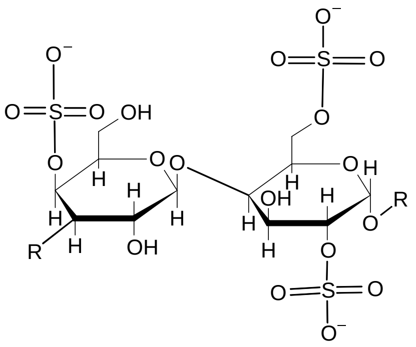
There are two main divisions of polysaccharides that contain unmodified galactose groups—arabinogalactans that contain many plant gums and carrageenans and agar. Seaweeds represent a source of many polysaccharides including alginic acid, agar, and carrageenan. Alginic acid is a polymer of D-mannuronic acid and L-guluronic acid that may be arranged in a somewhat random fashion or in blocks. It is used as a stabilizer for ice-cream, in paper coating, in the manufacture of explosives, and in latex emulsions.

The carrageenans and agar are generally linear galactans where the monomeric units are joined by alternating 1→4 and 1→3 bonds consisting then of disaccharide units. Carrageenan is the name given to a number of sulfated polysaccharides found in many red seaweeds where they play a structural role. The approximate repeat units for two industrially important carrageenans are given below (structure 9.30). Both are able to form double helices containing two parallel staggered chains creating a gel. There are three disaccharide units per helix turn. The sulfate units are located on the outside of the helix with the helical structure stabilized by internal hydrogen bonds. In nature, red seaweeds contain an enzyme that converts the galactose-6-sulfate of the k-carrageenan to 3,6-anhydrogalactose that causes a stiffening of the helix. It has been found that red seaweeds found where there is a strong wave action contain a high proportion of anhydrogalactose. Thus, it appears that the seaweed is able to control its structure in response to external stimuli to minimize shredding by the increased wave action.

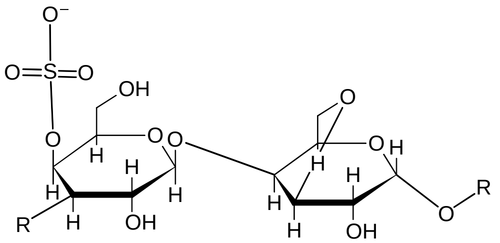
Because of its gelling ability, carrageenan is widely used as food thickeners and emulsion stabilizers in the food industry and is present in many dairy products including less expensive ice-cream and other dessert products providing a smooth, creamy texture. It is used as a stabilizer in foods, such as chocolate milk.



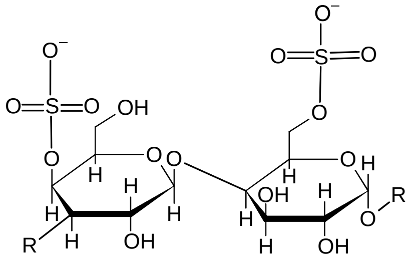
(9.30a)



(9.30b)



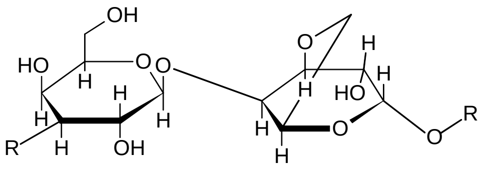
(9.31a)



(9.31b)

The name agar refers to a family of polysaccharides that contain alternating β-D-galactopyranose and 3,6-anhydro-α-L-galactopyranose units and is thus similar to a carrangeenan where the anhydro-L-galactose is substituted for the anhydro-D-galactose. It is employed as the basis of many microbiological media and in canned food because it can be sterilized. The latter is an advantage over gelatin, which is not able to withstand sterilization.

Agarose is the agar polysaccharide with the greatest gelling tendency. It contains no glucuronic acid units. It can form a compact double helix with the two chains being parallel and staggered, as in the case of carrageenan, forming a gel. Agarose gels are employed in GPC and gel electrophoresis.



(9.32)

Agarose

Glycoproteins contain both saccharide and protein moieties with the protein being the major component, but both portions are involved in the overall biological activities.

9.8 SYNTHETIC RUBBERS

NR has been known for over 1000 years. The Aztecs played a game using a "rubber" ball. NR was used by the Mayan civilization in Central and South America before the 20th century. In addition to using the latex from the ule tree for waterproofing of clothing, they played a game called "tlachtli" with large hevea rubber balls. The object of the game was to insert the ball into a tight-fitting stone hole in a vertical wall using only the shoulder or thigh. The game ended once a goal was scored, and the members of the losing team could be sacrificed to the gods.

Columbus, on his second voyage to America, is reported to have seen the Indians of Haiti using rubber balls. By the 18th century, Europeans and Americans used NR to "rub out" marks made by lead pencils. The "rubbing out" use led to the name "rubber." Because of the association of NR with the American Indian it was also called "Indian rubber."

Early progress towards its use in Europe is attributed to Charles Macintosh and Thomas Hancock. NR was dissolved in relatively expensive solvents such as turpentine and camphene. The earliest applications were made by pouring these solutions containing the NR onto objects to be "rubberized." Later, other less expensive solvents were discovered including the use of coal-tar naphtha. Macintosh poured naphtha solutions containing the NR onto layers of cloth producing "waterproof" material, which was the origin of the Macintosh raincoat, misspelled by the English as "Mackintoshes." The layering of the NR not only produced a material that was waterproof, but also got around the problem that NR was sticky, becoming more sticky on hot days. NR also had an unpleasant odor that was prevented by placement between pieces of cloth. Hancock, an associate of Macintosh, worked to develop other useful rubbers from NR. One of his first was a rubber thread obtained by cutting strips of NR and applied to cloths and footwear. He had lots of scrapes and found that by heating them he could reform sheets of the NR from which he could cut more strips. He also developed a crude mixing machine that allowed him to mix other materials, additives, into the rubber.

The development of rubber technology then shifted to North America in the early to mid-1800s. Mills were developed that allowed additives to be added to rubber and allowed rubber to be formed into sheets and small particles. Uses for NR were largely waterproof cloth items in Britain and waterproof boots in the United States.

But, the problem of stickiness remained until an accidental discovery by Charles Goodyear in 1839. As a young man, Goodyear started a lifelong affair with NR to "tame it" for use. He recorded thousands of experiments with NR mixing materials of the day with it and observing what happened. When working with sulfur some of his rubber happened to mix with sulfur and fire with the resulting mixture no longer sticky. After some effort, he worked with mixtures of NR, sulfur, and lead producing a "fireproof" gum that was later called "vulcanized rubber" after the god of fire Vulcan. At about the same time Hancock found a piece of Goodyear's vulcanized rubber and applied for a patent citing as the important ingredients heat, sulfur, and NR. Goodyear's combination included lead that allowed vulcanization to occur at lower temperatures. Goodyear applied for a British patent on January 30, 1844, 8 weeks prior to Hancock's application. Though in ill health and poverty, Goodyear battled to see that his contributions were recognized. Others entered the fight with related claims but history recognizes Goodyear for his scientific insight and Hancock for his applications of NR producing a number of products. (Chapter 1 contains more about the ventures of Charles Goodyear.)

Goodyear had trouble defending his patent, piling up huge debts before he died in 1860. Daniel Webster defended him in one of his patent infringement cases. By 1858, the yearly value of rubber goods produced in the United States was about $5 million. The major rubber producing plants clustered about Akron, Ohio with the Goodyear Company founded in 1870.

Vulcanized rubber had many applications but one of the greatest is probably the "rubber tire." Early tires were made of solid NR and gave a stiff ride. John B. Dunlap rediscovered the air-filled tire, pneumatic tire, in 1887. At this time the automobile was just beginning its ownership of the roads. Bicycles made by various small shops including those made by the Wright Brothers of Dayton, Ohio, were being viewed as a poor man's horse. It did not need food nor did you need to tend to it or its droppings. As roads, even gravel and dirt roads, became more commonplace in the cities, bicycles began to be the vehicle of choice in America and Europe. The air-filled tire gave a softer ride and became the tire of choice for cyclists. It also increased the value and need for NR. As cars and then trucks entered as major conveyers of people and goods, the need for greater amounts of rubber increased.

During this time, seeds from the Amazon valley were planted in British colonies in the east where plantations were founded using native labor, often enslaved, to harvest the NR (Figure 9.3). Of the various NR producing trees, *Hevea brasiliensis* was the best. With World War I, the need for rubber by the British and American forces was critical. To cope with this need several avenues were explored. Alternative rubber producing plants were explored emphasizing plants that would be producing within a year or less and which could survive under milder climates, milder with respect to temperature and need for water. While the exploration of such plants continues even today, this avenue was not successful in supplying the greatly increased rubber needs.

The second avenue involved developing an SR. English scientist Michael Faraday helped set the stage by analyzing NR finding that it was generally composed of repeat units originally described by Faraday as $C_{10}H_{16}$, which was latter rendered $(C_5H_8)_n$. NR was later separated

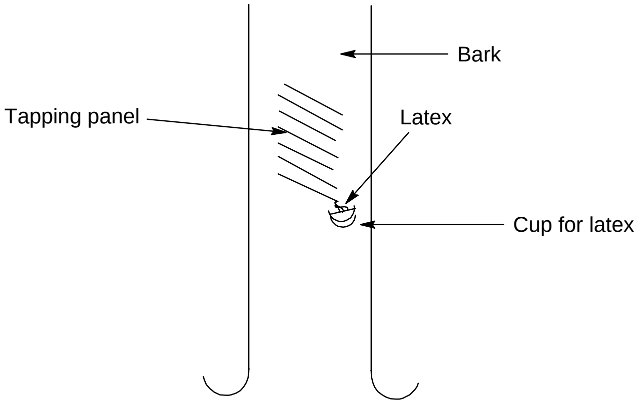


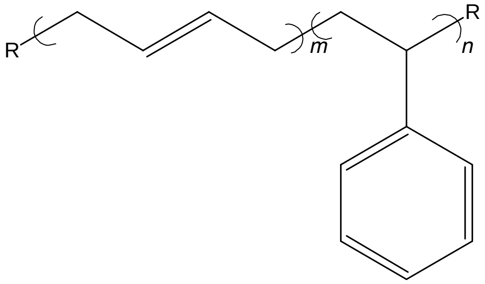
FIGURE 9.3 Harvesting of rubber latex from a rubber tree.

into three parts—oil, tar, and "spirit." The most volatile spirit portion was evaluated and found to contain largely the isoprene unit. The task then was to produce isoprene synthetically, and convert it to rubber. By 1900, the synthesis of isoprene had been achieved, though not easily. Often, isoprene samples spontaneously underwent addition forming a material similar to NR.

During this time, other materials that gave rubberlike materials were found. In 1901, I. Kondakov, a Russian, discovered that dimethyl butadiene when heated with potash formed a rubberlike material. In 1910, S.V. Lebedev, another Russian, reacted butadiene forming a rubberlike material (structure 9.33).

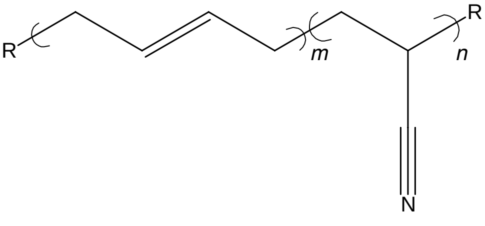
$$H_2C{=}CH{-}CH{=}CH_2 \rightarrow \text{Rubberlike product} \tag{9.33}$$

During World War I, Germany was cut off from the Far East sources of NR and so developed their own alternative rubbers. They focused on the Kondakov process making two rubberlike materials dubbed methyl "H," which was a hard rubber and methyl "W," which was a softer rubber. Before commencement of large-scale production, the war ended and Germany returned to natural sources of NR. Even so, Germany continued some research towards the production of rubber. By the 1930s, they produced three "Buna" rubbers. The name Buna comes from the first two letters of the main ingredients, butadiene and natrium (sodium), the catalyst. They also discovered another of today's rubbers, Buna-S, which is derived from butadiene and styrene. The British referred to Buna-S as SBR, while the United States referred to this as GR-S (Government rubber–styrene). Many of these SRs when vulcanized were superior to earlier synthesized rubbers and often to NR for some applications.



(9.34)

In 1937, Germany also developed Buna-N (N = nitrile; structure 9.35), which offered good resistance to oil. Most of these rubbers are still in use with small modifications.

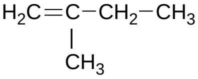


(9.35)

The USSR was producing SRs during this time using potatoes and limestone as starting materials. Thus, the move towards natural materials is not new.

As World War II approached, Germany and the USSR worked frantically to be free from outside need of rubber. The United States by comparison were conducting research in a number of areas that would eventually prove useful, but had made no real push for self-reliance in the issue of rubber. U.S. experiments with SR before 1939 lead to the discovery of neoprene, thiokol, and butyl rubber.

As noted above, chemists learned about the structure of rubber by degrading it through heating and analyzing the evolved products. One of the evolved products was isoprene, a five-carbon hydrocarbon containing a double bond. Isoprene is a basic building block in nature serving as the "repeat" unit in rubber and also the building block of steroids such as cholesterol.



$$H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2{-}CH_3 \qquad (9.36)$$

Isoprene

Again, with the knowledge that NR had isoprene units, chemists worked to duplicate the synthesis of rubber except using synthetic monomers. These attempts failed until two factors were realized. First, after much effort it was discovered that the methyl groups were present in a *cis* arrangement. Second, it was not until the discovery of stereoregular catalysts that the chemists had the ability to form NR-like material from butadiene.

The search for the synthesis of a pure SR, structurally similar to NR, continued and involved a number of scientists building upon one another's work—along with a little creativity. Nieuwland, a Catholic priest, President of Notre Dame University, and a chemist did extensive work on acetylene. He found that acetylene could be made to add to itself forming dimers and trimers.

$$\underset{\text{Acetylene}}{HC{=}CH} \rightarrow \underset{\text{Vinylacetylene}}{H_2C{=}CH{-}C{=}CH} + \underset{\text{Divinylacetylene}}{H_2C{=}CH{-}C{=}C{-}CH{=}CH_2} \qquad (9.37)$$

Calcott, a DuPont chemist, attempted to make polymers from acetylene, reasoning that if acetylene formed dimers and trimers, conditions could be found to produce polymers. He failed, but went to Carothers who had one of his chemists, Arnold Collins, work on the project. Collins ran the reaction described by Nieuwland, purifying the reaction mixture. He found a small amount of material that was not vinylacetylene or divinylacetylene. He set the liquid aside. When he came back, the liquid had solidified giving a material that seemed rubbery and even bounced. They analyzed the rubbery material and found that it was not a hydrocarbon, but had chlorine in it. The chlorine had come from HCl that was used in Nieuwland's procedure to make the dimers and trimers. The HCl added to the vinylacetylene forming chloroprene.

This new rubber was given the name Neoprene (Equation 9.38). Neoprene had outstanding resistance to gasoline, ozone, and oil in contrast to NR. Today, neoprene is used in a variety of applications including as electrical cable jacketing, window gaskets, shoe soles, industrial hose, and heavy duty drive belts.

$$H_2C{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH{=}CH_2 \rightarrow {-}({-}CH_2{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}CH{-}CH_2{-}){-} \qquad (9.38)$$

Chloroprene Polychloroprene (Neoprene)

Thiokol was developed by J.C. Patrick in 1926. Patrick was born in 1892 in Jefferson County, Missouri. He was a physician rather than a chemist. Before completing his medical school studies World War I began and he tried to join the U.S. Air Corps. Because of poor health, he could not meet the standards for combat service but was accepted in the U.S. Medical Corps and sent to serve in France. He was part of the influenza epidemic in France and was found in a coma surrounded by corpses awaiting shipment for interment. His escape from burial may have been the result of the administering of a large dose of quinine by a French nurse.

On returning to the United States he continued his medical education and accepted a position as a public health inspector in Kansas City, Missouri. Within a year he took a better paying job as an analytical chemist for Armor Packing Company in Buenos Aires, Argentina. He returned to the United States, and finally completed his medical training from the Kansas City College of Medicine and Surgery in 1922.

Rather than practicing medicine he helped establish the Industrial Testing Laboratory, Inc. in Kansas City by the mid-1920s. He developed a process for the production of pectin as a precipitate from apples from a vinegar plant.

Another project undertaken by the testing laboratory was an attempt to improve the synthesis of ethylene glycol, the major ingredient in antifreeze, from the hydrolysis of ethylene chlorohydrin. They used sodium sulfide in the process. Instead of getting the desired antifreeze, he got a gunk. Instead of throwing away the gunk, which was often done during this time, he studied it. The material was foul smelling, much like rotten eggs, and was stable in most solvents it was placed in. He called this material "thiokol" after the Greek for "sulfur" and "gum" (Kommi). He got funds from Standard Oil Company of Indiana to do further work with thiokol to try to eliminate its odor.

Sulfur naturally comes in packages of eight forming an octagon. Through varying the reaction conditions a variety of thiokols can be formed with the thiokol chains having varying averages of sulfurs. Thiokols are formed from the reaction of ethylene with chlorine forming ethylene dichloride that is reacted with sodium polysulfide.

$$\mathrm{H_2C{=}CH_2 - Cl_2 \rightarrow H_2C(Cl) - C(Cl)H_2} \tag{9.39}$$

$$\mathrm{H_2C(Cl) - C(Cl)H_2 + NaS_x \rightarrow -(CH_2 - CH_2 - S - S -) - + NaCl} \tag{9.40}$$

Butyl rubber was discovered by R.M. Thomas and W.J. Sparks in 1937, and was developed by the Standard Oil Company (New Jersey) and was part of an exchange of information between the German chemical giant I.G. Farbenindustrie AG and Standard Oil.

Butyl rubber is a copolymer of 1-butene, $(CH_3)_2C{=}CH_2$, and small amounts (about 2%–3%) of isoprene or other unsaturated compounds. The unsaturation allows subsequent cross-linking of the material.

As World War II loomed with America pushed into the war by the Pearl Harbor attack, the need for an independent rubber supply was critical. The government instituted several nationwide efforts including the Manhattan and Synthetic Rubber Projects. Carl "Speed" Marvel was one of the chemists involved in the Synthetic Rubber Project.

When I first met "Speed" Marvel, there was nothing "speedy" about his gait but he was speedy with his mind and pleasant personality. As with many of the polymer pioneers he was friendly and commented on the importance of my work before I could talk about my admiration of him and his efforts. Now that is a way to turn the tables on a young researcher. I had read about "Speed" and his part in "saving the war" and was anxious to simply meet him.

Carl Shipp "Speed" Marvel was born in 1894 on a farm in Waynesville, Illinois and spent much of his 93 years furthering synthetic polymer chemistry. When Marvel registered for his first semester as a graduate student, in 1915, at the University of Illinois it was believed that he lacked some of the basic chemistry background and so was given extra courses. He worked late into the night in the laboratory and studying but wanted to get to the breakfast table before the dining room door closed at 7:30 a.m. His fellow students commented that was the only time he ever hurried and hence gave him the name "Speed."

During this time, chemistry was prospering in Europe but not in America; so there was an effort by American chemists to establish routes to important chemicals, such as dyes, in academia and industry. There was a flow of chemists from academia to industry and from one academic institution to another. Roger Adams, one of the foremost organic chemists then, moved from Harvard to the University of Illinois. This was a time of rapid growth in the chemical industry because prior to World War I, much of the chemical industry was centered in Germany and because of the war, this was changing. The American Society membership grew from 7,400 in 1915 to over 10,600 in 1917. (Today, the ACS has a membership of about 160,000 and is the largest single discipline organization.) The shortage of chemicals was so severe that Adams had graduate students such as ‘‘Speed’’ Marvel actually work on the production of special chemicals related to the new chemical warfare that was introduced by the Germans. It was quite a task to make these dangerous chemicals because of the poor ventilating hoods used by the students.

America entered the war in 1917 and many university chemists were transferred to Washington, DC, to work on chemical warfare problems. Adams became a Major in a unit that emphasized chemical warfare problems and maintained contact with the group at Illinois asking them to furnish chemicals on a rush basis. Speed also helped in the preparation of steel providing steelmakers with a chemical needed to analyze nickel steel.

At the end of the war there was a lessening in the need for chemists as industry reorganized itself for peace. In 1921, Speed was able to complete his graduate work at Illinois in organic chemistry. He had wanted to work in industry, but industrial jobs were hard to get at this time; so he stayed on as an instructor. The academic hierarchy was similar to that present in Europe where junior faculty had bosses who were also part of the academic regime. Speed's boss was Oliver Kamm who left to become research director at Parke-Davis, so Speed was promoted. During this time, interest in chemistry was increasing so there was an increase in the number of graduate students in chemistry. In the fall of 1920, one of Speed's students, Wallace Carothers, went on to become one of the fathers of polymer chemistry. By 1924, Carothers became part of the organic faculty. There were evening seminars where the faculty discussed the latest trends and problems in chemistry. In 1927, Carothers left to join the Harvard faculty and eventually the DuPont Experimental Station.

In 1928, Speed became a consultant to the DuPont Experimental Station due to the nudging of Roger Adams. Chemistry was on the rise with the invention of the first SR (neoprene) and first truly synthetic fiber (nylon) both discovered by Carothers. The plastics industry developed rapidly with chemistry truly becoming an industrial giant, mainly on the back of giant molecules.

War broke out in Europe and it was obvious that America would become part of the conflict. The Office of Scientific Research and Development and the National Research and Development Committee were established in late 1941. Various universities furnished the people for these agencies and most university laboratories accepted contracts related to studying problems of interest to the Department of Defense. Adams was important in this effort and so included Speed as a participant.

When Japan attacked Hawaii in December 1941, the most critical chemical problem was the solution to the rubber shortage because the far Eastern suppliers were cut off. Since Speed had ‘‘become’’ a polymer chemist during 1930–1940, he became part of this rubber program. The major rubber companies, many universities, and other chemical companies put aside their competition and pooled their research efforts and in about a year's time developed a usable SR that was manufactured and used in smaller types of tires.

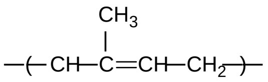
Speed helped organize, prior to the war years, a rubber program on the synthesis of rubber for the National Defense Research Committee under Adams, which was eventually responsible for the production of rubber during the war. He was also drafted and helped on a research program for the Committee on Medical Research dealing with malaria research.

In the 1950s, Speed was part of a large effort headed out of Wright Patterson Air Force Base aimed at developing thermally stable materials for a number of purposes including use for outer spacecraft. This effort acted as an early focal point for the synthesis of metal-containing polymers that lost out to the honey-combed ceramic tiles currently used on spacecrafts.

By 1953, Karl Ziegler and Giuilo Natta discovered a family of catalysts that allowed the introduction of monomer units onto growing polymer chains in an ordered manner. This allowed the synthesis of rubberlike polymers with greater strength and chemical stability in comparison with similar polymers made without the use of these stereoregulating catalysts.

9.9 NATURALLY OCCURRING POLYISOPRENES

Polyisoprenes occur in nature as hard plastics called gutta-percha (*Palaquium oblongifolium*) and balata (*Mimusops globosa*) and as an elastomer or rubber known as *H. brasiliensis*, or NR. Approximately 50% of the 500 t of gutta-percha produced annually is from trees grown on plantations in Java and Malaya. Balata and about 50% of the gutta-percha used are obtained from trees in the jungles of South America and the East Indies. The first gutta-insulated submarine cable was installed between England and France in 1859. Gutta-percha continues to be used for wire insulation and polyisoprene, balata, and gutta-percha are used as covers for some golf balls.



$$-\!\left(\mathrm{CH}-\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}=\mathrm{CH}-\mathrm{CH_2}\right)\!- \qquad (9.41)$$

The hardness of some of the polydisperse naturally occurring crystalline polymers is the result of a *trans* configuration in 1,4-polyisoprene (Figures 9.4 and 9.5). This geometry facilitates good fit between chains and results in inflexibility in the chains. The hevea or NR is, by comparison, soft because it is a *cis* configuration (Figures 9.4 and 9.5) that does not allow a

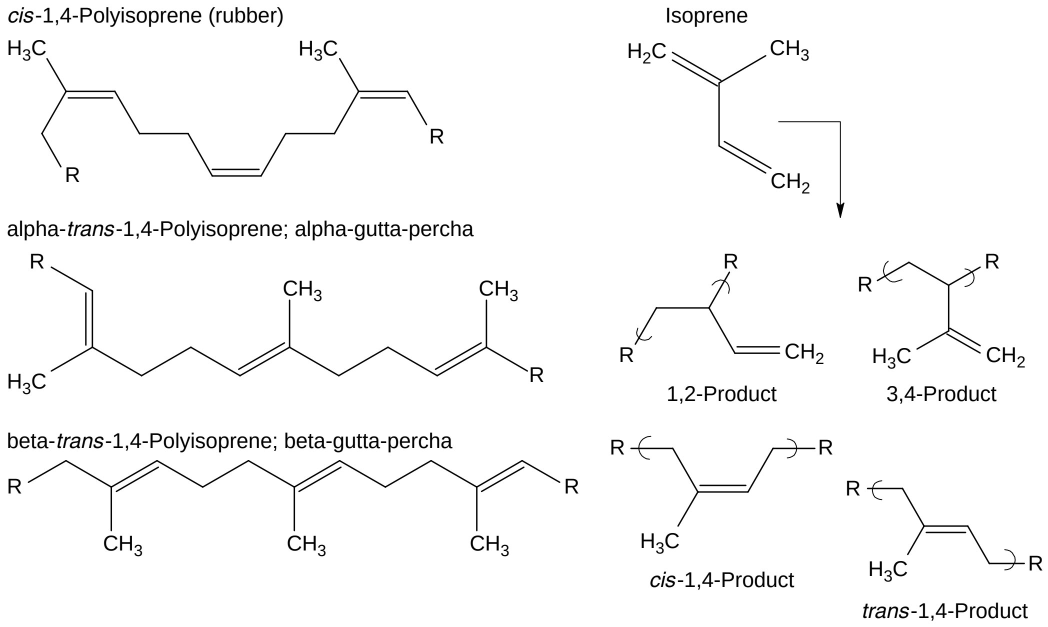


FIGURE 9.4 Abbreviated structural formulas for polyisoprenes.

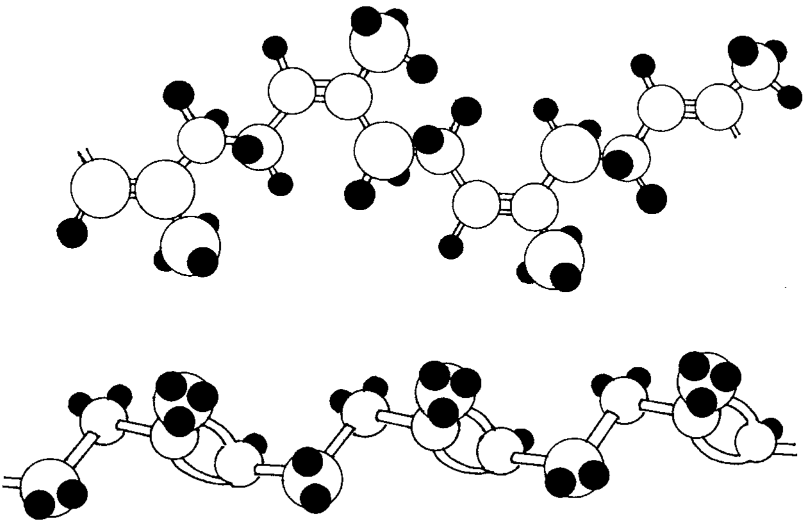


FIGURE 9.5 Ball-and-stick models of "soft" hevea rubber (*cis*-1,4-polyisoprene) (top) and "hard" gutta-percha (*trans*-1,4-polyisoprene) (bottom).

close fit between chains resulting in flexibility and a "rubbery" behavior. Both *cis* and *trans* isomers of polyisoprene are present in chicle, obtained from the *Achras sapota* tree in Central America. These isomers are also synthesized commercially.

Prior to the discovery of the vulcanization or cross-linking of hevea rubber with sulfur by Goodyear in 1838, Faraday has shown that the empirical formula of this elastomer is C_5H_8 making it a member of the terpene family. The product obtained by pyrolysis of rubber was named isoprene by Williams in 1860 and converted to a solid (polymerized) by Bouchardat in 1879.

NR crystallized when stretched in a reversible process. However, the sample remains in its stretched form (racked rubber) if it is cooled below its T_g. The racked rubber will snap back and approach its original form when it is heated above its T_g. The delay in returning to the original form is called *hysteresis*. These and other elastic properties of NR and other elastomers above the T_g are based on long-range elasticity. Stretching causes an uncoiling of the polymer chains, but these chains assume a more ordered microstructure creating crystalline domains acting to oppose further stretching. If the rubber is held in the stretched state for some time, slippage of chains occurs and precise return to its original shape does not occur when the stress is released.

The absence of strong intermolecular forces, the presence of pendant methyl groups discouraging close association, and crankshaft action associated with the *cis* isomer all contribute to the flexibility of NR. The introduction of a few cross-links by vulcanization with sulfur reduces slippage of chains but still permits good flexibility.

When a strip of NR or SR is stretched at a constant rate, the tensile strength required for stretching (stress, s) increases slowly until elongation (strain) of several hundred percent is observed. This initial process is associated with an uncoiling of the polymer chains in the uncross-linked regions. Considerably more stress is required for greater elongation to about 800%. This rapid increase in modulus (G) is associated with better alignment of the polymer chains along the axis of elongation, crystallization, and decrease in entropy (ΔS). The work done in the stretching process (W_l) is equal to the product of the retractile force (F) and the change in length (dl). Therefore, the force is equal to the work per change in length.

$$W_l = f\,dl \quad \text{or} \quad f = \frac{W_l}{dl} \tag{9.42}$$

Here, W_l is equal to the change in Gibbs free energy ($\mathrm{d}G$), which under the conditions of constant pressure is equal to the change in internal energy ($\mathrm{d}E$) minus the product of the change in entropy and the Kelvin temperature as follows:

$$f = \frac{W_l}{\mathrm{d}l} = \frac{\mathrm{d}G}{\mathrm{d}l} = \frac{\mathrm{d}E}{\mathrm{d}l} - T\left(\frac{\mathrm{d}S}{\mathrm{d}l}\right) \tag{9.43}$$

The first term ($\mathrm{d}E/\mathrm{d}l$) in Equation 9.43 is important in the initial low modulus stretching process, and the second term [$T(\mathrm{d}S/\mathrm{d}l)$] predominates in the second high modulus stretching process. For an ideal rubber, only the second term is involved.

As observed by Gough in 1805 and verified by Joule in 1859, the temperature of rubber increases as it is stretched, and the stretched sample cools as it snaps back to its original condition. (This can be easily confirmed by rapidly stretching a rubber band and placing it to the lips, noting that heating has occurred, and then rapidly releasing the tension and again placing the rubber band to the lips.) This effect was expressed mathematically by Kelvin and Clausius in the 1850s. The ratio of the rate of change of the retractive force ($\mathrm{d}f$) to the change in Kelvin temperature ($\mathrm{d}T$) in an adiabatic process is equal to the specific heat of the elastomer (C_p) per degree temperature (T) times the change in temperature ($\mathrm{d}T$) times the change in length ($\mathrm{d}l$).

$$\frac{\mathrm{d}f}{\mathrm{d}T} = -\left(\frac{C_\mathrm{p}}{T}\right)\left(\frac{\mathrm{d}T}{\mathrm{d}l}\right) \tag{9.44}$$

Equation 9.44 may be transformed to Equation 9.45.

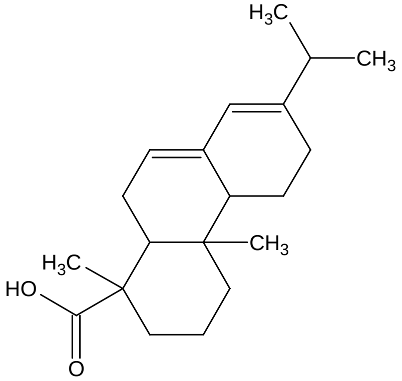
$$\frac{\mathrm{d}T}{\mathrm{d}f} = -\left(\frac{T}{C_\mathrm{p}}\right)\left(\frac{\mathrm{d}l}{\mathrm{d}T}\right) \tag{9.45}$$

Unlike most solids, NR and other elastomers contract when heated.

9.10 RESINS

Shellac, which was used by Edison for molding his first photograph records and is still used as an alcoholic solution (spirit varnish) for coating wood, is a cross-linked polymer consisting largely of derivatives of aleuritic acid (9,10,16-trihydroxyhexadecanoic acid). Shellac is excreted by small coccid insects (*Coccus lacca*), which feed on the twigs of trees in Southeast Asia. Over 2 million insects must be dissolved in ethanol to produce 1 kg of shellac.

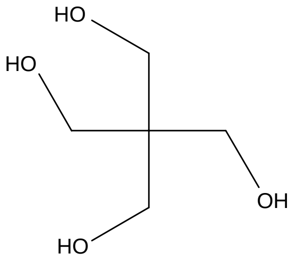
$$\mathrm{HOCH_2{-}(CH_2)_5{-}CH(OH){-}CH(OH){-}(CH_2)_7{-}COOH} \quad \text{Aleuritic acid} \tag{9.46}$$



(9.46)

Abietic acid

Rosin, the residue left in the manufacture of turpentine by distillation, is a mixture of the diterpene, abietic acid, and its anhydride. It is nonpolymeric but is used in the manufacture of synthetic resins and varnishes.



(9.47)

Pentaerythritol

Easter gum, a cross-linked ester, is obtained by the esterification of glycerol or pentaerythritol with rosin.

Many natural resins are fossil resins exuded from trees thousands of years ago. Recent exudates are called recent resins, and those obtained from dead trees called semifossil resins. Humic acid is a fossil resin found with peat, coal, or lignite deposits throughout the world. It is used as a soil conditioner, a component of oil drilling muds, and a scavenger for heavy metals. Amber is a fossil resin found in the Baltic Sea regions, and sandarac and copals are found in Morocco and Oceania, respectively. Casein, a protein from milk, under the name of Galalith, has been used as a molding resin and an adhesive.

9.11 BALLOONS

Balloons have been part of our everyday lives from birthdays to graduations. As with many simple objects, their origin is unknown. Balloon-like objects have been part of ancient stories and probably were initially used in sport. These early balloons were made of animal bladders and intestines, both being protein-based, and hence polymeric. European jesters inflated the animal entrails using them to entertain others. Galileo inflated a pig's bladder to help measure the weight of air.

Although there are also new world mentions of similar balloon construction, it was not until rubber arrived on the scene that the manufacture of balloons, as we know today, began.

In 1824, Michael Faraday used NR to produce balloons for his hydrogen experiments at the Royal Institution in London. He writes: "The caoutchouc is exceedingly elastic.... Bags made of it...have been expanded by having air forced into them, until the caoutchouc was quite transparent, and when expanded by hydrogen they were so light as to form balloons with considerable ascending power...." Faraday constructed his balloons by cutting two layered sheets of rubber and then pressing the edges together. Flour was applied to the inside of the balloons because the native rubber was tacky and would adhere preventing it from being inflated.

Toy balloons were introduced by Thomas Hancock in 1825 as a do-it-yourself kit that consisted of a rubber solution and a syringe. Vulcanized toy balloons were initially manufactured by J.G. Ingram of London in 1847. The vulcanizing caused the balloons to be nontacky and not susceptible to becoming excessively tacky on hot days. Montgomery Ward had balloons in their catalog by 1889.

In America, the story of the balloon coincided with the story of the tire, both requiring an understanding and use of rubber. The initial manufacture of balloons in the United States was in 1907 by the Anderson Rubber Company in Akron, Ohio. In 1912, Harry Rose Gill, founder of the National Latex Rubber Products of Ashland, Ohio, made a nonspherical cigar-shaped balloon. Gill also began packaging balloons in packs, the initial sanitary balloon package.

Neil Tillotson, at 16, began work at the Hood Rubber Company in Boston. After a 2-year period in the Seventh Cavalry during World War I, he returned to the Hood Rubber Company. Of about 25 Hood chemists, Neil was the only one without a college degree. But, he was inventive and with the first load of raw rubber latex in the 1920s, he started a lifelong romance with rubber. The company's initial efforts with the raw latex were unsuccessful and the company largely dropped its efforts to produce balloons. Tillotson persevered working out of his own home. Eventually, he managed to "tame" the latex sufficiently to make stylistic balloons using techniques similar to what is employed today. They cut a catlike face from cardboard. He dipped the catlike mold in latex and allowed it to dry. Inflated, it did resemble a cat. His first sale was an order for 15 gross for use at the annual Patriots Day Parade on April 19, 1931. Next, he formed a family business, incorporating later in 1931, using his family as an assembly line in the production of balloons. During the great depression, Neil traveled by bus around the country to sell his balloons. The Tillotson Rubber Company is still in operation with the balloon division named Dipco, a nice reminder of the way balloons are still made.

Rubber latex is sensitive to the influence of external forces or chemical agents. Thus, the so-called alligator balloon is formed when solid-colored balloons are dipped in an acid bath causing the balloon to turn into two shades, supposedly like an alligator. The radium balloon is produced by taking a solid-colored balloon and dipping it a second time into another color.

Commercially, inflated balloons held hydrogen and helium. Hydrogen was preferred because of its 10% greater lifting ability. Hydrogen balloons were first produced by Faraday, as noted earlier. But, along with its greater lifting power, hydrogen offers a danger. On ignition, hydrogen burns rapidly forming water and energy, generally producing a flame. As early as 1914, firemen tried to curtail the use of hydrogen-filled balloons. In 1922, New York City banned the use of hydrogen-filled balloons because a city official was badly injured due to a fire caused by hydrogen-filled balloons.

There is an experiment that is often used in polymer demonstrations. Pointed objects such as long pins and sticks are gently pushed into a blow-up balloon without exploding the balloon. This results because the rubber polymer chains form about the impacting object to seal up the "hole" created by the object. Thus, even in its seemingly solid state, the rubber balloon's polymer chains are sufficiently mobile to allow it to "heal" itself.

Balloons today are still made from the rubber latex from the rubber tree using molds. Color is added as desired.

Foil balloons are derived from the effort of National Aeronautics and Space Administration (NASA) Space Command with the concept and technology to metalizate plastic sheeting. While the balloons are often referred to as Mylar or silver Mylars, they are not made from Mylar, a trade name for certain polyester film. They should be simply referred to as foil balloons. They are made from nylon film coated on one side with PE and metallized on the other. The nylon film gives the balloon some strength and the PE gives it some flexibility and helps retard the release of the held gas.

9.12 LIGNIN

Lignin is the second most widely produced organic material, after the saccharides. It is found in essentially all living plants and is the major noncellulosic constituent of wood. It is produced at an annual rate of about 2×10^{10} t with the biosphere containing a total of about 3×10^{11} t. It contains a variety of structural units including those pictured in Figure 9.6.

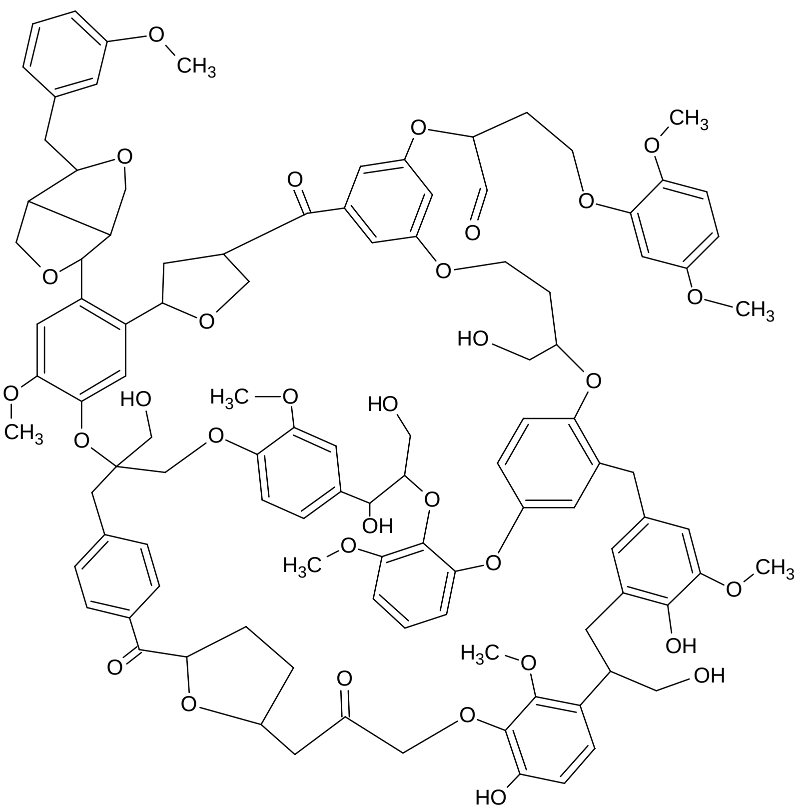


FIGURE 9.6 Representative structure of lignin.

Lignin has a complex structure that varies with the source, growing conditions, etc. This complex and varied structure is typical of many plant-derived macromolecules. Lignin is generally considered as being formed from three different phenylpropanoid alcohols—coniferyl, coumaryl, and sinapyl alcohols, which are synthesized from phenylalanine via various cinnamic acid derivatives and commercially is sometimes treated as being composed of a C_9 repeat unit where the superstructure contains aromatic and aliphatic alcohols and ethers, and aliphatic aldehydes and vinyl units.

Lignin is found in plant cell walls of supporting and conducting tissue, mostly the tracheids and vessel parts of the xylem. It is largely found in the thickened secondary wall but can occur elsewhere close to the celluloses and hemicelluloses.

The presence of rigid aromatic groups and hydrogen bonding by the alcohol, aldehyde, and ether groups gives a fairly rigid material that strengthens stems and vascular tissue in plants allowing upward growth. It also allows water and minerals to be conducted through the xylem under negative pressure without collapse of the plant. This structure can be flexibilized through introduction of a plasticizer, in nature mainly water. The presence of the hydrophilic aromatic groups helps ward off excessive amounts of water allowing the material to have a variable flexibility but to maintain some strength. This type of balance between flexibility and strength is also utilized by polymer chemists as they work to modify lignin, as well as synthetic polymers to give strong, semiflexible materials. Without the presence of water, lignin is brittle but with the presence of water the tough lignin provides plants with some degree of protection from animals.

Its chemical durability also makes it indigestible to plant eaters because of its bonding to cellulose and protein material. Formation of lignin also helps block the growth of pathogens and is often the response to partial plant destruction.

The role of transferring water by lignin makes the ability to produce lignin critical to any plants survival and permits even primitive plants to colonize dry land.

During the synthesis of plant cell walls, polysaccharides are generally initially laid down. This is followed by the biosynthesis of lignin that fills the spaces between the polysaccharide fibers acting to cement them together. The filling of cell wall spaces results in at least some of the lignin having a somewhat two-dimensional structure similar to a sheet of paper rather than the typical three-dimensional structure for most polysaccharides and other natural macromolecules. The lignin sheets act as a barrier towards the outside elements including marauding pests as noted above.

The lignin is generally considered as being insoluble but it can be solubilized utilizing special systems such as strong basic solutions that disrupt the internal hydrogen bonding. It is not clear even now if the undegraded lignin is solubilized or if degradations accompany lignin solubilization. Average molecular weights for some lignin samples vary depending on the type of solvent employed consistent with degradation occurring for at least some of these systems. Molecular weight values to about 10^7 have been reported for some alkali-extracted fractions.

Solubilized lignin solutions are easily oxidized and the presence of the aromatic units containing electron-withdrawing ether and alcohol moieties makes it available for electrophilic substitution reactions, such as nitration, halogenation, hydroxylation, etc.

Since its removal is the major step in the production of paper pulp, vast amounts of lignin are available as a by-product of paper manufacture. Its industrial use is just beginning and it remains one of the major underused materials. Its sulfonic acid derivative is used as an extender for phenolic resins, as a wetting agent for oil drilling muds, and for the production of vanillin. Combined, this accounts for less than 1% of this important "by-product." In the enlightened age of green chemistry, greater emphasis on the use of lignin itself and in products derived from it must occur.

9.13 MELANINS

Light is continuous ranging from wavelengths smaller than 10^{-12} cm (gamma radiation) to greater than 10^8 cm. Radiation serves as the basis for the synthesis of many natural macromolecules via photosynthesis. Radiation is used commercially to increase the wood pulp yield through cross-linking and grafting of lignin and other wood-components onto cellulosic chains. Radiation is also used in the synthesis and cross-linking of many synthetic polymers.

Radiation is also important in the synthesis and rearrangement of important "surface" macromolecules. Tanning of human skin involves the activation of the polypeptide hormone beta MSH that in turn eventually leads to the phenomena of tanning. Exposure to higher energy light from about 297 to 315 nm results in both tanning and burning, whereas exposure to light within the 315–330 nm region results mainly in tanning.

UV radiation activates enzymes that modify the amino acid tyrosine in pigment-producing cells, the melanocytes. The enzyme tyrosinase, a copper-containing oxygenase, catalyzes the initial step, which is the hydroxylation of tyrosine to 3,4-dihydroxyphenylalanine that is oxidized to dopaquinone subsequently forming the melanins (Figure 9.7). The concentration of tyrosine is relatively high in skin protein. These modified tyrosine molecules undergo condensation forming macromolecules known as melanins. Melanins have extended chain resonance where the pi-electrons are associated with the growing melamine structure.

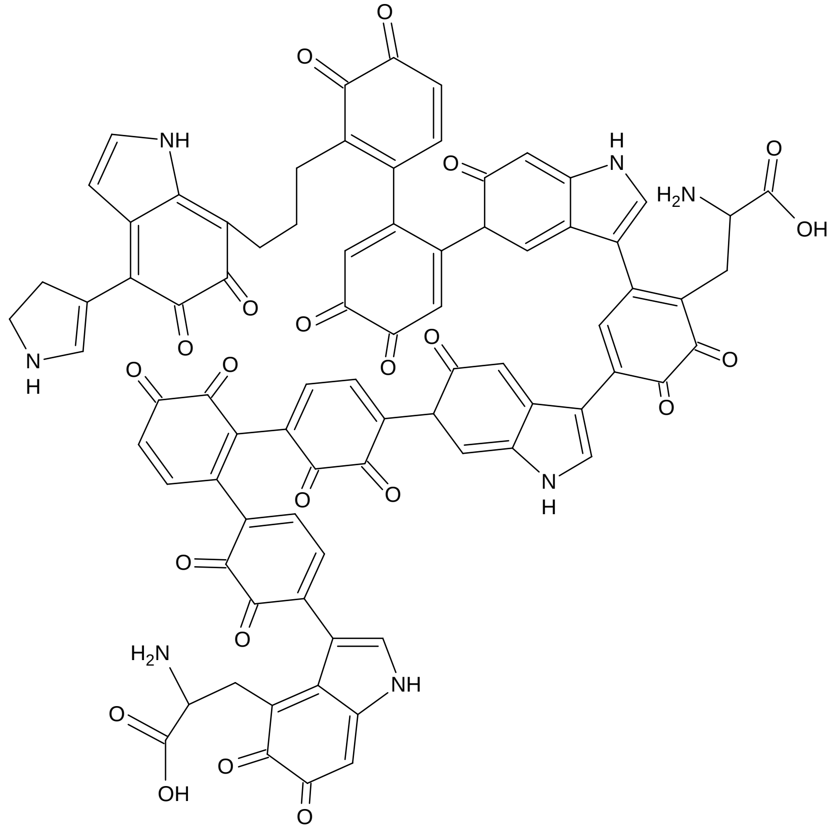


FIGURE 9.7 Representative structure of melanin.

As the melanin structure grows, it becomes more colored giving various shades of brown color to our skin. This brown coloration acts to help protect deeper skin elements from being damaged by the UV radiation. The absence of the enzyme tyrosinase that converts tyrosine to melanin can lead to albinism.

At least two colored melanins are formed—a series of black melanins and a series of so-called red melanins. Our skin pigmentation is determined by the relative amounts of these red and black melanins.

The concentration of melanin also contributes to the color of our hair (except for redheads where the iron-rich pigment trichosiderin dominates). The bleaching of hair, generally achieved through exposure to hydrogen peroxide, is a partial result of the oxidation of the melanin. A side reaction of bleaching is the formation of more sulfur cross-links leading to bleached hair being more brittle because of the increased cross-linking leading to a decrease in hair flexibility.

Melanin also provides a dark background in our eye's iris, is involved in animal color changes (such as the octopus and chameleon), is formed when fruit is bruised, and is partially responsible for the coloration of tea.

9.14 SUMMARY

1. Polysaccharides are the most abundant, on a weight basis, naturally occurring organic polymer. They are truly complex molecules with most structures representable on only an "average" basis. They are diverse with respect to both occurrence and size. The most

important, on a knowledge, weight, and use basis are cellulose and starch. Cellulose is composed largely of D-glucose units that are associated with other materials such as lignin. Cotton is one of the purest forms of cellulose though we get most of our cellulose from wood pulp. Cellulose becomes soluble in aqueous solutions only when the hydrogen bonding within the cellulose is broken.

2. While cellulose is used extensively itself in the form of paper and paper-based products, it also forms the basis of a number of synthetic materials, including a variety of acetylated products such as rayon.
3. Starch is composed of two major components—amylopectin and amylose. It is the second most abundant polysaccharide and is found largely within plants.
4. Polyisoprenes form the basis of many natural polymers including the two most widely known natural plastics gutta-percha and balata and an elastomer known as *H. brasiliensis*, or NR. The hard plastics balata and gutta-percha are *trans* isomers, while NR is the *cis* isomer of 1,4-polyisoprene. The polymer chain of amorphous NR and other elastomers uncoils during stretching and returns to its original low-entropy form when the material is above its T_g. Chain slippage is minimized through the presence of cross-links. Unlike other solids, stretched rubber contracts when heated. The long-range elasticity is dependent on the absence of strong intermolecular forces. Eventually, NR formed the basis of the rubber industry through knowledge of such factors as cross-linking that allowed the material to remain coherent but elastomeric even when exposed to moderate temperatures.
5. Melamines are polymeric agents that play many roles in nature including forming our skin pigmentation and with its growth through exposure to sunlight, acting to protect us from the harmful effects of the sunlight.
6. Lignin is a noncellulosic resinous component of wood. It is the second most abundant renewable natural resource. It has alcohol and ether units with many aromatic units. Much of lignin is sheetlike in structure.

GLOSSARY

accelerator Catalyst for the vulcanization of rubber.

alkali cellulose Cellulose that has been treated with a strong basic solution.

α-cellulose Cellulose that is not soluble in 17.5% basic solution.

α-helix Right-handed helical conformation.

amylopectin Highly branched starch polymer with branches or chain extensions on carbon 6 of the anhydroglucose repeating unit.

amylose Linear starch polymer.

antioxidant Compound that retards polymer degradation.

balata Naturally occurring *trans*-1,4-polyisoprene.

β arrangement Pleated sheetlike conformation.

β-cellulose Cellulose soluble in 17.5% basic solution but not soluble in 8% caustic solution.

Boeseken–Haworth projections Planar hexagonal rings used for simplicity instead of staggered chain forms.

carbohydrate Organic compound often with an empirical formula CH_2O; sugars, starch, cellulose are carbohydrates.

carbon black Finely divided carbon used for the reinforcement of rubber.

carboxymethylhydroxyethylcellulose (CMHEC) Made from the reaction of sodium chloroacetate and hydroxyethylcellulose.

carrageenan Mixture of several polysaccharides containing D-galactose units; obtained from seaweed.

casein Milk protein.

cellobiose Repeat unit in cellulose.

cellophane Sheet of cellulose regenerated by the acidification of an alkaline solution of cellulose xanthate.

celluloid Product from a mixture of cellulose nitrate (CN) and camphor.

cellulose Linear polysaccharide consisting of many anhydroglucose units joined by beta-acetal linkages.

cellulose acetate Product from the acetylation of cellulose.

cellulose nitrate (CN) Made from the reaction of cellulose and concentrated nitric acid; also known as gun cotton.

cellulose xanthate Product of soda cellulose and carbon disulfide.

chitin Polymer of acetylated glucosamine present in the exoskeletons of shellfish.

collagen Protein present in connective tissue.

compounding Processing of adding essential ingredients to a polymer such as rubber.

cyclodextrins Oligomeric cyclic products formed from the reaction of starch treated with a certain enzyme.

degree of substitution (DS) Number that designates the average number of reacted hydroxyl groups in each anhydroglucose unit in cellulose or starch.

dextran Branched polysaccharide synthesized from sucrose by bacteria.

drying Jargon used to describe the cross-linking of unsaturated polymers in the presence of air and a heavy metal catalyst (drier).

ester gum Ester of rosin and glycerol.

ethylhydroxyethylcellulose (EHEC) Nonionic mixed ether formed from HEC and ethyl chloride.

fibrils Threadlike strands or bundles of fibers.

fossil resins Resins obtained from the exudate of prehistoric trees.

galalith Commercial casein plastics.

γ-cellulose Cellulose soluble in 8% caustic solution.

glycogen Highly branched polysaccharide which serves as the reserve carbohydrate in animals.

guayule Shrub that produces *cis*-1,4-polyisoprene rubber.

gutta-percha Naturally occurring *trans*-1,4-polyisoprene.

Hevea Brasiliensis Natural rubber (NR).

humic acid Polymeric aromatic carboxylic acid found in lignite.

hydrocellulose Cellulose degraded by hydrolysis.

hydroxyethylcellulose (HEC) Produced from alkaline cellulose and ethylene oxide.

hydroxypropylcellulose Thermoplastic cellulose ether formed from alkaline cellulose and propylene oxide.

latex Stable dispersion of polymer particles in water.

lignin Noncellulosic resinous component of wood.

mercerized cotton Cotton fiber that has been immersed in caustic solution, usually under tension, and washed with water removing the excess caustic.

methylcellulose (MC) Formed from alkaline cellulose and chloromethane.

native cellulose Naturally occurring cellulose; like cotton.

oligosaccharide Low molecular weight polysaccharide.

racked rubber Stretched rubber cooled below its T_g.

rayon Cellulose regenerated by acidification of a cellulose xanthate (viscose) solution.

recent resins Resins obtained from the exudates of living trees.

regenerated cellulose Cellulose obtained by precipitation from solution.

retrogradation Process whereby irreversible gel is produced by the aging of aqueous solutions of amylose starch.

shellac Natural polymer obtained from the excreta of insects in Southeast Asia.

starch Linear or branched polysaccharides of many anhydroglucose units joined by an α-linkage; amylose is the linear fraction and amylopectin is the branched fraction.

tenacity Term used for the tensile strength of a polymer.

terpene Class of hydrocarbons having the empirical formula C_5H_8.

viscose Alkaline solution of cellulose xanthate.

EXERCISES

1. Why is starch digestible by humans? Why is cellulose not digestible by humans?
2. How does cellobiose differ from maltose?
3. Why is cellulose stronger than amylose?

4. How does the monosaccharide hydrolytic product of cellulose differ from the hydrolytic product of starch?
5. What is paper made from?
6. How many hydroxyl groups are present on each anhydroglucose unit in cellulose?
7. Which would be more polar—tertiary or secondary cellulose acetate?
8. Why would you expect chitin to be soluble in hydrochloric acid?
9. Which is more apt to form a helix: (a) amylose or (b) amylopectin?
10. Why is amylopectin soluble in water?
11. How do the configurations differ for (a) gutta-percha and (b) NR?
12. The formation of what polymer is responsible for tanning?
13. Will the tensile force required to stretch rubber increase or decrease as the temperature is increased?
14. Does a stretched rubber band expand or contract when heated?
15. List three requirements for an elastomer.
16. Why is there an interest in the cultivation of guayule?
17. Are the polymerization processes for synthesis and natural *cis*-polyisoprene (a) similar or (b) different?
18. What does the presence of C_5H_8 units in NR indicate?
19. Why does a rubber band become opaque when stretched?
20. What is the most important contribution to retractile forces in highly elongated rubber?
21. What is present in so-called vulcanized rubber compounds?
22. When a rubber band is stretched, what happens to its temperature?
23. Why are natural plastics not used more?
24. What type of solvent would you choose for shellac?
25. Why is lignin sometimes referred to as being a two-dimensional polymer?
26. Which is a polymer: (a) rosin or (b) ester gum?
27. If the annual production of paper is over 100 million tons, how much lignin is discarded from paper production annually?
28. Is an article molded from Galalith valuable?
29. What are some of the obstacles to using polymer-intensive plants as feedstocks for the preparation of fuels such as ethanol?
30. Since there are many plants that give a rubberlike latex, what are the impediments to their use as replacements for NR?
31. If you were beginning an industrial research project aimed at obtaining useful products from lignin what might be some of the first areas of research you might investigate?
32. How is melanin related to race?
33. It is interesting that while a number of suntan lotion ingredients are used, which of the more recent ones that offer broad range protection is titanium dioxide. What are the other major use of titanium dioxide?

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10 Naturally Occurring Polymers: Animals

The field of natural polymers is one of the strongest, most rapidly growing areas of science and polymers. Our bodies are largely composed of polymers: DNA, RNA, proteins, and polycarbohydrates. Aging, awareness, mobility, strength, etc.—all the characteristics of being alive—are related to the "health" of these polymers. Many medical, health, and biological projects focus on polymers. There is an increasing emphasis on such natural polymers. The importance of the human genome and relationships between genes, proteins, and our health underlies much of this movement. Thus, an understanding of polymeric principles is advantageous to those desiring to pursue a career related to their natural environment, be it medicine, biomedical, biological, bioengineering, etc.

Physically, there is no difference in the behavior, study, or testing of natural and synthetic polymers. Techniques suitable for application to synthetic polymers are equally applicable to the study and behavior of natural polymers.

While the specific chemistry and physics dealing with synthetic polymers is complicated, the chemistry and physics of natural polymers is even more complex because of a number of related factors, including (1) the fact that many natural polymers are composed of different, often similar but not identical, repeat units; (2) a greater dependency on the exact natural polymer environment; (3) the question of real structure of many natural polymers in their natural environment is still not well known for many natural polymers; and (4) the fact that polymer shape and size are even more important and complex in natural polymers than in synthetic polymers.

Biological polymers represent successful strategies that are being studied by scientists as avenues to different and better polymers and polymer structure control. Sample "design rules" and approaches that are emerging include:

- Identification of mer sequences that give materials with particular properties
- Identification of mer sequences that cause certain structural changes
- Formation of a broad range of materials with a wide variety of general or specific properties and function (such as proteins and enzymes) through a controlled sequence assembly from a fixed number of feedstock molecules (proteins—about 20 different amino acids, five bases for nucleic acids, and two sugar units)
- Integrated, *in situ* (in cells) polymer productions with precise nanoscale control
- Repetitive use of proven strategies with seemingly minor structural differences but resulting in quite divergent results (protein for skin, hair, and muscle)
- Control of polymerizing conditions that allows steady-state production far from equilibrium

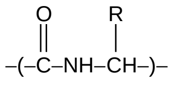
There often occurs a difference in "mind-set" between the nucleic acid and protein biopolymers covered in this chapter and other biopolymers and synthetic polymers covered in other chapters. Nucleic acids and proteins are structure-specific with one conformation. Generally, if a molecule differs in structure or geometry from the specific macromolecule needed, it is discarded. Nucleic acids and proteins are not a statistical average, but rather a specific material with a specific chain length and conformation. By comparison, synthetic and many other biopolymers are statistical averages of chain lengths and conformations. All of these distributions are often kinetic and/or thermodynamic-driven.

This difference between the two divisions of biologically important polymers is also reflected in the likelihood that there are two molecules with the exact same structure. For molecules such as polysaccharides and those based on terpene-like structures the precise structures of individual molecules vary, but for proteins and nucleic acids the structures are identical from molecule to molecule. This can be considered a consequence of the general function of the macromolecule. For polysaccharides the major, though not the sole, functions are energy and structure. For proteins and nucleic acids, the main functions include memory and replication, in addition to proteins sometimes also serving a structural function.

Another difference between proteins and nucleic acids and other biopolymers and synthetic polymers involves the influence of stress–strain activities on the materials properties. Thus, application of stress on many synthetic polymers and some biopolymers encourages realignment of polymer chains and regions, often resulting in a material with greater order and strength. However, application of stress to certain biopolymers, such as proteins and nucleic acids, causes a decrease in performance (through denaturation etc.) and strength. For proteins and nucleic acids, this is a result of the biopolymer already existing in a compact and "energy-favored" form and already existing in the "appropriate" form for the desired performance. The performance requirements for the two classifications of polymers are different. For one set, including most synthetic and some biopolymers, performance behavior involves response to stress–strain application with respect to certain responses such as chemical resistance, absorption enhancement, and other physical properties. By comparison, the most cited performances for nucleic acids and proteins involve selected biological responses requiring specific interactions occurring within a highly structured environment with specific shape and electronic requirements.

10.1 PROTEINS

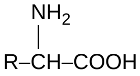
The many different monodisperse polymers of amino acids, which are essential components of plants and animals, are called proteins. This word is derived from the Greek *porteios* meaning "of chief importance." The 20 different alpha-amino acids are joined together by peptide linkages (Table 10.1).



$$-(-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\overset{\overset{\displaystyle R}{|}}{C}H-)- \tag{10.1}$$

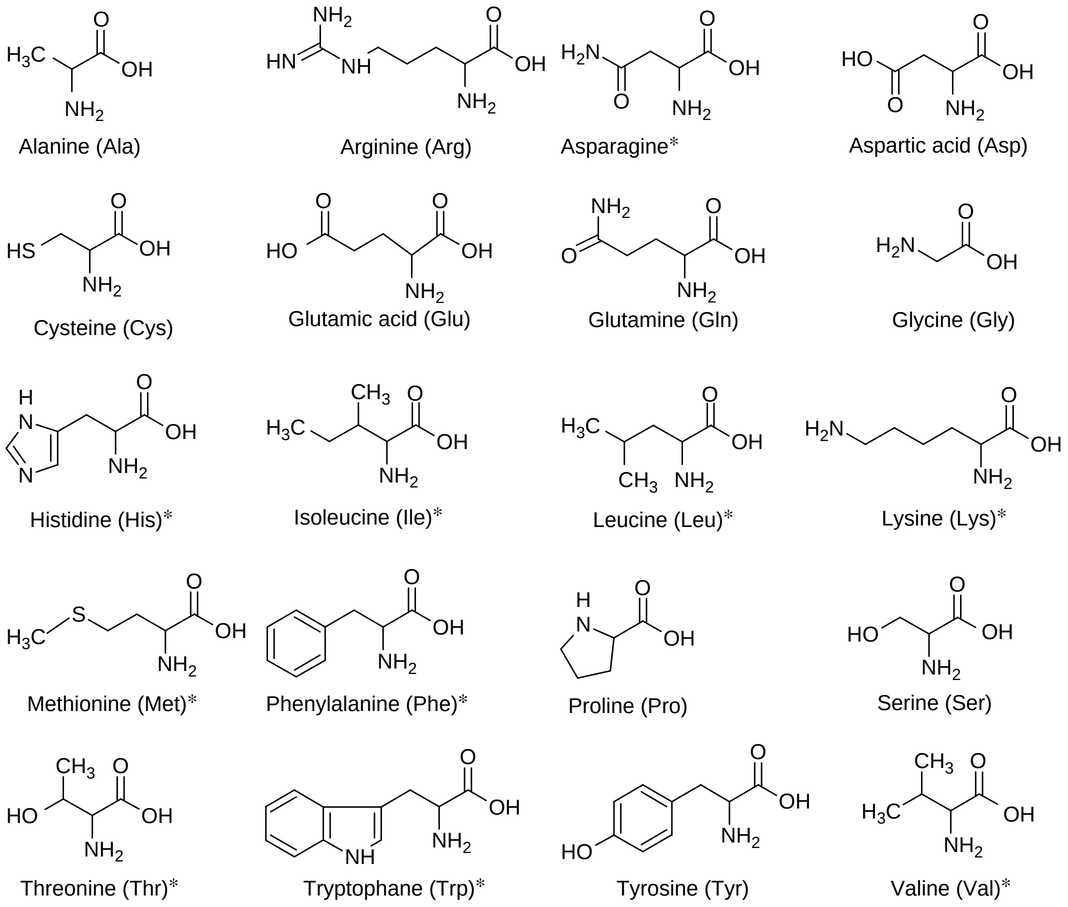
These are also called polyamides or polypeptides. The latter term is often used by biochemists to denote oligomers or relatively low molecular weight proteins. (Note the structural similarities and differences between proteins and polyamides—nylons (Section 4.8).)

All alpha-amino acids found in proteins are of the following general structure:

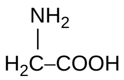


$$R-\overset{\overset{\displaystyle NH_2}{|}}{C}H-COOH \tag{10.2}$$

TABLE 10.1
Structures of the 20 Common Amino Acids. Essential Amino Acids Are Marked with *

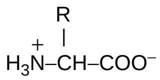


except glycine



$$\begin{array}{c} NH_2 \\ | \\ H_2C\text{–}COOH \end{array} \tag{10.3}$$

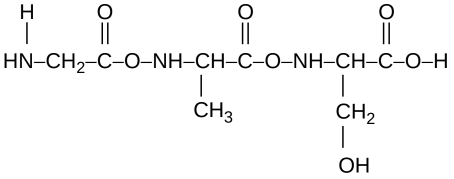
and they contain a chiral carbon atom and are L-amino acids. The net ionic charge of an amino acid varies with the changes in the solution pH. The pH at which an amino acid is electrically neutral is called the isoelectric point. For simple amino acids (containing only one acid and one amine), this occurs at a pH of about 6 with the formation of a dipolar or zwitterion as shown in the following structure:



$$\overset{+}{H_3N}\text{–}\overset{\overset{R}{|}}{C}H\text{–}COO^- \tag{10.4}$$

Hence, alpha-amino acids, like other salts, are water-soluble, high-melting, polar compounds which migrate toward an electrode at pH values other than that of the isoelectric point in a process called electrophoresis.

In writing out sequences for polypeptides it is usual to use a three-letter abbreviation or a one-letter abbreviation starting with the N-terminus to the left and going to the C–O terminus to the right. Thus, the trimer



$$\mathrm{HN(H){-}CH_2{-}C({=}O){-}O{-}NH{-}CH(CH_3){-}C({=}O){-}O{-}NH{-}CH(CH_2OH){-}C({=}O){-}O{-}H}$$

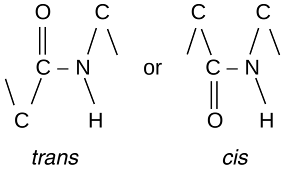
(10.5)

becomes Gly-Ala-Ser or GlyAlaSer or EGAS where E signals the N-terminus.

It is important to remember that all proteins are polypeptides composed of generally one of the 20 amino acids given in Table 10.1. While all of the amino acids have only one variation, with that variation being a lone substituent on the alpha-carbon, this variation is sufficient to produce the variety of proteins critical to life. Some of these contain an "excess" of acid groups such as aspartic acid while others contain one or more additional basic groups such as arginine. Still others possess sulfur-containing moieties, namely cysteine and methionine, that account for the need for sulfur to be present in our diets, and eventually end up in our fossil fuels producing sulfur oxides on burning. All possess nitrogen-containing moieties and these also eventually end up in our fossil fuels and produce nitrogen oxides on burning. The presence of these two elements is then connected to acid-rain production.

The amino acids may be neutral, acidic, or basic, in accordance with the relative number of amino and carboxylic acid groups present. Cations can be formed with amino acids like tryptophane, lysine, histidine, and arginine which have "extra" amine groups, while others that contain additional acid groups like aspartic acid and glutamic acid can be hydrolyzed to form anions. The presence of varying amounts of these additional amino acid moieties within a protein are primary driving forces for the separation of proteins using electrophoresis and results in polypeptides having different isoelectric points. If there are a number of "extra" acidic and/or basic groups on the polypeptide, the molecule is said to be a polyampholyte, or if they contain only positive or negative charges, they are called polyelectrolytes. The behavior of these charged polypeptides is similar to the behavior of other charged polymers. Thus, a fully hydrolyzed poly(acrylic acid) acts as a rod because the negative sites repeal one another while a polypeptide with a large number of negative sites will also be elongated. The spacing and number of these charged sites help determine the tertiary structure of such polypeptides.

Even though the atoms within a peptide bond are coplanar, they can exist in two possible configurations, *cis* and *trans*:



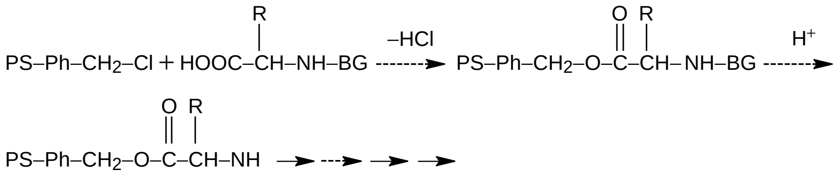
(10.6)

The *trans* form is usually favored whenever there is a bulky group on the adjacent alpha-carbon(s) because bulky groups will interfere more in the *cis* structure.

While humans synthesize about 12 of the 20 amino acids needed for good health, the other 8 are obtained from outside our bodies, generally from eating foods that supply these essential amino acids (Table 10.1). Different foods are good sources of different amino acids. Cereals are generally deficient in lysine. Thus, diets that emphasize cereals will also have other foods that can supply lysine. In the orient, the combination of soybean and rice supplies the essential amino acids, while in Central America bean and corn are used.

Almost all of the sulfur needed for healthy bodies is found in amino acids as cysteine and methionine. Sulfur serves several important roles including as a cross-linking agent similar to that served by sulfur in the cross-linking, or vulcanization, of rubber. This cross-linking allows the various chains, which are connected by these cross-links, to "remember" where they are relative to one another. This cross-linking allows natural macromolecules to retain critical shapes to perform necessary roles.

The most widely used technique for producing polypeptides with specific sequences is the solid-phase technique developed by Nobel Prize winner Bruce Merrifield in which all reactions take place on the surface of cross-linked PS beads. The process begins with the attachment of the C-terminal amino acid to the chloromethylated polymer. Nucleophilic substitution by the carboxylate anion of an N-blocked protected C-terminal amino acid displaces chloride from the chloromethyl group forming an ester, protecting the C site while attaching it to the solid support. The blocking group is removed by addition of acid and the polymer containing the nonprotected N-terminus is washed to remove unwanted byproducts. A peptide bond is formed by condensation to an N-blocked protected amino acid. Again, the solid-phase system is washed and the by-products removed. The blocking group is removed and the site is ready for attachment by another amino acid. This cycle is repeated eventually producing the desired polypeptide without isolation of intermediate products. These steps are outlined below.



$$\begin{gathered}\mathrm{PS{-}Ph{-}CH_2{-}Cl + HOOC{-}\overset{\displaystyle R}{\overset{|}{C}}H{-}NH{-}BG \xrightarrow{-HCl} PS{-}Ph{-}CH_2{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle R}{\overset{|}{C}}H{-}NH{-}BG \xrightarrow{H^+}} \\ \mathrm{PS{-}Ph{-}CH_2{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle R}{\overset{|}{C}}H{-}NH} \longrightarrow \dashrightarrow \longrightarrow \longrightarrow\end{gathered} \qquad (10.7)$$

where PS = polystyrene bead, Ph = phenyl group, BG = blocking group.

10.2 LEVELS OF PROTEIN STRUCTURE

The shapes of macromolecules, both synthetic and natural, can be described in terms of primary, secondary, tertiary, and quaternary structure (Figure 10.1), and these will be illustrated with protein structures.

10.2.1 Primary Structure

The term primary structure is used to describe the sequence of amino acid units (configuration) in a polypeptide chain. Structure 10.5 is an example of a primary structure.

10.2.2 Secondary Structure

The term secondary structure is used to describe the molecular shape or conformation of a molecule. The most important factor in determining the secondary structure of a material is its precise structure. For proteins, it is the amino acid sequence. Hydrogen bonding is also an important factor in determining the secondary structures of natural materials and those synthetic materials that can hydrogen-bond. In fact, for proteins, secondary structures are

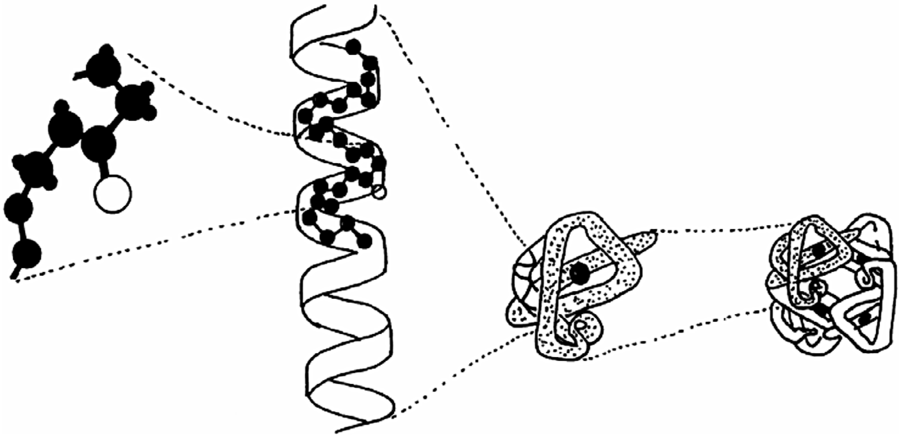


FIGURE 10.1 Four levels of structure elucidation. From left to right: primary, secondary, tertiary, and quaternary structures illustrate using a globular protein segment.

generally those that allow a maximum amount of hydrogen bonding. This hydrogen bonding also acts to stabilize the secondary structure while cross-linking acts to lock in a structure.

In nature, the two most common secondary structures are helices and sheets. In nature, extended helical conformations appear to be utilized in two major ways: to provide linear systems for the storage, duplication, and transmission of information (DNA, RNA); and to provide inelastic fibers for the generation and transmission of forces (F-actin, myosin, and collagen). Examples of the various helical forms found in nature are single helix (messenger and ribosomal DNA), double helix (DNA), triple helix (collagen fibrils), and complex multiple helices (myosin). Generally, these helices are readily soluble in dilute aqueous solution. Often solubility is only achieved after the inter- and intrahydrogen bonding is broken.

There are a variety of examples in which linear or helical polypeptide chains are arranged in parallel rows. The two major forms that exist for proteins are illustrated in Figures 10.2 through 10.5. The chains can have the N→C directions running parallel, making a parallel beta sheet (Figure 10.4), or they can have the N→C directions running antiparallel, giving antiparallel beta sheets (Figure 10.5).

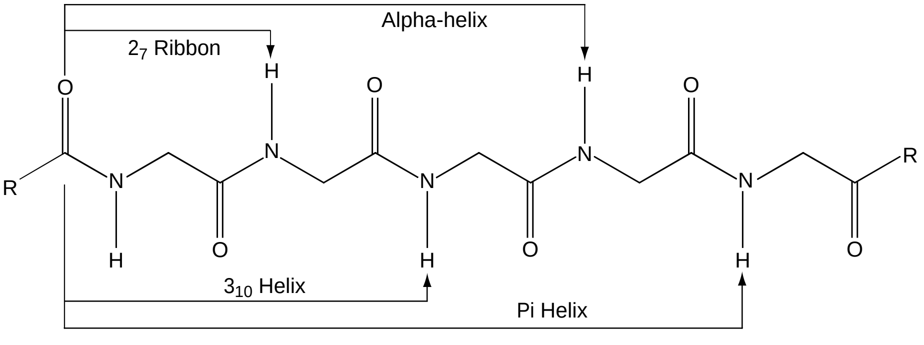


FIGURE 10.2 Commonly occurring repetitive helical patterns for polypeptides. (From Coates J. and Carraher, C. *Polymer News*, 9(3), 77, 1983. With permission.)

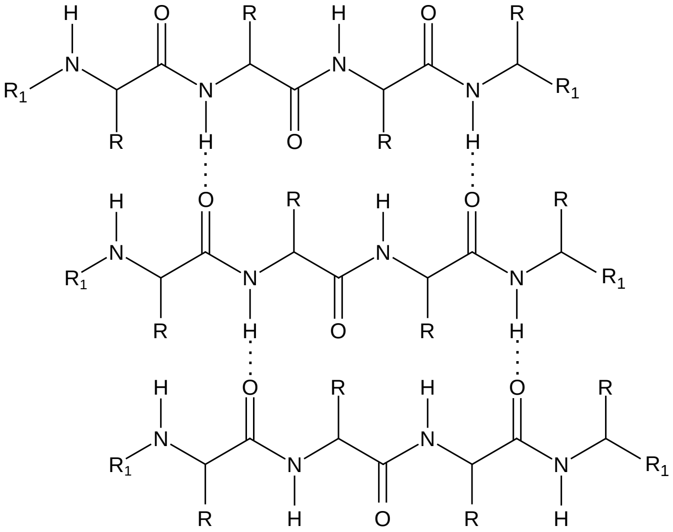


FIGURE 10.3 A beta arrangement or pleated sheet conformation of proteins.

As noted earlier, the structures of proteins generally fall into two groupings: fibrous and globular. The structural proteins such as the keratins, collagen, and elastin are largely fibrous. A recurring theme with respect to conformation is that the preferential secondary structure of fibrous synthetic and natural polymers approximates that of a pleated sheet (or skirt) or helix. The pleated sheet structures in proteins are referred to as beta arrangements (Figure 10.5). In general, proteins with bulky groups take on a helical secondary structure while those with less bulky groups exist as beta sheets.

Helices can be described by the number of amino acid residues in a complete "turn." In order to fit into a "good" helix, the amino acids must have the same configuration. For proteins, that configuration is described as an L-configuration, with the helix being a "right-handed" helix, referred to as an alpha-helix.

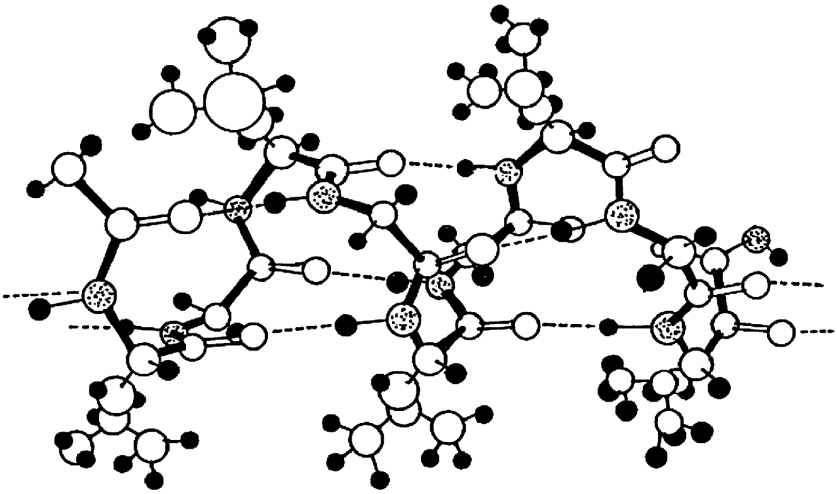


FIGURE 10.4 Alpha-keratin helix for the copolymer derived from glycine and leucine.

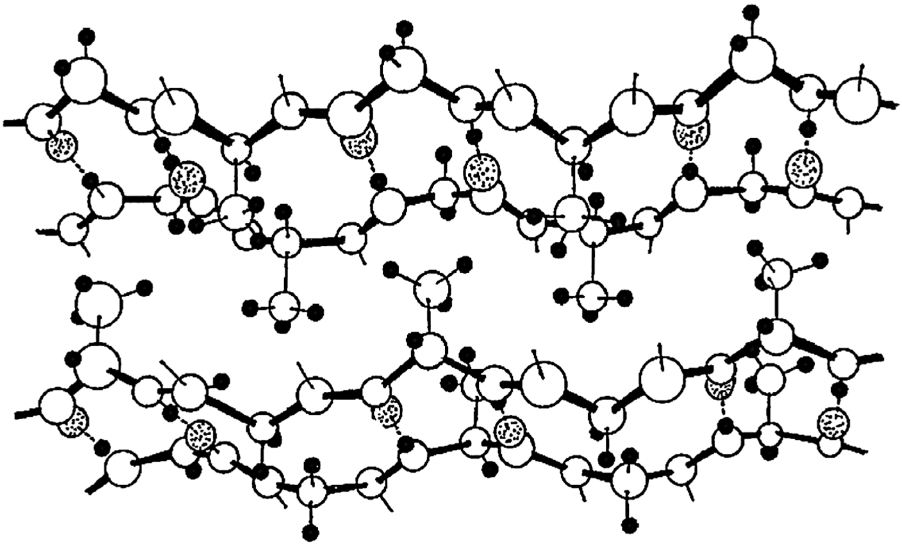


FIGURE 10.5 Beta-keratin sheet for the copolymer derived from glycine and alanine.

10.2.2.1 Keratins

As noted above, two basic "ordered" secondary structures predominate in synthetic and natural polymers. These are helices and the pleated sheet structures, which are illustrated by the group of proteins called the keratins. It is important to remember that hydrogen bonding is critical in both structures. For helices, the hydrogen bonding occurs within a single strand, whereas in the sheets, the hydrogen bonding occurs between adjacent chains.

Helices are often described in terms of a repeat distance—the distance parallel to the axis in which the structure repeats itself; pitch—the distance parallel to the helix axis in which the helix makes one turn; and rise—the distance parallel to the axis from the level of one repeat unit to the next.

Helices generally do not have an integral number of repeat units or residues per turn. The alpha-helix repeats after 18 amino acid residues taking five turns to repeat, resulting in $18/5 = 3.6$ residues/turn. For polypeptides, each carbonyl oxygen is hydrogen-bonded to the amino proton on the fourth residue, giving a "hydrogen-bonded loop" with 13 atoms. Helices are often described in terms of this number n. Thus, the alpha-helix is described as a 3.6_{13} helix. Because hydrogen bonds tend to be linear, the hydrogen bonding in proteins approximates this with the $-N-H\cdots O{=}C$ in a straight line. The rise h of alpha-keratin (Figure 10.4) is found by x-ray spectroscopy to be about 0.15 nm for each amino acid residue. The pitch p of a helix is given by $p = nh$. For alpha-keratin $p = 3.6$ amino acid residues/turn × 0.15 nm/amino acid residue = 0.54 nm/turn.

Hair and wool are composed of alpha-keratin. A single hair on our head is composed of many strands of keratin. Coiled, alpha-helices, chains of alpha-keratin intertwine to form protofibrils, which in turn are clustered with other protofibrils forming a microfibril. Hundreds of these microfibrils, in turn, are embedded in a protein matrix giving a macrofibril, which in turn combines to form a human hair. While combing will align the various hairs in a desired shape, after a while, the hair will return to its "natural" shape through the action of the sulfur cross-links pulling the hair back to its original shape.

Secondary bonding is involved in forming the helical structures allowing the various bundles of alpha-keratin to be connected by weak secondary interactions, which in turn allow them to readily slide past one another. This sliding or slippage along with the "unscrewing" of the helices allows our hair to be flexible. Some coloring agents and most permanent waving of our hair involve breakage of the sulfur cross-links and a reforming of the sulfur cross-links at new sites to "lock in" the desired hair shape.

Our fingernails are also composed of alpha-keratin, but keratin with a greater amount of sulfur cross-links giving a more rigid material. In general, for both synthetic and natural polymers, increased cross-linking leads to increased rigidity.

The other major structural feature is pleated sheets. Two kinds of pleated sheets are found. When the chains have their N→C directions running parallel, they are called parallel beta sheets. The N→C directions can run opposite to one another giving what is called an antiparallel beta sheet. The beta-keratin (Figure 10.5) that occurs in silk produced by insects and spiders is of the antiparallel variety. While alpha-keratin is especially rich in glycine and leucine, beta-keratin is mostly composed of glycine and alanine with smaller amounts of other amino acids including serine and tyrosine. Size-wise, leucine offers a much larger grouping attached to the alpha-carbon than does alanine. The larger size of the leucine causes the alpha-keratin to form a helical structure to minimize steric factors. By comparison, the smaller size of the alanine allows the beta-keratin to form sheets. This sheet structure is partially responsible for the "softness" felt when we touch silk. While silk is not easily elongated because the protein chains are almost fully extended, beta-keratin is flexible because of the low secondary bonding between sheets, allowing them to flow past one another.

10.2.2.2 Silk

Silk is a protein fiber that is woven into fiber from which textiles are made including clothing and high-end rugs. It is obtained from the cocoon of silkworm larvae. While most silk is harvested from commercially grown silkworms, some is still obtained from less well-established sources.

Silk was first developed as early as 6000 B.C. The Chinese Empress, Xi Ling-Shi, developed the process of retrieving silk filaments by floating the cocoons on warm water. This process and the silkworm itself were monopolized by China until about A.D. 550 when two missionaries smuggled silkworm eggs and mulbetty seeds from China to Constantinople (Istanbul). First reserved for use by the Emperors of China, it eventually spread to the Middle East, Europe, and North America until now when its use is worldwide. The history of silk and the silk trade is interesting and can be obtained at http://en.wikipedia.org/wiki/Silk.

The early work focused on a particular silkworm, *Bombyx mori*, that lives on mulberry bushes. There are other silkworms each with its own special properties, but in general most silk is still derived from the original strain of silkworm. Crystalline silk fiber is about four times stronger than steel on a weight basis.

In the silk fibroin structure almost every other residue is glycine, with either alanine or serine between them allowing the sheets to fit closely together (Table 10.1). While most of the fibroin exists as beta sheets, regions that contain more bulky amino acid residues interrupt the ordered beta structure. Such disordered regions allow some elongation of the silk. Thus, in the crystalline segments of silk fibroin there exists directional segregation using three types of bonding: covalent bonding in the first dimension, hydrogen bonding in the second dimension, and hydrophobic bonding in the third dimension. The polypeptide chains are virtually fully extended; there is a little puckering to allow for optimum hydrogen bonding. Thus, the structure is not extensible in the direction of the polypeptide chains. By comparison, the less specific hydrophobic (dispersive) forces between the sheets produce considerable flexibility. The crystalline regions in the polymers are interspersed with amorphous regions in which glycine and alanine are replaced by amino acids with bulkier pendant groups that prevent the ordered arrangements to occur. Furthermore, different silkworm species spin silks with differing amino acid compositions, and thus with differing degrees of crystallinity. The correlation between the extent of crystallinity and the extension at the break point is given in Table 10.2.

TABLE 10.2
Selected Properties as a Function of Silk Worm Species

Silk Worm Species	Approximate Crystallinity (%)	Extension at Break Point (%)
Anaphe moloneyi	95	12.5
Bombyx mori	60	24
Antherea mylitta	30	Flows then extend to 35

Another natural key that illustrates the tight relationship between structure and property is found in spiderwebs. The composition within a spiderweb is not all the same. We can look briefly at two of the general types of threads. One is the network or frame threads, also called the dragline fabric. It is generally stiff and strong. The second is the catching or capture threads, which are made of viscid silk that is strong, stretchy, and covered with droplets of glue. The frame threads are about as stiff as nylon-6,6 thread and stronger than steel cable on a weight basis. Capture thread is not stiff but is more elastomeric and about one-third as strong as frame thread on a weight basis. While there are synthetic materials that can match silk in both stiffness and strength, there are few that come near silk threads in toughness and their ability to withstand a sudden impact without breaking. Kevlar, which is used in bullet-resistant clothing, has less energy-absorbing capacity in comparison to either frame or capture threads. In fact, when weight is dropped onto frame silk, it adsorbs up to 10 times more energy than Kevlar. On impact with frame thread, most of the kinetic energy dissipates as heat, which, according to a hungry spider, is better than transforming into elastic energy that might simply act to ‘‘bounce’’ the prey out of the web.

The frame threads are composed of two major components: highly organized microcrystals comprise about one-quarter of the mass and amorphous spaghetti-like tangles comprise the other three-quarters. The amorphous chains connect the stronger crystalline portions. The amorphous tangles are dry and glasslike, acting as a material below its T_g. The amorphous chains are largely oriented along the thread length as are the microcrystals giving the material good longitudinal strength. As the frame threads are stretched, the tangles straighten out allowing it to stretch without breaking. Because of the extent of the tangling there is a lessening in the tendency to form micro-ordered domains as the material is stretched, though that also occurs. Frame thread can be reversibly stretched to about 5%. Greater stretching causes permanent creep. Thread rupture does not occur until greater extension, such as 30%. By comparison, Kevlar fibers break when extended only 3%.

The capture threads also comprise similar components but here the microcrystals compose less than 5% of the thread, with both the amorphous and microcrystalline portions arranged in a more random fashion within the thread. Hydrated glue, which coats the thread, acts as a plasticizer imparting greater mobility and flexibility to the chains. It stretches several times its length when pulled and is able to withstand numerous shocks and pulls appropriate to contain the prey as it attempts to escape. Further, most threads are spun as two lines so that the resulting thread has a kind of built-in redundancy.

The spinning of each type of thread comes from a different emission site on the spider and the spider leaves little to waste, using unwanted and used web parts as another source of protein.

Cloning of certain spider genes has been included in goats to specify the production of proteins that call for the production of silklike fibroin threads that allow the production and subsequent capture of spider-like threads as part of goat’s milk.

The beta-keratin structure is also found in the feathers and scales of birds and reptiles.

10.2.2.3 Wool

Wool, while naturally existing in the helical form, takes on a pleated sheet-like structure when stretched. If subjected to tension in the direction of the helix axes, the hydrogen bonds parallel to the axes are broken and the structure can be irreversibly elongated to an extent of about 100%.

Wool is the fiber from members of the Caprinae family that includes sheep and goats. It is produced as an outer coat with the inner coat being more hairlike. Since it is removed without damaging the sheep's skin, it is renewable without sacrificing the animal. The fiber has two distinguishing characteristics that separate it from fur and hair. It has scales that overlap like shingles on a roof and it is curly, with many fibers having over 20 bends per inch. This crimp has both advantages and disadvantages. The disadvantage is that the fiber tends to mat and gather cockleburs when on the sheep. The curly nature gives the fiber lots of bulk and associated insulation ability. It retains air, assisting the wearer to maintain temperature. Thus, in the cold the body retains needed heat, while in hot weather it can remain somewhat cool with respect to the surroundings. Thus wool is a staple material for extreme temperatures.

The shingle nature results in a somewhat rough surface that helps the fibers to remain together. In turn, this allows the fibers to be easily formed into yarn.

As noted above, the inner coat is more hairlike with little scale or crimp. This hair is called kemp, while the fiber portion is the wool. Combined they are referred to as the fleece.

A common theme with natural products is the variability of the fiber with the particular plant or animal and the particular conditions under which they were grown. The proportion of kemp to wool varies from breed to breed as does the number of crimps per inch. Thus, wool from different breeds raised in different parts of the world will have different properties and contributions to the fiber. Generally, the wool and kemp are physically separated. In fact, after shearing, the wool is divided into five groups: fleece (which is the largest), pieces, bellies, crutchings, and locks. The last four are packaged and sold separately. The desired part, the fleece, is further classified.

As the wool is removed from the sheep, it contains a high amount of grease that has valuable lanolin. Natives make yarn out of this wool. But, for most commercial use, the lanolin is removed by washing with detergents and basic solutions.

A number of different wools are special and sold under different names such as cashmere wool. These wools have their own special characteristics that increase their cost and value. It is interesting that many animals have developed their own special coats to overcome their native environment. Thus, because cashmere goats live in a cold mountain temperature, their wool is an effective material to protest against the cold.

10.2.2.4 Collagen

Collagen is the most abundant single protein in vertebrates making up to one-third of the total protein mass. Collagen fibers form the matrix or cement material in our bones where mineral materials precipitate. Collagen fibers constitute a major part of our tendons and act as a major part of our skin. Hence, it is collagen that is largely responsible for holding us together.

The basic building block of collagen is a triple helix of three polypeptide chains called the tropocollagen unit. Each chain is about 1000 residues long. The individual collagen chains form left-handed helices with about 3.3 residues/turn. In order to form this triple-stranded helix, every third residue must be glycine because glycine offers a minimum of bulk. Another interesting theme in collagen is the additional hydrogen bonding that occurs because of the presence of hydroxyproline derived from the conversion of proline to hydroxyproline. The conversion of proline to hydroxyproline involves vitamin C. Interestingly, scurvy, the consequence of a lack of vitamin C, is a weakening of collagen fibers giving way to lesions in the skin and gums and weakened blood vessels. Collagen fibers are strong. In tendons, the collagen fibers have a strength similar to that of hard-drawn copper wire.

Much of the toughness of collagen is the result of the cross-linking of the tropocollagen units to one another through a reaction involving lysine side chains. These chains are oxidized to aldehydes that react with either a lysine residue or with one another through an aldol condensation and dehydration resulting in a cross-link. This process continues throughout our life resulting in our bones and tendons becoming less elastic and more brittle. Again, a little cross-linking is essential, but more cross-linking leads to increased fracture and brittleness.

Collagen is a major ingredient in some "gelation" materials. Here, collagen forms a triple helix for some of its structure while other parts are more randomly flowing single-collagen chain segments. The bundled triple-helical structure acts as the rigid part of the polymer while the less-ordered amorphous chains act as a soft part of the chain. The triple helix also acts as a noncovalently bonded cross-link.

10.2.2.5 Elastin

Collagen is found where strength is needed, but some tissues, such as arterial blood vessels and ligaments, need materials that are elastic. Elastin is the protein of choice for such applications. Elastin is rich in glycine, alanine, and valine and it is easily extended and flexible. Its conformation approaches that of a random coil so that secondary forces are relatively weak, allowing elastin to be readily extended as tension is applied. The structure also contains some lysine side chains that are involved in cross-linking. The cross-linking is accomplished when four lysine side chains are combined to form a desmosine cross-link, which prevents the elastin chains from being fully extended and causes the extended fiber to return to its original dimensions when tension is removed. One of the areas of current research is the synthesis of polymers with desired properties based on natural analogues. Thus, elastin-like materials have been synthesized using glycine, alanine, and valine, as well as some cross-linking. These materials approach elastin in its elasticity.

We are beginning to understand better how we can utilize the secondary structure of polymers as tools of synthesis. One area where this is being applied is "folded oligomers." Here, the secondary structure of the oligomer can be controlled through its primary structure and use of solvents. Once the preferred structure is achieved, the oligomers are incorporated into larger chains eventually forming synthetic polymers with several precise structures "embedded" within them. The secondary structure of the larger polymers can also be influenced by the nature of the solvent allowing further structural variety. Further, other species, such as metal ions, can be added to assist in locking in certain desired structures and they can also be used to drive further structure modifications.

10.2.3 TERTIARY STRUCTURE

The term tertiary structure is used to describe the shaping or folding of macromolecules. These larger structures generally contain elements of the secondary structures. Often hydrogen bonding and cross-linking lock in such structures. As noted above, proteins can be divided into two broad groups: fibrous or fibrillar proteins and globular proteins that are generally soluble in acidic, basic, or neutral aqueous solutions. Fibrous proteins are long macromolecules that are attached through either inter- or intrahydrogen bonding of the individual residues within the chain. Solubility, partial or total, occurs when these hydrogen bonds are broken.

10.2.3.1 Globular Proteins

There is a wide variety of so-called globular proteins. Many of these have alpha and beta structures imbedded within the overall globular structure. Beta sheets are often twisted or wrapped into a "barrel-like" structure. They contain portions that are beta sheet structures and portions that are in an alpha conformation. Further, some portions of the globular protein may not be conveniently classified as either an alpha or a beta structure.

These proteins are often globular in shape so as to offer a different "look" or polar nature to their outside. Hydrophobic residues are generally found in the interior while hydrophilic residues are found on the surface interacting with the hydrophilic water-intense external environment. (This theme is often found for synthetic polymers that contain both polar and nonpolar portions. Thus, when polymers are formed or reformed in a regular water-filled atmosphere, many polymers will favor the presence of polar moieties on their surface.)

Folding depends on a number of interrelated factors. The chain-folding process involves going from a system of random beta and alpha conformations to a single-folded structure. This change involves a decrease in the entropy or randomness. For folding to occur, this increase in order must be overcome by energy-related factors to allow the overall free energy to be favorable. These energy factors include charge–charge interactions, hydrogen bonding, van der Waals interactions, and hydrophilic or hydrophobic effects.

Within a particular globular polymer there may be one or more polypeptide chains folded backward and forward forming quite distinct structural domains. Each domain is characterized by a particular style of coiling or "sheeting" which may be nonrepetitive with respect to its peptide chain geometry or may be repetitive, conforming to one of several now well-recognized patterns. The specific chain conformations are determined by the side chain interactions of the amino acids superimposed on intrapeptide hydrogen bonding along the chain. The form of chain folding is thus ultimately determined by the amino acid sequence and the polymeric nature of the polypeptide chains, and is fundamental to the specific geometry of the given protein.

Protein units can be either negatively or positively charged. Attractions between unlike charges are important as are the repulsions between like changed units. As expected, these associations are pH-dependent, and control of pH is one route for conformation changes to occur. The ability to hydrogen-bond is also an important factor with respect to the internal folding scheme. Because the proteins are tightly packed, the weak van der Waals interactions can also play an important role in determining chain folding. The tendency for polarity-like segments to congregate can also be an important factor in chain folding. Thus, hydrophilic groupings are generally clustered on the outside of the globular protein allowing them to take advantage of hydrogen bonding and other polar bonding opportunities with the water-rich environment, while hydrophobic clusters of amino acid units occupy the internal regions of the protein taking advantage of hydrophobic interactions.

Globular proteins act in maintenance and regulatory roles—functions that often require mobility and thus some solubility. Within the globular grouping are enzymes, most hormones, hemoglobin, and fibrinogen that are changed into an insoluble fibrous protein fibrin, which causes blood clotting.

Denaturation is the irreversible precipitation of proteins caused by heating, such as the coagulation of egg white as an egg is cooked, or by addition of strong acids, bases, or other chemicals. This denaturation causes permanent changes in the overall structure of the protein and because of the ease with which proteins are denatured it makes it difficult to study natural protein structure. Nucleic acids also undergo denaturation.

Small changes in the primary structure of proteins can result in large changes in the secondary structure. For instance, researchers have interchanged the positions of two adjacent amino acid residues of a globular protein portion resulting in a beta strand becoming a right-handed helix.

Molecular recognition is one of the keys to life. Scientists are discovering ways both to modify molecular recognition sites and to "copy" such sites. One approach to modifying molecular recognition sites, namely enzymatic protein sites, is through what is referred to as "directed evolution." Arnold and coworkers have employed the combinatorial approach by taking an enzyme with a desired catalytic activity and encouraging it to undergo mutation, selecting out those mutations that perform in the desired manner; and repeating this cycle until the new enzymes perform as desired. Ratner and coworkers have taken another approach whereby templates containing the desired catalytic sites are made. First, the protein is mounted on a mica support. The target protein is coated with a sugar monolayer that allows for specific recognition. A fluoropolymer plasma film is deposited over the sugar monolayer. The fluoropolymer reverse image is attached to a support surface using an epoxy resin. Solvents are then added to etch away the mica, sugar, and original protein leaving behind a ‘‘nanopit’’ template that conforms to the shape of the original protein.

10.2.4 QUATERNARY STRUCTURE

The term quaternary structure is employed to describe the overall shape of groups of chains of proteins, or other molecular arrangements. For instance, hemoglobin is composed of four distinct but different myoglobin units, each with its own tertiary structure that comes together giving the hemoglobin structure. Silk, spiderwebs, and wool, already described briefly, possess their special properties because of the quaternary structure of their particular structural proteins.

Both synthetic and natural polymers have superstructures that influence or dictate the properties of the material. Many of these primary, secondary, tertiary, and quaternary structures are influenced in a similar manner. Thus, the primary structure is a driving force for the secondary structure. Allowed and preferred primary and secondary bondings influence structure. For most natural and synthetic polymers, hydrophobic and hydrophilic domains tend to cluster. Thus, most helical structures will have either a hydrophobic or hydrophilic inner core with the opposite outer core resulting from a balance between secondary and primary bonding factors and steric and bond angle constraints. Nature has used these differences in domain character to create the world around us.

As noted earlier, some proteins are linear with inter- and intrachain associations largely occurring because of hydrogen bonding. Influences on globular protein structures are more complex, but again the same forces and features are at work. Globular proteins have irregular three-dimensional structures that are compact but which, when brought together, form quaternary structures that approach being spherical. While the overall structure is spherical the surface is irregular, with the irregularity allowing the proteins to perform different specific biological functions.

The preferred folding confirmation is again influenced by the same factors of bonding type, polarity, size, flexibility, and preferred bond angles. The folded conformations are possible because of the flexibility of the primary bonding present within proteins. Thus, polar portions, namely the amine and carbonyl moieties, are more fixed, but the carbon between them is more flexible. Again, the folding characteristic conformations are driven by secondary bonding. Some folding is chemically ‘‘fixed’’ through use of cross-links. In hair, these cross-links are often disulfides, –S–S–.

As noted earlier, the flexibility of proteins allows them to carry out a wide variety of tasks. Our cells often build about 60,000 different kinds of proteins. A bacterial cell will synthesize only a little over 1000 different kinds of proteins.

When a protein contains more than about 200 amino acid groups, it often assumes two or more somewhat spherical tertiary structural units. These units are often referred to as domains. Thus, hemoglobin is a combination of four myoglobin units with each of the four units influenced by the other three, and where each unit contains a site to interact with oxygen.

The specificity of enzymatic catalytic activity is dependent on tertiary structure. Phosphoglycerate kinase (Figure 10.6) is a protein composed of 415 amino acids. The protein chain is folded backward and forward forming a clawlike structure that has two rigid domains divided by a more flexible hinge region. Phosphoglycerate kinase binds to phosphoglycerate,

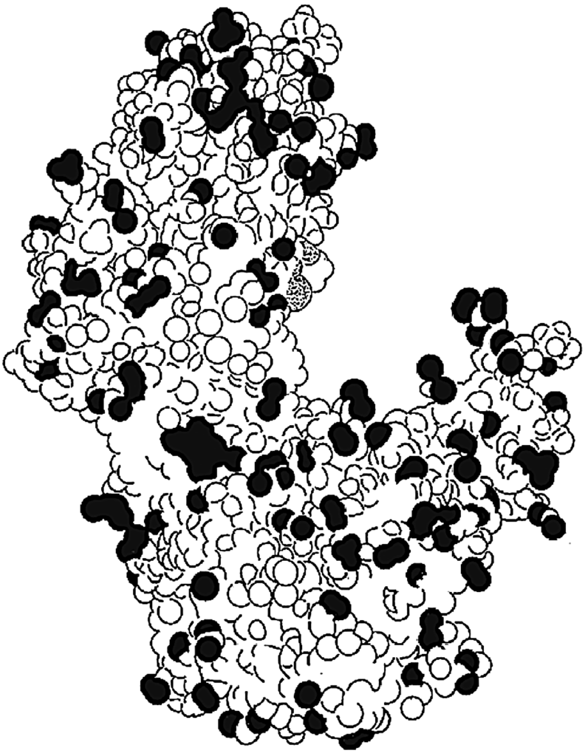


FIGURE 10.6 Protein enzyme phosphoglycerate kinase involved in the formation of adenosine-5′-triphosphate (ATP) from adenosine-5′-diphosphate (ADP).

a fragment of glucose, transferring the phosphate forming adenosine triphosphate (ATP). If the enzyme binds to the phosphoglycerate and water, the phosphate could react with the water rather than forming ATP. The protein is designed to circumvent this by having the essential parts present in both halves of the claw. As the enzyme binds the phosphoglycerate and the adenosine diphosphate (ADP), the claw closes bringing together the two necessary active parts, excluding water and other nonessential compounds. In Figure 10.6 the active site phosphoglycerate is indicated by the "dotted" area about half way up one of the two sections of the claw.

The structure given in Figure 10.6 also illustrates the usual arrangement whereby hydrophilic areas, noted as darkened areas, radiate outward from the enzyme surface, while the less hydrophilic and hydrophobic areas tend to reside within the enzyme.

Table 10.3 contains a listing of some important proteins. Protein purification must be done under conditions in which conformational and configurational changes are minimal. Such purification is most often carried out using varieties of chromatography including affinity chromatography and electrophoresis. Some of the common features of enzymes are:

- Alpha-helix content is not as high as myoglobin, but areas of beta sheeting are not unusual.
- Water-soluble enzymes have a large number of charged groups on the surface and those not on the surface are involved in the active site; large parts of the interior are hydrophobic.
- The active site is found either as a cleft in the macromolecule or as a shallow depression on its surface.

TABLE 10.3
Shapes of Selected Biologically Important Proteins

Protein	Shape	Molecular Weight	Comments
Myoglobin	3D, oblate spheroid	1.7×10^4	Temporary oxygen storage in muscles
Hemoglobin	3D, more spherical than myoglobin	6.4×10^4	Oxygen transport through body
Cytochrome C	3D, prolate spheroid	$1.2–1.3 \times 10^4$	Heme-containing protein, transports electrons rather than oxygen
Lysozyme	3D, short alpha-helical portions, region of antiparallel pleated sheets	1.46×10^4	Well studied, good illustration of structure-activity
Chymotrypsin and trypsin	3D, extensive beta structure	—	Hydrolysis of peptide bonds on the carboxyl side of certain amino acids
Insulin	3D, two alpha-helical section in A chain, B chain has alpha-helix and remainder is extended linear central core	6×10^3	Regulation of fat, carbohydrate, and amino acid metabolism
Somatotropin (human) collagen	3D, 50% alpha-helix	2.2×10^4	Pituitary hormone
Keratin	Varies with source, 3D or 2D; most contain alpha-helix sections	$10^4–10^5$	Most abundant protein; major part of skin, teeth, bones, cartilage, and tendon
Fibroin	Varies with source, fibrous-linear with cross-links; crystalline regions contain antiparallel, pleated sheets	3.65×10^5	Major constituent of silk
Elastin	Varies with source; cross-linked, mostly random coil with some alpha-helix	$>7 \times 10^4$	Many properties similar to rubber; gives elasticity to arterial walls and ligaments

While enzymes are effective catalysts inside in the body, we have developed techniques for "capturing" some of this activity by immobilizing enzymes. The activity of many enzymes continues in this immobilized condition. In one approach, the enzyme is isolated and coupled to gels that can swell in solvent using polyacrylamide copolymers that contain N-acryloxysuccinimide repeat units. The pendant groups react with the amino "ends" of the enzyme effectively coupling or immobilizing the enzyme. Modifications of this procedure have been used to immobilize a wide variety of enzymes. For instance, the particular reactive or anchoring group on the gel can be especially modified for a particular enzyme. Spacers and variations in the active coupling end are often employed. Amine groups on gels are easily modified to give other functional groups including alcohols, acids, nitriles, and acids. Recently, other entities, such as fungi, bacteria, and cells, have been immobilized successfully. This technique can be used for the continuous synthesis of specific molecules.

10.3 NUCLEIC ACIDS

Nucleoproteins, which are conjugated proteins, may be separated into nucleic acids and proteins. The name "nuclein," which was coined by Miescher in 1869 to describe products isolated from nuclei in pus, was later changed to nucleic acid. Somewhat pure nucleic acid was isolated by Levene in the first decade of the 20th century. He showed that either D-ribose or D-deoxyribose (Figure 10.7) was present in what are now known as RNA and DNA.

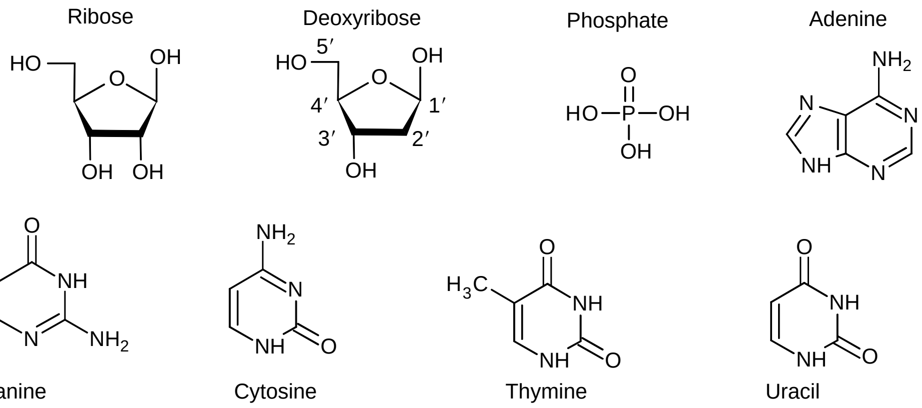
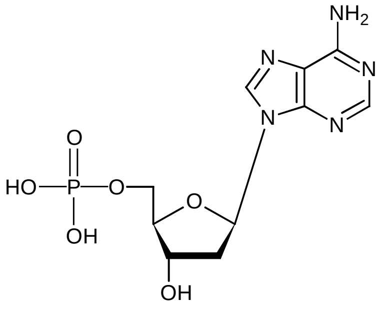


FIGURE 10.7 Components of nucleic acids.

They consist of two sugars that are identical except that the deoxyribose contains a hydrogen on carbon 2 (thus the name deoxy or without one "oxy" or hydroxyl; Figure 10.7). These specific compounds were originally obtained from yeast (DNA) and the thymus gland (RNA).

In 1944 Avery showed that DNA was able to change one strain of bacteria to another. It is now known that nucleic acids direct the synthesis of proteins. Thus, our modern knowledge of heredity and molecular biology is based on our knowledge of nucleic acids. Recently, it was announced that the human genome was decoded. This is one of the most important events to date. The human genome is composed of nature's most complex, exacting, and important macromolecules. It comprises nucleic acids that appear complex in comparison to simpler molecules such as methane and ethylene, but simple in comparison to their result on the human body. Each unit is essentially the same, containing a phosphate and a deoxyribose sugar and one of four bases (Figure 10.7), with each base typically represented by the capital of the first letter of its name, G, C, A, and T. In fact, it is less complex than having four separate and independent bases because the bases come in matched sets, i.e., they are paired. The mimetic Gee CAT allows an easy way to remember this pairing (G–C and A–T). The base, sugar and phosphate combine, forming nucleotides such as adenylic acid, adenosine-3′-phosphate shown in the following structure and represented by the symbols A, dA, and dAMP.

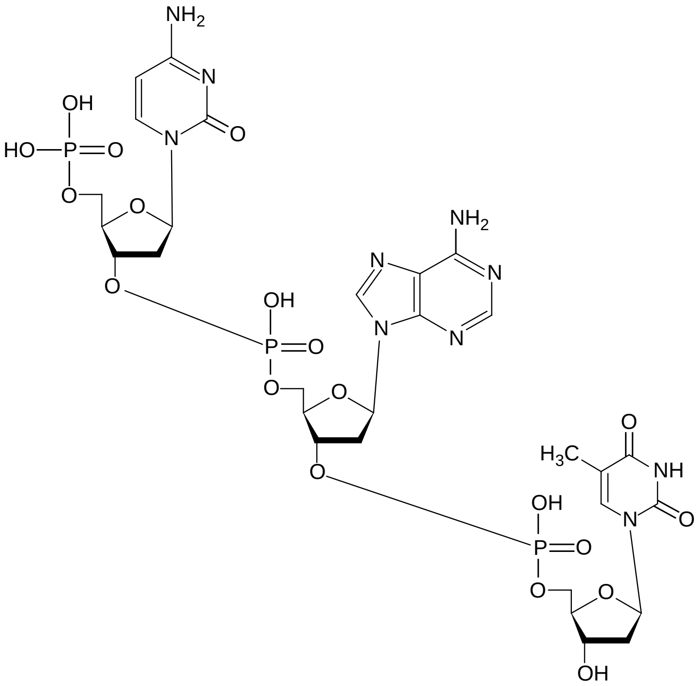


(10.8)

Adenylic acid, adenosine-3′-phosphate

The backbone of nucleic acids is connected through the 3′ and 5′ sites on the sugar with the base attached at the 1′ site. Because the sugar molecule is not symmetrical each unit can be connected differently, but there is order (also called sense or directionality) in the sequence of this connection so that phosphodiester linkage between units is between the 3′ carbon of one unit and the 5′ carbon of the next unit. Thus, nucleic acids consist of units that are connected so that the repeat unit is a 3′–5′ (by agreement we consider the start to occur at the 3′ and end at the 5′ though we could just as easily describe this repeat as being 5′–3′) linkage. Thus, the two ends are not identical—one contains an unreacted 3′-hydroxyl and the other an unreacted 5′-hydroxyl.

A shorthand representation is used to describe sequences. The following structure shows a trimer containing in order the bases cytosine, adenine, and thymine.



(10.9)

This sequence is described as p–5′–C–3′–p–5′–A–3′–p–5′–T–3′ or pCpApT or usually as simply CAT.

Nobel Laureates Watson and Crick correctly deduced that DNA consisted of a double-stranded helix in which a pyrimidine base on one chain or strand was hydrogen-bonded to a purine base on the other chain (Figure 10.8). The bonding distances are not the same as the G–C paring is more compact. This uneven pairing distances result in a DNA with a characteristic twisting giving unique structures. It is this twisting, and the particular base sequence, that eventually results in the varying chemical and subsequently biological activities for various combinations.

The stability of the DNA is due to both internal and external hydrogen bonding as well as ionic and other bonding. First, the internal hydrogen bonding is between the complementary purine–pyrimidine base pairs. Second, the external hydrogen bonding occurs between the polar sites along exterior sugar and phosphate moieties and water molecules. Third, ionic bonding occurs between the negatively charged phosphate groups situated on the exterior surface of the DNA and electrolyte cations such as Mg^{+2}. Fourth, the core consists of the base pairs, which, along with being hydrogen-bonded, stack together through hydrophobic interactions and van der Waals forces. In order to take good advantage of pi-electron cloud interactions the bases stack with the flat "sides" over one another so that they are approximately perpendicular to the long axis.

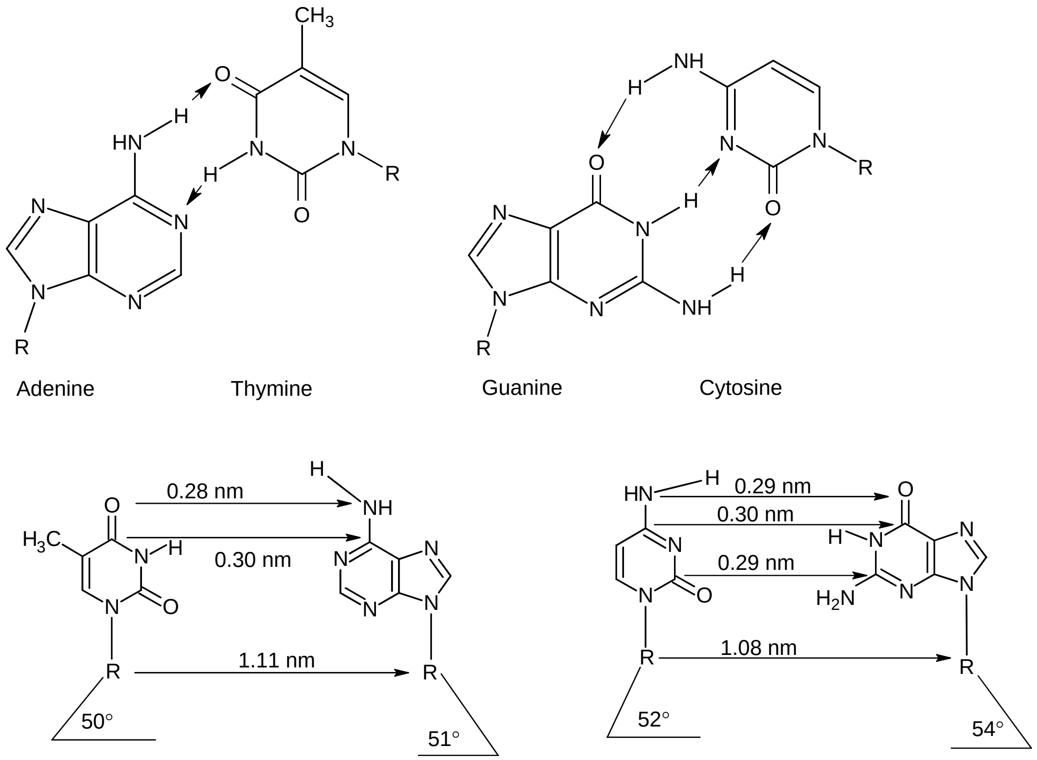


FIGURE 10.8 Hydrogen bonding between preferred base pairs in DNA. Top structures illustrate the number of hydrogen bonds and the bottom the bond distances between preferred base pairs.

The A–T and C–G base pairs are oriented in such a manner that the sugar–phosphate backbones of the two twined chains are in opposite or antiparallel directions, with one end starting at the 5′ and ending at the 3′ and the other starting from the 3′ and ending at the 5′ so that opposite one 3′ end is the other 5′ end. Thus, the two chains "run" in opposite directions.

The glucose bonds holding the bases onto the backbone are not directly across the helix from one another. Thus, the sugar–phosphate repeat units are not the same. This dislocation creates structures referred to as major and minor grooves. It is known that at least some proteins that bind to DNA recognize the specific nucleotide sequences by "reading" the hydrogen-bonding pattern presented by the edges of these grooves.

In solution, DNA is a dynamic, flexible molecule. It undergoes elastic motions on a nanosecond timescale most closely related to changes in the rotational angles of the bonds within the DNA backbone. The net result of these bendings and twistings is that DNA assumes a roughly globular or spherical tertiary shape. The overall structure of the DNA surface is not that of a recurring "barber pole" but rather because of the particular base sequence composition each sequence will have its own characteristic features of hills, valleys, bumps, etc.

As the two strands in a double helix separate, they act as a template for the construction of a complementary strand. This process occurs enzymatically, with each nucleotide being introduced into the growing chain through matching it with its complementary base on the existing chain. Thus, two identical strands are produced when one double-helix combination replicates.

DNA chains can contain 1 million subunits with an end-to-end contour length of about 1 mm. Even with the complexity of these large macromolecules, synthesis of new chains generally occurs without any change in the molecule. Even when changes occur, these giant machines have built-in "correcting" mechanisms that rectify mistakes.

The transcription product of DNA is always single-stranded RNA. The single strand generally assumes a right-handed helical conformation mainly caused by base-stacking interactions also present in the DNA. The order of interaction is purine–purine $\gg$ purine–pyrimidine $>$ pyrimidine–pyrimidine. The purine–purine interaction is so strong that a pyrimidine separating two purines is often displaced from the stacking order to allow the interaction between the two purines to occur. Base paring is similar to that of the DNA except that uracil generally replaces thymine. For coupled RNA the two strands are antiparallel as in DNA. Where complementary sequences are present, the predominant double-stranded structure is an A form right-handed double helix. Many RNAs are combinations of complementary double-stranded helices, single-stranded segments, as well as other complex structures. Hairpin curves are the most common type of more complex structure in RNA. Specific sequences, such as UUCG, are generally found at the ends of RNA hairpin curves. Such sequences can act as starting points for the folding of an RNA into its precise three-dimensional structure. The tertiary structures for RNAs are complex and several combinations are present. For instance, the tertiary structure for the tRNA of yeast for phenylalanine consists of a cloverleaf including three loops formed by hairpin curves and double-helix regions stabilized by hydrogen bonding. Hydrogen-bonding sites that are not significant in the DNA structures are important. Thus, the free hydroxyl on the ribose sugar moiety can hydrogen-bond with other units.

There are four major kinds of RNA. Messenger RNA (mRNA) varies greatly in size from about 75 units to over 3,000 nucleotide units, giving a molecular weight of 25,000–1 million. It constitutes about 2% of the total RNA in a cell. Transfer RNA (tRNA) has about 73–94 nucleotides with a corresponding molecular weight range of 23,000–30,000. It is present in the cell at a level of about 16%. The most abundant RNA, comprising 82%, is the ribosomal RNA (rRNA), which has several groupings of molecular weight with the major ones being 35,000 (about 120 nucleotide units), 550,000 (about 1550 units) and 1,100,000 (about 2,900 units). Eukaryotic cells contain an additional type called small nuclear RNA (snRNA).

There are generally 73–94 nucleotides in a single chain of tRNA, with a majority of the bases hydrogen-bonded to one another. Hairpin curves promote complementary stretches of base bonding, giving regions in which helical double-stranding occurs. The usual overall structure can be represented as a cloverleaf with each cloverleaf containing four of these helical double-stranded units. One of the loops acts as the acceptor stem that serves as the amino acid–donating moiety in protein synthesis.

rRNA is a part of the protein-synthesizing machinery of cells, ribosomes. Ribosomes contain two subunits called "small" and "large" with rRNAs being part of both these units. rRNAs contain a large amount of intrastrand complementary sequences and are generally highly folded. Interestingly, there is a similarity between the folded structures of rRNA from many different sources even though the primary structure, base sequence, is quite varied. Thus, there appears to be preferred folding patterns for rRNAs.

mRNA carries messages that are encoded in genes to the sites of protein synthesis in the cell where this message is translated into a polypeptide sequence. Because mRNAs are transcribed copies of the genetic unit, they are sometimes referred to as the "DNA-like RNA." mRNA is created during transcription, when an enzymatic sequence in which a specific RNA sequence is "copied" from a gene site. rRNA and tRNA are also made by transcription of DNA sequences but unlike mRNA they are not subsequently translated to form proteins.

Actual reproduction steps involving DNA and RNA often occur in concert with protein where the protein can act as a clamp or vice holding the various important members involved with the particular reproduction step in place. Thus, the protein complex acts as an assembly line tunnel or doughnut with the reactants present within the interior.

10.4 FLOW OF BIOLOGICAL INFORMATION

Nucleic acids, proteins, some carbohydrates, and hormones are informational molecules. They carry directions for the control of biological processes. With the exception of hormones, these are macromolecules. In all these interactions, secondary forces such as hydrogen bonding and van der Waals forces, ionic bonds, and hydrophobic or hydrophilic characteristics play critical roles. "Molecular recognition" is the term used to describe the ability of molecules to recognize and interact—bond—specifically with other molecules. This molecular recognition is based on a combination of the interactions just cited and on structure.

Molecular recognition interactions have several common characteristics. First, the forces that are involved in these interactions are relatively weak and noncovalent. They are on the order of about 1–8 kcal/mol (4–30 kJ/mol) compared with covalent bonds on the order of about 80 kcal/mol (300 kJ/mol) for a C–C sigma bond. A single noncovalent bond is generally not capable of holding molecules together for any length of time. But for macromolecules, there is a cumulative effect so that the forces are not singular but are multiplied by the number of such interactions that are occurring within the particular domain. Second, these interactions are reversible. Initial contact occurs as the molecules come into contact with one another often through simple diffusion or movement of the molecules or segments of the molecules. These initial contacts are often not sufficient to cause the needed binding though some transitory interactions do occur. This complex can then begin a specific biological process. Eventually thermal motions and geometrical changes cause the complex to dissociate. Ready reversibility is an important key that allows a relatively few "signaling" molecules to carry out their mission. Third, bonding between the particular molecular sites is specific. There must exist a combination of complementary bonding, hydrophobic or hydrophilic sites, ionic charge, and geometry that allows effective long-term (generally no more than several seconds) interactions to occur.

In general, the flow of biological information can be mapped as follows:

$$\text{DNA} \rightarrow \text{RNA} \rightarrow \text{Protein} \rightarrow \text{Cell structure and function}$$

The total genetic information for each cell, called the genome, exists in the coded double-stranded DNA. This genetic information is expressed or processed either through duplication of the DNA so it can be transferred during cell division to a daughter cell or by transfer to manufactured RNA, which in turn transfers the information to proteins that carry out the activities of the cell.

Duplication of double-stranded DNA is self-directed. The DNA, along with accessory proteins, directs the replication or construction of two complementary strands forming a new, exact replicate of the original DNA template. As each base site on the DNA becomes available through the unraveling of the double-stranded helix, a new nucleotide is brought into the process and held in place by hydrogen bonding and van der Waals forces so that the bases are complementary. It is then covalently bonded through the action of an enzyme called DNA polymerase. After duplication, each DNA contains one DNA strand from the original double-stranded helix and one newly formed DNA strand. This is called semiconservative replication and increases the chance that if an error occurs, the original base sequence will be retained.

How is DNA suitable as a carrier of genetic information? While we do not entirely understand them, several features are present in DNA. First, because of the double-stranded nature and mode of replication, retention is enhanced. Second, DNA is particularly stable within both cellular and extracellular environments, and has a good stability to hydrolysis within an aqueous environment. Plant and animal DNAs have survived thousands of years. Using polymerase chain reactions (PCRs) we can reconstruct DNA segments allowing comparisons to modern DNA.

"Transcription" is the term used to describe the transfer of information from DNA to RNA. The genome is quite large, on the order of 1 mm in length if unraveled, but within it are coding regions called genes. Transcription is similar to DNA replication, except that ribonucleotides are the building units instead of deoxyribonucleotides; the base thymine is replaced by uracil; the DNA/RNA duplex unravels, releasing the DNA to again form its double-stranded helix and the single-stranded RNA; and the enzyme linking the ribonucleotides together is called RNA polymerase.

Many viruses and retroviruses have genomes that are single-stranded RNA instead of DNA. These include the acquired immunodeficiency syndrome (AIDS) virus and some retroviruses that cause cancer. Here, an enzyme called reverse transcriptase converts the RNA genome of the virus into the DNA of the host cell genome, thus infecting the host.

The transcription of the DNA gives three kinds of RNA: ribosomal, messenger, and transfer. The most abundant RNA is rRNA. Most rRNAs are large and are found in combination with proteins in the ribonucleoprotein complexes called ribosomes. Ribosomes are subcellular sites for protein synthesis.

The smallest of the RNAs, tRNA, is less than 100 nucleotides long. It combines with an amino acid incorporating it into a growing protein. There is at least one tRNA for each of the 20 amino acids used in protein synthesis. Although mRNAs vary in size, each carries the message found in a single gene or group of genes. The sequence of bases in mRNAs is complementary to the sequence of DNA bases. mRNAs are unstable and short-lived so that their message for protein synthesis must be rapidly decoded. The message is decoded by the ribosomes that make several copies of the protein for each mRNA.

The ultimate purpose of DNA expression is protein synthesis. mRNAs serve as the intermediate carrier of the DNA genetic information for protein synthesis. The DNA message is carried in the form of base sequences that are transferred to RNA, also in terms of base sequences, and finally these are transferred into amino acid sequences through a translation process based on the genetic code. This process of information from the RNA to the protein is called translation.

A set of coding rules are in action as in the translation process. First, a set of three adjacent nucleotides compose the code for each amino acid. A single amino acid can have several triplet codes or codons. Since there are four different nucleotides (or four different bases) in DNA and RNA, there exist $4^3 = 64$ trinucleotide combinations. For instance, using U as a symbol for uracil, which is present in RNA, the triplet or code or codon UUU is specific for phenylalanine.

Second, the code is nonoverlapping so that every three nucleotides code for an amino acid, the next three code for a second amino acid, the third set codes for a third amino acid, etc. Third, the sets of nucleotides are read sequentially without punctuation. Fourth, the code is nearly universal. Fifth, there are codes for other than amino acids including stop or terminate (UAG), and start or initiate (AUG).

In essence, tRNA has two active sites: one that is specific for a given amino acid and the other that is specific for a given set of three bases. The tRNA "collects" an appropriate amino acid and brings it to the growing polypeptide chain inserting it as directed by the mRNA. There is then a collinear relationship between the nucleotide base sequence of a gene and the amino acid sequence in the protein.

The amount, presence, or absence of a particular protein is generally controlled by the DNA in the cell. Protein synthesis can be signaled outside or within the cell. Growth factors and hormones form part of this secondary messenger service.

The translation and transcription of DNA information is polymer synthesis and behavior, and the particular governing factors and features that control these reactions—synthetic and biological—are present in the synthesis and behavior of other macromolecules.

For the human genome there exist coding or active regions called exons and noncoding regions called introns. The average size of an exon is about 120–150 nucleotide units long or coding for about 40–50 amino acids. Introns vary widely in size from about 50 to over 20,000 units. About 5% of the genome is used for coding. It was thought that the other 95% was silent or junk DNA. However, it is found that the intron regions play essential roles. Interestingly, introns are absent in the most basic prokaryotes, only occasionally found in eukaryotes, but common in animals.

10.5 RNA INTERFERENCE

RNA interference (RNAi) is a somewhat newly discovered part of our body's natural immune system. RNAi is not another form of RNA, but rather a sequence involving protein enzymes that block the action of certain foreign RNA, thus its name. Andrew Fire and Craig Mello won the 2006 Nobel Prize in Medicine for their work with RNAi.

Following is a general discussion of what RNAi is and does including some of its potential applications.

While DNA is the depository of our genetic information, it is "held captive" or "protected" by the nuclear envelope remaining within this envelope. Yet the information held by the double-stranded DNA is transferred throughout the cell with results felt throughout the body. Briefly, polymerase transcribes the information on the DNA into single-stranded mRNA. The single strands of the mRNA move from the cell nucleus into the cell cytoplasm through openings in the nuclear envelope called nuclear pore complexes.

In the cytoplasm, ribosome, another protein enzyme, translates the information on the mRNA into protein fragments eventually giving entire proteins. This "normal" sequence is depicted in Figure 10.9.

Viruses are genetic materials enclosed in a protein "coat." They show a very high specificity for a particular host cell, infecting and multiplying only within those cells. Viral genetic

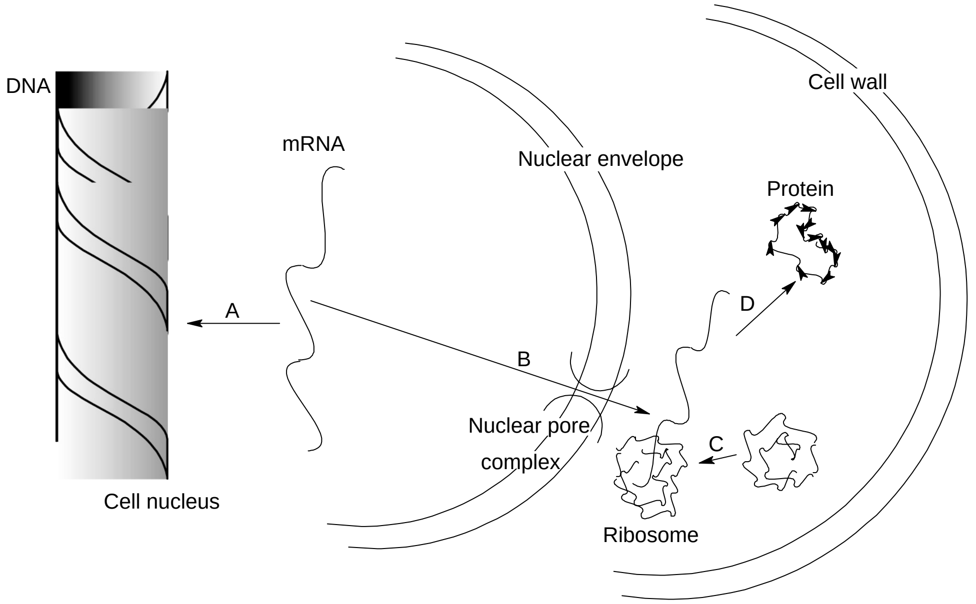


FIGURE 10.9 Normal protein formation sequence. First, mRNA is formed from the cell's DNA (A). Second, the mRNA enters into the cell's cytoplasm (B). Third, ribosome forms around the mRNA (C) resulting in the formation of the desired protein (D).

material can be either DNA or RNA but is almost always double-stranded. Viral attacks generally result in a virus infecting a cell by depositing its own genetic material, here RNA, into the cell's cytoplasm. The purpose of depositing this viral-derived RNA is to have it replicated as rapidly as possible in an attempt to hijack the cell into producing viral-directed protein. We need to remember that almost all of the viral-derived RNAs are double-stranded, rather than single-stranded.

By accident, it was discovered about a decade ago that the cell had a new weapon in its autoimmune system. Although there had been prior hints, the first reasonable evidence that something was present was the work of Jorgensen and coworkers in 1996. Their effort to darken the purple color of petunias, toward a black color, showed that some sort of suppression was at work giving variegated to white petunias instead of a darkened purple variety. They called this phenomenon co-suppression since the expression of both the introduced gene and the seed's own color gene was suppressed. Evidence for co-suppression was not new and had already been found for fungi.

Eventually, it was discovered that the cell has its own ability to combat viral attacks. The initial step in the RNAi process is the use of an enzyme, nicknamed Dicer, which cuts the double-stranded viral-derived RNA into small (about 20 units) strands. The second part of the RNAi system involves the unwinding of these short sections again using a protein enzyme called RNA-induced silencing complex (RISC). This results in short chains of single-stranded RNA being present with the RISC referred to as a RISC–RNA complex. This complex floats around the cell looking for complementary RNA segments in the much longer cellular mRNA. When such a fit is found, the complex deposits its viral-derived segment onto the mRNA rendering it either incapable or much less capable of creating viral-related protein. Thus, the cell has built into it its own antiviral weaponry. This sequence is shown in Figure 10.10.

The discovery of the RNAi sequence has led to researchers employing it to identify the activity of various gene segments as well as working on cures for a number of diseases. More about this will be discussed later.

RNAi activity is most often induced using relatively small (generally 21–23 nucleotides long) segments of RNA that interfere with the activity (silence) of an endogenous

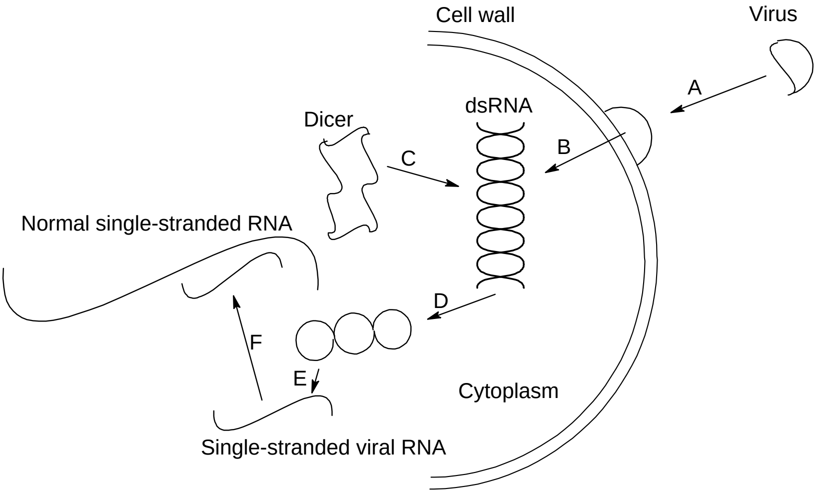


FIGURE 10.10 RNAi sequence. First the virus approaches and attaches itself to the cell wall (A). The virus injects double-stranded RNA (B) into the cell cytoplasm. The dicer attacks the dsRNA, breaking it into smaller units (C and D). These smaller units are then acted on by RISC, forming single-stranded viral RNA (E), which are rendered incapable of forming their own protein by attachment to a complement contained within the cell's own single-stranded RNA (F).

gene. This silencing is called posttranscriptional gene silencing (PTGS), and the interference is called silence-interfering RNA (siRNA). Thus, gene-specific siRNAs are prepared and their effect monitored "downstream."

RNAi is used as a tool to help decipher the gene. Eventually, this may allow us to better understand the purpose of the various segments contained within specific genes. The basis of this is the ability of RNAi to curtail the activity of the cell to supply specific proteins. This loss of function then identifies the role that the particular RNAi has rendered inactive. Briefly, various double-stranded RNAs are created. Each of these is tested to see where on the normal RNA they become attached and which function is impaired. This then tells us about the particular function of that particular part of the normal RNA which is then traced back to the cell's DNA and its location in a particular gene.

10.6 POLYMER STRUCTURE

Linus Pauling, in 1954, received the Nobel Prize for his insights into the structure of materials, mainly proteins. Pauling showed that only certain conformations are preferred because of intermolecular and intramolecular hydrogen bonding. While we know much about the structures of natural macromolecules, there is still much to be discovered.

The two major secondary structures found in nature—the helix and the sheet—are also major secondary structures found in synthetic polymers. The helix takes advantage of both the formation of intermolecular secondary bonding and relief of steric constraints. Some materials utilize a combination of helix and sheet structures such as wool, which consists of helical protein chains connected to give a "pleated" sheet.

The Watson and Crick model for DNA as a double helix is only a generalized model to describe much more complex structures. Along with the typical double helix there exist structural elements such as supercoils, kinks, cruciforms, bends, loops, and triple strands as well as major and minor grooves. Each of these structural elements can vary in length, shape, location, and frequency. Even the "simple" DNA double helix can vary in pitch (number of bases per helical turn), sugar pucker conformation, and helical sense (whether the helix is left- or right-handed).

Electron microscopy shows that DNA consists of either linear or circular structures. The chromosomal DNA in bacteria is a closed circle, a result of covalent joining of the two ends of the double helix (Figure 10.11). Note the presence of supercoils, branch points, intersections, and the generally thin and open structure. The chromosomal DNA in eukaryotic cells, like ours, is believed to be linear.

The most important of the secondary structures is supercoiling. Supercoiling is simply the coiling of a coil or in this case a coiling of the already helical DNA. The typical DNA structure is the thermally stable form. Two divergent mechanisms are believed responsible for supercoiling. The first, and less prevalent, is illustrated by a telephone cord. The telephone cord is typically coiled and represents the "at rest" or "unstressed" coupled DNA. As I answer the telephone I have a tendency to twist it in one direction and after answering and hanging up the telephone for a while it begins forming additional coils. Thus, additional coiling tends to result in supercoiling. The second, and more common form, involves the presence of less than normal coiling. This can be illustrated by taking a rubber band, breaking one end, and then tying it around a stationary object. Begin bradding the two ends until just prior to a bunching or formation of supercoiling caused by overcoiling. Then separate the two ends pulling them apart. The resulting strain produces supercoiling and illustrates how supercoiling may result in undercoiling or underwinding. Thus, underwinding occurs when there are fewer helical turns than would be expected. Purified DNA is rarely relaxed.

Supercoiling with bacterial DNA gives a largely open, extended, and narrow, rather than a compacted, multibranched structure. By comparison, the DNA in eukaryotic cells is present

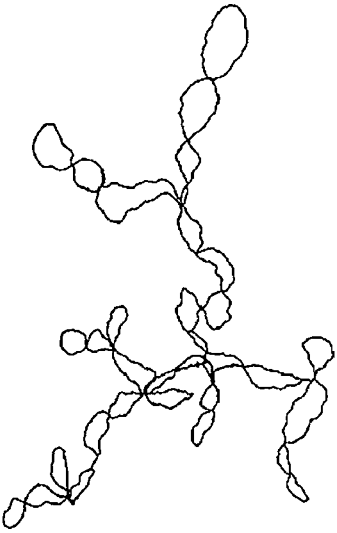


FIGURE 10.11 Description of a typical bacterial chromosome.

in very compacted packages. Supercoiling forms the basis for the folding pattern in eukaryotic cells that eventually results in this very compacted structure. Subjection of chromosomes to treatments that partially unfold them shows a structure where the DNA is tightly wound around "beads of proteins," forming a necklace-like arrangement where the protein beads represent precious stones imbedded within the necklace (Figure 10.12). This combination forms the nucleosome, the fundamental unit of organization upon which higher-order packing occurs. The bead of each nucleosome contains eight histone proteins. Histone proteins are small basic proteins with molecular weights between 11,000 and 21,000 that are specified by names such as H1, H2, etc. H1 is especially important and its structure varies to a good degree

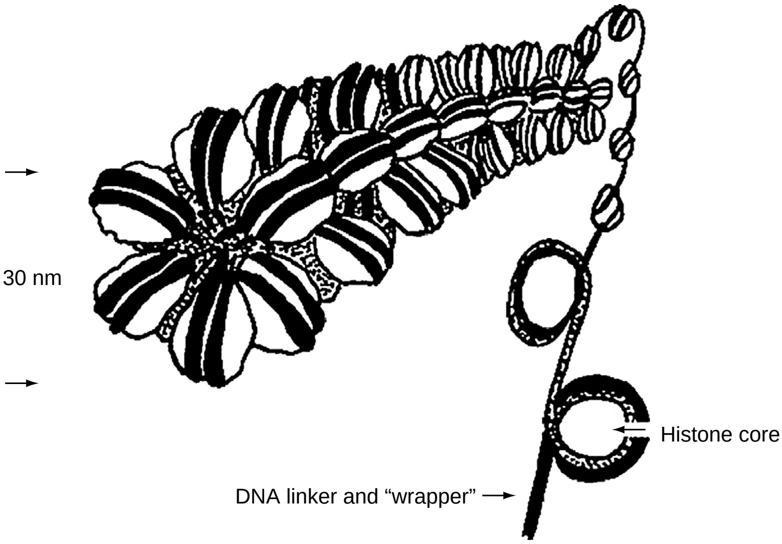


FIGURE 10.12 Illustration of regularly spaced nucleosomes consisting of histone protein bound to supercoiled DNA, with DNA links between the histone bound units forming a 30 nm higher-order fiber.

from species to species, whereas some of the other histones, such as H3 and H4, are very similar. Histones are rich in the amino acid residues from arginine and lysine.

Wrapping of DNA around a nucleosome core compresses the DNA length about sevenfold. The overall compacting, however, is about 10,000-fold. Additional compacting of about 100-fold is gained from the formation of 30 nm fibers. These fibers contain one H1 for nucleosome core. This organization does not occur over the entire chromosome but rather is punctuated by areas containing sequence-specific (non-histone-containing) DNA-binding proteins. The term "30 nm fibers" is used because the overall shape is of a fiber with a 30 nm thickness. The additional modes of compaction are just beginning to be understood but may involve scaffold-assisting. Thus, certain DNA regions are separated by loops of DNA which have about 20,000–100,000 base pairs in each loop possibly containing sets of related genes.

The scaffold contains several proteins, especially H1 in the core and topoisomerase II. Both appear important to the compaction of the chromosome. In fact, the relationship between topoisomerase II and chromosome folding is so vital that inhibitors of this enzyme can kill rapidly dividing cells; thus, several drugs used in the treatment of cancer are topoisomerase II inhibitors.

The central theme concerning the major secondary structures found in nature is also illustrated with the two major polysaccharides derived from sucrose: cellulose and the major component, starch-amylose. Glucose exists in one of two forms: an alpha and a beta form where the terms alpha and beta refer to the geometry of the oxygen connecting the glucose ring to the fructose ring.

Cellulose is a largely linear homosaccharide of the beta-D-glucose. Because of the geometry of the beta linkage, individual cellulose chains are generally found to exist as sheets, i.e., the individual chains connected through hydrogen bonding. The sheet structure gives cellulose-containing materials good mechanical strength, allowing them to act as structural units in plants. Amylose, by comparison, is a linear poly(alpha-D-glucose). Its usual conformation is as a helix with six units per turn (Figure 10.13). Amylose is a major energy source occurring in plants as granules.

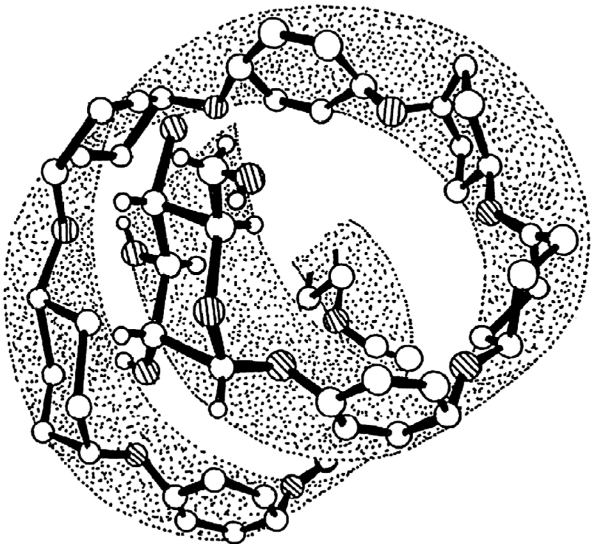


FIGURE 10.13 Helical structural arrangement of amylose derived from alpha-D-glucose units.

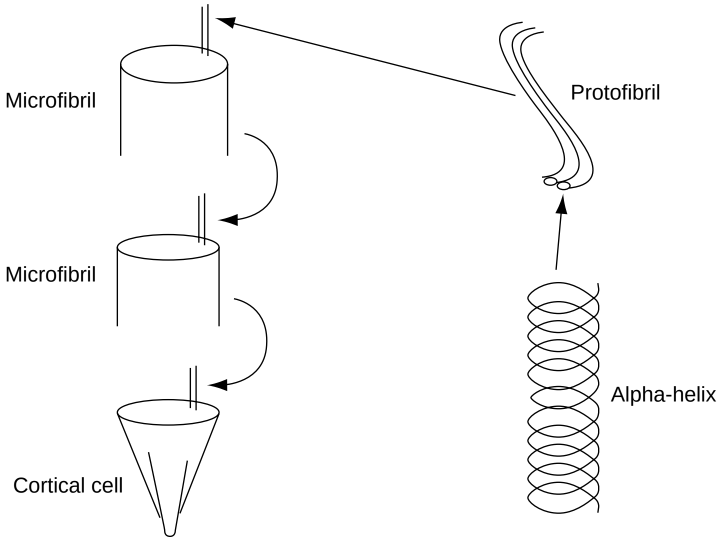


FIGURE 10.14 Buildup of wool hair.

A number of repeating features occur in nature. Along with the ones noted earlier, another depends on the buildup of structure from individual polymer chains to structures that are seen by our human eye. One of these assemblies is illustrated in Figure 10.14 where individual alpha-helix chains form slowly curving protofibril bundles. These bundles form microfibril structures, which in turn form macrofibril structures and finally the cortical cell of a single wool fiber. The bundling and further bundling eventually gives the wool fiber. A similar sequence can be described in the formation of our hair as well as our muscles. The difference for muscle is that the basic structure is not the alpha-helix but rather a sheetlike actin filament connected together by myosin filaments. In all cases, flexibility is achieved through several features, and one of the major modes is simply sliding past the various bundles of protein. For the muscle, the sliding of the various sheets is also a factor.

These assemblies of more simple structures to form more complex structures are also found in the plant world. Thus, plant fibers often contain various cellulose-intense layers that are not placed on top of one another, but rather at some angle to one another resulting in increased strength and flexibility for the fiber.

10.7 PROTEIN FOLDING

Just as the functioning of nucleic acids depends in part on its overall structure, so does the activity of proteins depend on its overall structure. Protein folding is one of the ‘‘hot’’ areas today in science. To the synthetic polymer chemist, understanding the influences of factors, basic or fundamental, which produce protein chain folding will allow the creation of new synthetic polymers that possess specifically desired properties. For biochemists, understanding these factors allows us to better understand other factors and to combat particular diseases related to chain folding.

The particular shape of protein chains is known as a fold and the process is called chain folding. While chain folding is often referred to as a self-assembly process, it also involves other specialized separate proteins that assist in this chain folding, so it is not truly self-assembly. Chain folding occurs rapidly in the timescale of 1–10 μsec.

Chain folding depends on the primary and secondary structures of materials. Thus, the particular atomic composition of a chain dictates, under equilibrium conditions, its tertiary and quaternary structures.

Proteins act as structural and "enzyme-type" materials. Much of the present discussion focuses on the folding of enzyme-type materials, but it is equally applicable to structural proteins. While the human genome has less than about 30,000 genes, these genes account for as many as one million proteins, most of which are nonstructural in nature. Proteins also undergo maturing or, to be more truthful, aging, as it carries out its function(s). As with much of nature, after extended use and associated damage related to chemical and partial unfolding, the protein is degraded and its parts often become part of a newly synthesized protein.

As already noted, protein folding is dependent on the primary chemical structure. Chain folding begins even as it is being synthesized by ribosomes. The assembly area is crowded, thus increasing the risk of nonspecific association and aggregation. A primary driving force for aggregation is simply the push to bury hydrophobic portions of the molecule away from the influences of the hydrophilic, water-rich, surrounding. Thus, left to themselves, folded proteins have a hydrophilic surface, which contains within it the more hydrophobic portions. But this tendency must be moderated otherwise simple aggregation of the hydrophobic and hydrophilic portions—ribbons—may occur and, even worse, unwanted aggregation of the proteins themselves may occur.

Crowding is one factor that is not easily achieved away from the native environment. Lack of crowding is one of the major reasons why *in vivo* and *in vitro* syntheses often result in proteins with different activities.

While we characterize nonstructural proteins as being globular in shape, these shapes vary considerably according to their use. Again, this overall shape is governed by a combination of factors including primary and secondary structures.

A family of proteins assist in the folding process in general. These proteins are called molecular chaperones. As in the case of a date, the chaperones help guide appropriate interactions and discourage unwanted associations. Chaperones are found in all of our cells. Many of them are designated as Hsp for heat shock protein. They are also designated by the relative mass in kilodaltons so that Hsp70 means it is a chaperone molecule that is about 70 kDa in mass. The main chaperones are Hsp60 (chaperonins), Hsp70, and Hsp90.

Typically, a series of steps is involved in the work carried out by chaperone molecules. Hsp70 operates on the protein as it is being formed on the ribosome. It recognizes extended or exposed protein chain regions that are more hydrophobic and acts to discourage unwanted association of these parts. It also acts to maintain the growing protein in a somewhat unfolded state.

Hsp70 hands off the protein to another class of chaperones known as Hsp60 or simply chaperonins. Chaperonins create a protected environment sometimes known as an "Anfinsen cage" because it creates an enclosed environment in which the protein segments spontaneously fold, free from aggregating with other proteins and somewhat free from aqueous influences. These are large proteins that are somewhat cylindrical in shape. Chaperonins are composed of two major units, or stacked rings.

There are two different classes of chaperonins. Class I includes eukaryotic cells and class II includes certain prokaryotic cells. Eukaryotic cells have nuclei and include organelles. Prokaryotic cells do not contain nuclei and other organelles. We will focus on eukaryotic cells. Much of the information we have on chaperonins is derived from studying bacteria such as *Escherichia coli*. The chaperonin in *E. coli* is given the designation GroES–GroEL. The GroEl is composed of two stacked 7-membered rings of 60 kDa mass that form a cylinder about 15 nm high and 14 nm wide, with a 5 nm central cavity capable of holding proteins to 60 kDa. GroES is a co-chaperonin that acts as a dome or cap for one end of the GroEL portion. It is composed of a single 7-membered ring of about 10 kDa mass. Thus, there is considerable knowledge about the structures of at least a few of the molecules involved in the folding process. Much is also known concerning the function of these molecules, but this is beyond the scope of this chapter.

Human cells contain about 1%–2% Hsp90 of the total cytosolic proteins. This is a huge percentage in comparison to most other proteins and signals their importance. Their action depends on the cyclic binding and hydrolysis of ATP. Hsp90 is involved with conformational regulation of signal transduction molecules.

Along with the guiding of chaperon molecules there are some "native" or natural tendencies with respect to chain folding, at least for smaller proteins. One of these only recently described involves the closeness of various segments and folding rate. Briefly, protein segments that are located close to one another and in a generally close orientation to the final folding location promote rapid chain folding. This is reasonable since it takes more time to organize protein segments that are further from one another relative to organization of structures that will be close to one another after folding. Even so, not all of what we discover is the most "reasonable." For instance, interatomic interactions are not as important as previously believed. This suggests that local sequences, the primary structures, are most important in determining the final folded structures and rates at which these structures are achieved. These findings have been found for smaller groups to about 150 units in length. It is not known if they will be true for larger proteins. At times one tendency may be influenced by other factors. Thus, for beta-lactoglobulin, the local structure favors a helical structure but this tendency is overcome by tertiary interactions.

What is known is that we have not yet mastered the art of chain folding. We are aware that several groups of factors are involved with the folding and more will probably become apparent. We also know that there is a balance between these factors and again an understanding of factors influencing this balance will also become better known.

An added importance to understanding and being able to influence chain folding involves the number of diseases that are related to misfolds. For instance, misfolding can result in aggregation of the proteins, which is a symptom of mad cow, Creutzfeldt–Jakob and Alzheimer's diseases.

It has been suggested that about 50% of cancers involve some chain misfolding. A key protein in this is the p53 protein which exerts tumor suppression. A single DNA strand break can result in uncontrolled cell division but it normally activates p53 activity, which promotes the production of other proteins that block cell division or bring about cell death, and thus the cessation of the precancer activity. Mutation of a single nucleotide in p53 is believed to result in a misfold resulting in the protein's inability to recognize when it is needed or a failure to act correctly.

Diabetes can involve misfolding of proteins that form in the endoplasmic reticulum (ER). The ER secretes certain hormones, enzymes, and antibodies, and so is a key player in our health. In some cases, the misfolded proteins interfere with carbohydrate metabolism leading to diabetes.

Other protein misfolding-associated diseases include lung diseases such as cystic fibrosis and hereditary emphysema, blood coagulation, certain infectious diseases, and liver diseases. Thus, a better understanding of chain folding is important for our health.

10.8 GENETIC ENGINEERING

Genetic engineering is the alteration of an organism's genetic material. The aim is to introduce into the organism's genetic material some desirable trait that is otherwise absent. Alternation of genetic material entails the use of polymer chemistry on a molecular (or nano) level making use of somewhat straightforward chemical reactions, many of them employing biological entities, such as enzymes, to carry out these reactions.

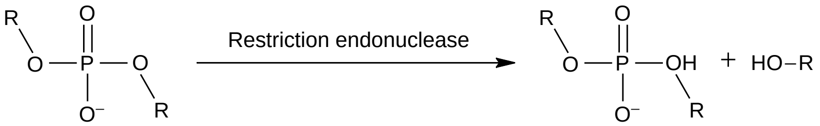
Essentially, gene segments are replaced to inject into the altered microorganism genetic material that expresses the desired trait. Routine gene alteration is now taught in undergraduate laboratories. Even so, specific gene alteration requires extensive planning and is conducted in major research laboratories.

In the broadest sense, genetic engineering refers to any artificial process that alters the genetic composition of an organism. Such alterations can be carried out indirectly through chemical methods, radiation, or selective breeding. The term usually refers to the process whereby genes or portions of chromosomes are chemically altered.

After the alteration of a single, or few, genes, the altered genes reproduce, giving much larger numbers of genes with the alternation incorporated in the their genome. The term "clone" comes from the Greek *klon*, meaning "a cutting used to propagate a plant." Cell cloning is the production of identical cells from a single cell. In like manner, gene cloning is the production of identical genes from a single gene, introduced into a host cell. The term cloning now refers to one special type of genetic engineering.

Genes are a chromosomal portion that codes for a single polypeptide or RNA. Gene splicing is currently practiced as the enzymatic attachment of one gene or gene segment to another gene or gene segment. Genes are composed of DNA, which can be considered as a specialized polyphosphate polymer. The manipulation of DNA can occur for many reasons. One of these is the production of recombinant DNA, which we will focus on in this chapter. DNA cannot be directly transferred from one organism, the donor, to another recipient organism, the host. Instead, the donor DNA segment is cut and then recombined with a DNA from a host. *E. coli* is typically employed as the host cell since it is itself a harmless bacterium that reproduces rapidly. (But under the wrong conditions *E. coli* is responsible for many food poisonings.) The *E. coli* then acts as a "factory" that reproduces bacteria which contain the desired modification.

Enzymes, specialized proteins, are used as designing tools for genetic engineering. One of these enzyme tools consists of "restriction endonucleases" that recognize a specific series of base pairs. They split the DNA at these specific points. This splitting is called "lysing", which in reality is simply the hydrolysis of DNA units as shown in the following structure:



(10.10)

Organisms produce restriction endonucleases that are specific for that organism. Certain restriction endonucleases cut double-stranded DNA asymmetrically in regions called palindromes, which "read" (have identical sequences) the same way from left to right on one strand as right to left on the other strand. This produces what is referred to as "sticky ends" that form not only a "cleft" for attachment but also a single-stranded end that has the ability to pair with another complementary single-stranded end. Both strands of the original donor twin strand have a tendency to recombine with complementary strands of DNA from a host that has been treated to produce the complementary strands. The sticky ends, when mixed under the proper conditions in the presence of another enzyme, DNA-ligase, combine. The hydrogen bonding between complementary sticky ends reinforces the recombination reaction. This reaction results in a variety of products including the desired recombination of host and donor DNA as well as the combination of the original donor strands and uncombined DNA. The mixture is often treated in one of two manners. The simplest case requires a chemical-resistant gene that is resistant to the employed chemical agent, such as tetracycline. The desired recombinant genes survive and are then transferred into the host organism so the new gene can express itself.

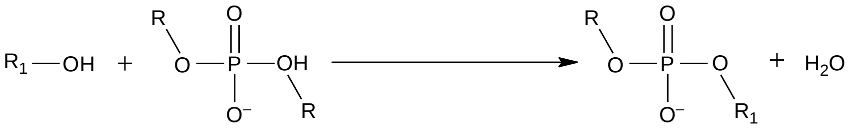
In some cases, such as the synthesis of insulin, the recombination mixture is added to a host organism, here *E. coli*. This infected mixture is then plated out and the individual colonies tested for insulin production. Those colonies that produce insulin are further plated out and grown for mass insulin production. Cells that accept the recombinant DNA are called "transformed." More specialized sequences have been developed to increase the probability of gene incorporation and its successful reproduction.

A second tool employed by the genetic engineer is the enzyme terminal transferase that adds deoxyribonuclease residues to the 3′ end of DNA strands creating 3′ tails of a single type of residue.

Special modified plasmid DNAs, called vectors or carriers, are used as hosts or targets for gene modification. These circular vectors reproduce autonomously in host cells. Plasmids have two other important properties. First, they can pass from one cell to another allowing a single "modified" bacterial cell to inject neighboring bacterial cells with this "modification." Second, gene material from other cells can be easily formed into plasmids, allowing ready construction of modified carriers.

The steps involved in gene splicing, emphasizing the chemical nature of the individual steps, are as follows:

1. Lysing (which is simply the hydrolysis of DNA units as shown above)
2. Construction of staggered, sticky ends
3. Recombination or lysation, the reverse of lysing, for the chemical formation of a phosphate ester as shown in the following structure connecting the desired segment to the DNA of the host cell



(10.11)

4. Chemical recombination of vector insertion into the host cell; recombining plasmid genes into the host genetic complement
5. Replication of host cell

There are many uses of recombinant DNA. As noted above, one technique that produces recombinant DNA is called cloning. In one cloning technique used for the production of the sheep Dolly in 1996, the DNA nucleus from a female's egg was replaced with a nucleus from another sheep. The egg was placed in the uterus of a third animal, known as the surrogate mother. Dolly is nearly genetically identical to the animal from which the nucleus was obtained but not genetically related to the surrogate mother.

Recombinant DNA has been used in a variety of ways. The growth hormone gene of rainbow trout has been transferred into carp eggs, resulting in the transgenic carp producing larger fish. The milk production of dairy cows has been increased by cloning and introducing into the cows the cattle growth hormone bovine somatotropin.

Transgenic strawberry and potato plants have been produced that are frost-resistant. Cotton, corn, and soybean have been produced with increased resistance to herbicides allowing herbicide use without killing the transgenic crop-producing plants. Larger and smaller varieties of other food-producing plants have been produced using recombinant DNA as have plants that produce certain amino acids needed for our nutrition.

Transgenic bacteria have been produced that can metabolize petroleum products including certain synthetic polymers.

Along with the production of insulin, many other medical uses have been achieved for recombinant DNA. This includes the production of erythropoetin, a hormone used to stimulate production of red blood cells in anemic people; tissue plasminogen activator, an enzyme that dissolves blood clots in heart attack victims; and antihemophilic human factor VIII, used to prevent and control bleeding for hemophiliacs. These three important genetically engineered proteins were all cloned in hamster cell cultures.

Gene engineering is the basis of gene therapy where genes are removed, replaced, or altered producing new proteins for the treatment of diseases such as muscular dystrophy, some cancers, adenosine deaminase deficiency, cystic fibrosis, and emphysema.

10.9 DNA PROFILING

DNA profiling is also referred to as DNA fingerprinting and DNA typing. It is used in paternity identification, classification of plants, criminal cases, identification of victims, heredity (of living, recently deceased, and anciently deceased), etc. DNA profiling is a tool that allows comparison of DNA samples.

While about 99.9% of our DNA is alike, the 0.1% is what makes us different individuals, and it is this 0.1% that allows for our identification as individuals. It is interesting to note that it is not the portions within the gene that make up our different physical and mental characteristics, but DNA profiling employs DNA taken from what is referred to as the "junk DNA."

Identification generally occurs because of the formation of different lengths of this junk DNA after appropriate treatment. This junk DNA contains the same sequence of base pairs, but in different repeat numbers. Thus, the sequence ATTCGG may appear four times, five times, six times, etc. There are typically some statistical number of repeats. Other sequences such as GGCATCC and AATGCAAT also appear in some statistical number of repeats. While all of us have these different run sequences, individually we have unique run lengths of these different run sequences. These run sequences are called variable number of tandem repeats (VNTRs). The repeat runs used for identification are generally from specific locations within a chromosome. Enzymes "cut" the associated DNA at specific locations leading to decreases in DNA molecular weight. In fact, these DNA chain length decreases are apparent as band shifts in DNA gels. The combination of the differences in decreased DNA chain lengths becomes unique as results obtained from different enzymes are accumulated. These changes in the movement of DNA segments are then compared with results from different individuals and identification as to whether the individuals are the same or different. The identity results are often given as some percentage or ratio.

There are two basic types of DNA profiling: one that uses PCR enzymes and the other employs the restriction fragment length polymorphism (RFLP) enzymes. The PCR approach utilizes a sort of molecular copying process in which a specific region is selected for investigation. The PCR approach requires only a few nanograms of DNA. The DNA polymerase makes copies of DNA strands in a process that mimics the way DNA replicates naturally within the cell. Segments are selected for special study and the results used to identify the DNA pattern.

With the exception of identical twins, each individual has a DNA profile that is unique. As previously noted, more than 99.9% of the over 3 billion nucleotides in human DNA are the same. But, for every 1000 nucleotides there is an average of one site of variation or polymorphism. These DNA polymorphisms change the length of the DNA fragments produced by certain restriction enzymes. The resulting fragments are called RFLPs. Gel electrophoresis is typically employed to separate the fragments according to size and thus to create a pattern of RFLPs. The number and size of the fragments is used to create the DNA profile.

Several steps are involved in creating the genetic fingerprint. First, a sample of cells is obtained from a person's blood, bone, semen, hair roots, or saliva. The individual cells from the sample are split open and DNA isolated. The DNA is treated with restriction enzymes that cleave the DNA strands at specific locations creating fragments of varying lengths and composition. The resulting fragments undergo electrophoresis using a gel which allows the separation of the fragmented DNA. Because the gel is fragile, a thin nylon membrane covered by a towel is laid over the gel. As moisture is drawn by the towel from the electrophoresis gel, the DNA fragments are transferred to the nylon membrane. This process is called blotting. The DNA bands are visible to the eye but they are too numerous to be useful. Thus, a radioactive solution is poured over the nylon membrane that binds to like fragments, generally to only 6–20 of the DNA clusters. A sheet of photographic film is placed on top of the nylon membrane that records these cluster sites. The film is then developed producing a pattern of thick-and-thin bands. This pattern is the genetic pattern for that particular sample. This process can take a month or more at commercial laboratories for routine analysis, but when needed, the analysis can be made in only a day or two.

There are different restriction enzymes that cut DNA at different sites. The previous sequence can be repeated several times for the same DNA sample. From a study of each restriction enzyme, a probability that another person will have the same profile is assigned. Thus, one restriction enzyme may have the possibility that another person has the same match of 1 in 100 or 1%. A second restriction enzyme may have the probability of 1 in 1000 or 0.1%. A third restriction enzyme may have a probability for a match of 1 in 500 or 0.2%. If there is a match with all three restriction enzymes, the probability would be $0.01 \times 0.001 \times 0.002$ or 0.00000002% or 0.000002% or 1 part in 50,000,000. There is a caution to using the "multiplication rule," in that DNA sequences are not totally random. In fact, DNA sequence agreements generally diverge as one's ancestors are less closely related.

The RFLP method requires a sample about 100 times larger than that required for the PCR approach, but with repeated sequences using different restriction enzymes, RFLP is more precise.

It must be noted that factors leading to DNA degradation, such as moisture, chemicals, bacteria, heat, and sunlight will impact negatively on DNA profiling since the precise sequences and length of the DNA and DNA fragments may be changed. While DNA, in general, is robust and can exist "alive" over thousands of years (such as the germination of seeds found in the pyramids of Egypt), DNA degradation decreases the probability of precise matches. Also, DNA contamination by addition of DNA from another source greatly confuses the final results.

DNA sequencing has found importance in a wide range of areas. It is used to identify individuals at greater risk for having certain diseases such as breast cancer. It is used for the screening of certain diseases such as the presence of the sickle-cell gene.

The initial VNTRs were several hundred nucleotide units long requiring extended laboratory periods for the various segments to separate on the gel. Today, most tests employ shorter, 3–5 nucleotides long, VNTRs that allow for more rapid movement on the gel, resulting in faster and less costly results. It also allows for the production of a greater number of sequences that are looked at, and hence a greater ability to match or not match the results. These shorter sequences are called short tandem repeats (STRs).

While DNA is more robust than often depicted in movies, age and extreme conditions such as a fire can substantially degrade it. In such cases, mitochondrial DNA (mtDNA) is best used. Unlike nuclear DNA, mitochondrial genome exists in thousands of copies, is less apt to degrade, and is inherited only from the mother. Here, STRs are not analyzed, but rather the focus is on variable regions of the mitochondrial genome. Such analyses take much longer but are used for situations where time is not essential.

This type of DNA profiling has allowed taxonomists to determine evolutionary relationships among plants, animals, and other life forms. Currently it is a basis for the so-called

Eve theory that says all of us are related to one woman, Eve, after the Biblical Eve. It is also being used to trace the (ancient) movement of people around Earth.

DNA profiling was used to determine whether bones unearthed that were said to belong to Jesse James were in fact his. DNA samples were taken from his grandchildren and compared to those obtained from the bone material and shown to be similar, so that while it cannot be absolutely said that they were Jesse James' bones, DNA evidence was consistent with them being his bones. DNA profiling has also been used in the identification of 9/11 victims, and a number of mass graves throughout the world.

In 1998 the Combined DNA Index System (CODIS) was begun by the Federal Bureau of Investigation (FBI). It is an automated forensic data bank that contains DNA profile data related to most of the recent major crimes. It is also connected with state systems as well as similar worldwide data bases.

10.10 THE HUMAN GENOME: GENERAL

The unraveling of much of the human genome is one of the most important advances ever made. An online tour of the human genome is found at a number of web sites allowing access to some of this valuable information. Some of these sites are http://genome.ucsc.edu, www.nature.com/genomics/human/papers, www.sciencemag.org/contents/vol291/issue5507, www.ncbi.nlm.nih.gov/sitemap/index.html#humangenome, www.nhgri.nih.gov/data/, www.celera.com, www.ensembl.org/genome/central/, http://genome.ucsc.edu, http://genome.cse.ucsc.edu, and http://genome.wustl.edu/gsc/human/mapping.

There are two general kinds of cells: those having a membrane-bounded nucleus called eukaryotic cells, and those without a nuclear envelope called prokaryotic cells. Humans have eukaryotic cells. All eukaryotic cells contain a nucleus that contains the genome, the complete set of genes. Unless noted otherwise, our discussion will be restricted to eukaryotic cells.

The human genome and other mammalian cells contain about 600 times as much DNA as *E. coli*. But many plants and amphibians contain an even greater amount. While eukaryotic cells contain more DNA than do bacterial cells (prokaryotic cells), the gene density of bacterial cells is greater. For instance, human DNA contains about 50 genes/mm while *E. coli* contains more than 2,500 genes/mm. Although the human genome contains a lot of nongene material, this nongene material appears to be active in the organization of the chromosome structure, playing a number of roles including supplying hyperfine contours to assist in the replication, protection, and selectivity of the sites. The contour length, i.e., the stretched-out helical length, of the human genome material in one cell is about 2 m in comparison with about 1.7 m for *E. coli*. An average human body has about 10^{14} cells giving a total length that is equivalent to traveling from the earth to the sun and vice versa about 500 times or 1,000 one-way trips.

Replication occurs with a remarkably high degree of fidelity such that errors occur only once in about 1,000–10,000 replications or an average single missed base for every 10^9–10^{10} bases added. This highly accurate reproduction occurs because of a number of reasons including probably some that are as yet unknown. As noted earlier, the G–C group has three hydrogen bonds while the A–T has two. *In vitro* studies have found that DNA polymerases insert one incorrect base for every 10^4–10^5 correct bases. Thus, other features are in place that assist in this process. Some mistakes are identified and then corrected. One mechanism intrinsic to virtually all DNA polymerases is a separate $3'$–$5'$ exonuclease activity that double-checks each nucleotide after it has been added. This process is very precise. If a wrong base has been added, this enzyme prevents addition of the next nucleotide removing the mispaired nucleotide and then allowing the polymerization to continue. This activity is called proofreading and it is believed to increase the accuracy by another 10^2- to 10^3-fold.

Combining the accuracy factors results in one net error for every 10^6–10^8 base pairs, still short of what is found. Thus, other factors are at work.

In general, replication occurs simultaneously as both strands are unwound. It is bidirectional with both ends of the loop having preferentially active starting points or sites. A new strand is synthesized in the $5'$–$3'$ direction with the free $3'$ hydroxyl being the point at which the DNA is elongated. Because the two DNA strands are antiparallel, the strand serving as the template is read from its $3'$ end toward its $5'$ end. If DNA replication always occurs in the $5'$–$3'$ direction, how can it occur simultaneously? The answer is that one of the strands is synthesized in relatively short segments. The leading strand, or the strand that "naturally" is going in the correct direction, replicates somewhat faster than the lagging strand, which is synthesized in a discontinuous matter with the required direction and occurs at the opposite end of the particular segment, consistent with the observation that all new strands, and here strand segments, are synthesized in a $5'$–$3'$ manner.

From a scientist's point of view, knowledge comes along with questions, which in turn lead to gathering more information, and so the cycle continues. We have already noted that the precise folding and compaction for chromosomal DNA is not yet fully known (Section 10.11). Further, as noted above, we are not fully aware of how replication occurs in such a precise manner.

A third major area of evolving knowledge involves how so much information is packed into the relatively small number of genes we believe we now have. In the past we believed that the number of human genes was on the order of 100,000, a number that appeared appropriate even after the first two animal genomes were deciphered. The roundworm, sequenced in 1998, has 19,098 genes, and the fruit fly, in 2000, was found to have 13,601 genes. Currently the number of human genes is believed by many, but not all, to be on the order of 30,000–40,000, less than half of the original number. This means that the genes are probably more complex than originally believed. It is now believed that the reason we are able to function with such few genes is that our genes carry out a variety of activities. This ability is a consequence of several features. One involves the coordinated interactions between genes, proteins, and groups of proteins, with variations of the interactions changing with time and on different levels. There is then a complex network with its own dynamics, which is probably largely absent in lower species such as the roundworm. The roundworm is a small tubed animal with a body composed of only 959 cells of which 302 are neurons in what passes for a brain. Humans, by comparison, have 100 trillion cells including 100 billion brain cells. While protein domains exist in primitive animals such as the roundworm, they are not as "creative" as those found in more advanced animals. The domains that we have allow the "creation" of more complex proteins.

It appears that another way to gain complexity is the division of genes into different segments and by using them in different combinations, increasing the possible complexity. These protein-coding sequences are known as exons and the DNA in between them as introns. The initial transcript of a gene is processed by a splicesome, which strips out the introns and joins the exons together into different groupings governed by other active agents in the overall process. This ability to make different proteins from the same gene is called alternative splicing, which is more common with the higher species. Related to this is the ability of our immune system to cut and paste together varying genetic segments that allow the immune system to be effective against unwanted invaders.

In eukaryotic cells transcription and translation occur in two distinct temporal and spacial events, whereas in prokaryotic cells they occur in one step. As humans have eukaryotic cells, we will look at this process. Transcription occurs on DNA in the nucleus and translation occurs on ribosomes in the cytoplasm.

Our genes are split into coding or exon regions and noncoding or intron regions. The introns are removed from the primary transcript when it is made into a mature or completed RNA such as mRNA, tRNA, and rRNA.

Such split genes occur in a wide variety of sizes and interruptions. Even so, the transcription must be precise. Several features are worth noting about this process. First, the order of the exons is fixed as is the size and order of the introns. Also, the order of the exons on the mature RNA is the same as in the original DNA. Second, each gene has the same pattern and size of exons and introns in all tissues and cells of the organism and, with the exception of the immune response and the major histocompatibility complex, no cell-specific arrangements exist. Third, many introns have nonsense codons in all three reading frames, so nuclear introns are nontranslatable. Introns are found in the genes of mitochondria and chromoplasts as well as in nuclear genes.

We must remember that each of these steps consists of simple, though complex when considered as a whole, chemical reactions.

Another source of increased complexity involves the fact that human proteins often have sugars and other chemical groups attached to them allowing subtle, and possibly not so subtle, changes in behavior.

It has also been found that at least some, about 75%, of the DNA sequences in our genome are apparently nonactive material. The coding regions may occupy only about 1%–1.5% of the genome. (It must be remembered that while only a small amount contains coding regions, the structure around these regions is also important to the overall activity of the gene.) These active regions are not evenly distributed across the cell's 23 pairs of chromosomes but are arranged in patches or regions, some gene-rich and others gene-poor or deprived. They appear to be sticky and like to associate with one another. It is similar to the USA where most of the people occupy a small fraction of the land area, with large areas having only a low population. There are even preferred base sequences for these different regions. The populated regions tend to be high in C–G sequences, whereas nonpopulated areas, regions in which there are few active areas, have higher amounts of A–T sequences. These differences in preferential sequencing actually help account for the banding found in chromosome patterns. The light bands are rich in C and G and the dark ones in A and T.

Gene expression simply refers to its transcription, resulting, in most cases, in the synthesis of a protein or protein part. The flow of information is typically DNA → RNA → protein → cell structure and function. Transcription is the term used to describe the transfer of information form DNA to RNA; the flow of information from RNA to protein is called translation. Genes whose product is needed essentially all the time are present at a constant amount in virtually every cell. Genes for enzymes of the central metabolic pathways are of this type and are often called housekeeping genes. Unvarying expression of a gene is called constitutive gene expression.

The cellular levels of some gene products vary with time in response to molecular signals. This is called regulated gene expression. Gene products that increase in concentration are called inducible and the process of increasing their expression is called induction. Conversely, gene products that decrease in concentration in response to a molecular signal are said to be repressible and the process is called repression. Transcription is mediated and regulated by protein–DNA interactions. Thus, while we will focus on DNA, protein interactions are critical to the operation and expression of genes.

We are beginning to understand some of the language of the genes. We are already aware of the sequences that code for particular amino acids. We are also becoming more aware of the meaning of other sequences. Many of these sequences are involved with transcription regulation. Promoters are DNA sites where the RNA polymerase can bind, leading to initiation of transcription. They are generally located near the gene. There are a number of these sequences. The CAAT box has a consensus sequence of GGCCAATCT and its presence indicates a strong promoter site. One or more copies of the sequence GGGCGG, called the GC box, are often found upstream from transcription start sites of housekeeping genes. The TATA box has a sequence of TATAAAA.

Enhancers are DNA sequences that assist in the expression of a given gene and may be located several hundred or thousand base pairs away from the gene. They are also called upstream activation sequences because they exist somewhat removed from transcription start sites. Their location varies between genes. Such sequences are bidirectional, i.e., they occur in the same way in both directions.

Response elements are promoter modules in genes that are responsive to common regulation. Examples include the heat shock element (HSE), with a sequence of CNNGAANNTCCNNG (where "N" is unspecified); the glucocorticoid response element (GRE), with a sequence of TGGTACAAATGTTCT; and the metal response element (MRE), with a sequence of CGNCCCGGNCNC. HSEs are located about 15 base pairs upstream from a transcription start site of a variety of genes whose expression dramatically changes in response to elevated temperatures. The response to steroid hormones depends on the presence in certain genes of a GRE positioned about 250 base pairs upstream from the transcription start point.

The complexity of these response elements can be seen in considering the metallothionein gene. Metalothionein is a metal-binding protein produced by the metallothionein gene. It protests against heavy metal toxicity by removing excess amounts from the cell. Its concentration increases in response to the presence of heavy metals such as cadmium or in response to glucocorticoid hormones. The metallothionein gene promotion package consists of two general promoter elements, namely a TATA box and a GC box; two basal level enhancers; four MREs; and one GRE. These elements function independently of one another, with any one able to activate transcription of the gene to produce an increase in the metallothionein protein.

As expected, it is both the composition and the shape which are driven by the composition that are important. This shape is maintained through a combination of hydrophilic and hydrophobic interactions, cross-links, preferred bond angles, as well as inter- and intrachain interactions. It is a complex combination but one in which we are beginning to understand some of the basics.

The age distribution for various genome sequences is done by comparing changes in similar sequences found in "older" species. This dating has several important assumptions: first, that the rate of sequence divergence is constant over time and between lineages; and second, that the "standard" older sequence is in fact a source of the sequence and that the date for this source is appropriate. These assumptions are at best appropriate so that results derived from such studies need to be considered in this light.

Our genomes contain a history of their development including incorporation, infection, by viruses and bacteria. Some of these "additions" form part of the so-called dead regions while others may allow desired activities to occur. Thus, it is possible that a foreign incorporated bacterial sequence allows the encoding of monoamine oxidase, which is an important degradative enzyme for the central nervous system. The presence of such apparently foreign information in our genome may mean that there is a dynamic nature to our genome that allows for the inclusion of new information into present genomes, and probably also the converse, the removal of segments of information from our genome.

Even so, the large majority of our genome is not borrowed, but has rather developed on its own, possibly through what are called jumping genes or transposons that caused themselves to be reproduced and inserted into the genomes. The euchromatic portion of the human genome has a higher density of transposables than found for other species. Further, the human genome has more ancient transposables, whereas other species have more recent transposables.

Most of these transposons move so that the new location is almost selected at random. Insertion of a transposon into an essential gene could kill the cell so that transposition is somewhat regulated and not frequent. Transposons are one of the simplest molecular parasites. In some cases, they carry gene information that is of use to the host.

The most important group of transposons is believed to be the long interspersed element (LINE) grouping (there are three LINE families with only the LINE1 family active) that encodes instructions for whatever it needs including copying its DNA into RNA, and copying the RNA back into DNA, and finally moving out of and into the chromosome. LINEs are only about 6000 base pairs in length (6 kb). Interestingly, most of these LINEs are found in the C and G gene-rich or gene-poor regions of the genome. LINEs have other "parasites" called Alu elements accompanying them that are only about 300 base pairs long and are the most abundant sequences in our genome. (They are given the name Alu because their sequence generally includes one copy of the recognition sequence for the restriction endonuclease AluI.) While Alu elements cannot replicate on their own, they "borrow" the needed hardware from the LINE segments to reproduce. Because of their active nature, they can cause trouble. For instance, in the development of an egg or sperm cell, a replicating Alu segment can be inserted resulting in a child with a genetic disease. But Alu segments do perform positive functions. They become activated, helping modulate the body's response when it is exposed to stresses such as sudden changes in temperature and light as well as to alcohol. Alu segments are found only in the higher primates and are responsive to a large family of receptor proteins that allow cells to recognize potent hormones like estrogen, retinoic acid, and thyroid hormone. Their presence appears to allow the surrounding site to be more flexible and to slightly change in shape when exposed to these hormones and hormone-like chemical agents.

In humans, the LINE and Alu families account for about 60% of all interspersed repeat sequences, but there are no dominant families in the other species thus far studied. Alu segments compose about 1%–3% of the total DNA and Alu and similar dispersed repeating sequences comprise about 5%–10% of human DNA.

In humans, while less than 5% of the genome contains coding sequences, about 50% contains repeat sequences. Such sequences are often included in the category of junk DNA, yet they provide lots of information and some provide function. Such segments act as a kind of paleontological record of past interactions with various bacteria and virus, and as passive markers for studying mutation and selection; they can be active in providing shape and function, allowing the same sequence to behave in a different fashion because of the presence of these junk sequences.

Repeats can be divided into five classes. The first are transposon-derived repeats, some of which have been briefly dealt with earlier. About 45% of our genome is derived from transposable elements. It is possible that some of the other "unique" DNA may also be derived from ancient transposable element copies that we have not yet recognized. The second are partially inactive retroposed copies of cellular genes called processed pseudogenes. The third are short simple repeating sequences such as AAAAAA and CACACACACA. The fourth are short segmental duplications that have been copied from one region of the genome into another region. These sequences are typically 10,000–300,000 base pairs long (10–300 kb). The fifth are blocks of tandem repeated sequences.

There are four types of transposon-derived repeating sequences, of which three transpose through RNA intermediates and one transposes directly as DNA (the last one is considered below). We have already identified the LINEs. The second set is called short interspersed elements (SINEs), of which the Alus are the only active members that exist in the human genome.

The third group is the long terminal repeat (LTR) retrotransposons that are flanked by long terminal direct repeats that contain all the transcriptional regulatory elements. LTR genes can encode a protease, reverse transcriptase, RNAse H, and integrase. Transposition occurs through a retroviral mechanism with reverse transcription occurring in a cytoplasmic virus-like particle. While a wide variety of LTRs exist it is believed that only the endogenous retroviruses (ERVs) are active in humans.

The last group of transposable elements is the DNA transposons that resemble bacterial transposons. They tend to have short life spans within a species. Humans have at least seven families of DNA transposons. Their replication is lessened by the presence of inactive copies, so as the inactive copies accumulate, transposition becomes less efficient.

As part of the overall human genome, the LINEs, SINEs, LTRs, and DNA retroposons make up 20%, 13%, 8%, and 3% (total of 44%) of the repeat sequences.

Such repeats are often included as "junk." Again, the so-called junk in our genome may not be junk but rather part of a complex of shape and electrical nature that forms the basis for the chemistries of the various polymeric molecules.

This massive amount of information should not be considered as insurmountable or only material to be marveled at but not understood. Much of the chemistry is already available to "mine" this information successfully. Much of it is understandable in somewhat simple terms, generally only after we have discovered the key to this simplicity. For instance, there is a marked decrease in the frequency of the dinucleotide CpG in some areas of the genome. The deficiency is believed to be due to the fact that most CpG nucleotides are methylated on the cytosine base, and spontaneous deamination of the methyl-cytosine residue creates T residues. Thus, CpG dinucleotide sequences mutate to TpG dinucleotides. But there still remain some questions. There are certain regions or islands where the CpG sequences exist in a nonmethylated form and where the frequency of CpG occurs within the expected or normal rate. Why? These CpG islands are of particular interest because they are associated with the 5′ ends of genes.

Another broad finding in examining the human genome concerns the rate of recombination. Recombination involves the cleavage and rejoining, i.e., the insertion, of sequences of nucleic acids by enzymes. In fact, recombinant DNA is the result of such recombination. In general, the average recombination rate increases as the length of the chromosome arm decreases. Long chromosome arms have a recombination rate that is about half that of shorter arms. Second, the recombination rate is less near the centromere and greater in the more distant portions of the chromosomes. This effect is most pronounced for males. The centromere is an essential site for the equal and orderly distribution of chromosomal units during cell formation, meiosis.

Why these differences? A higher rate of recombination increases the likelihood of at least one crossover during meiosis of each chromosome arm. Such crossovers are necessary for normal meiotic disjunction of homologous chromosome pairs in eukaryotic cells. Recombination occurs with the greatest frequency during meiosis, the process in which diploid cells with two sets of chromosomes divide, producing haploid gametes—sperm cells or ova—with each gamete having only one member of each chromosome pair.

The "crossing over" is not entirely random. Even so, in general, the frequency of homologous recombination in any region separating two points on a chromosome is proportional to the distance between the points. A homologous genetic recombination is simply the recombination between two DNAs of similar (not necessarily the same) sequence. Homologous recombination serves several functions. First, it contributes to the repair of certain types of DNA damage. Second, it provides a transient physical link between chromatids that encourages orderly segregation of chromosomes during the first meiotic cell division. Third, it enhances genetic diversity.

Since such crossover sequences are important, it is possible that they are present to an extent in each arm to ensure that crossover occurs, but the full answer is not currently known and since shorter arms are shorter, their density or frequency is greater.

We need to remember that the present knowledge of the human genome is a rough map without complete information of the stoplights, detours, alternative routes, potholes, etc., to use the metamorphic language relating a paper map to the actual physical terrain. Scaffolds are being built to fill these knowledge gaps with time, allowing the scaffolding to become part of a solid building.

10.11 CHROMOSOMES

The preliminary investigation of chromosomes has resulted in several recurring themes. One is that nature magnifies small differences; often the difference in only a single base pair can lead to marked differences in our overall predicted health. The second involves the interrelatedness of the genes with one another and with various proteins that are created by them. A third theme will not be dealt with at great extent as it concerns the fact that even though we talk about a common human genome, there are within it sufficient differences to make each of us individuals with our own aspirations and dreams, tendencies toward particular foods and diseases, etc. Even so, most of the human genome is the same with small variances, including our outward environment, resulting in a diverse population of human beings.

We often think of chromosomes as being flat with little or no geographical topology because the sheet of paper or screen we view them on is flat. However, it is the three-dimensional structure that assists the various genes to perform their function in designing the necessary proteins. The secondary structure of these features is more or less helical, with the different clefts causing the DNA to have these varying structures. The transfer of information from the DNA template to protein, and less so RNA, synthesis is described in Section 10.4.

Our bodies have about 100 trillion cells, and inside each cell is the nucleus and, except for egg and sperm cells, inside the nucleus are two copies of the human genome made from DNA with protein-building genes contained within chromosomes that compose the human genome. There are, however, a few exceptions. Not all genes are DNA, and some contain RNA. Not all genes code for proteins. Some are transcribed into RNA that becomes part of an rRNA or tRNA. While most gene-associated reactions are catalyzed by proteins, a few are catalyzed by RNA. Again, while many proteins are designed by a single gene, some are designed by several genes.

The human genome comes in 23 packages where each package is a chromosome. This number 23 is important. If we have more or less than 23, we may well be in great trouble. Only chromosome 21 can be present with more than one copy with the occupant having a healthy body, but unfortunately those with an extra chromosome 21 are not normal but rather have Down syndrome. The chromosomes are named in general order of size starting from the largest as chromosome 1 through 22, though it has recently been found that chromosome 21 is smaller than chromosome 22. We also have as the remaining chromosome the twined sex chromosomes, with women having two large X chromosomes and men having one large X and a small Y. The X chromosome, in size, falls between chromosomes 7 and 8, while the Y chromosome is indeed the smallest. Note that even though the XY chromosome combinations are together only a part of the total twined sex chromosome, chromosome researchers often refer to each part in terms of a chromosome. The variation from the smallest to the largest of the chromosomes is about 25-fold.

While 23 chromosomes is a relatively large number it is by no means the largest number of chromosomes within a species. The normal number of chromosomes for selected organisms appears in Table 10.4.

All eukaryotic cells in our bodies contain the same 23 chromosomes with the same DNA base sequences. The lone differences are the mitochondria. The mitochondria in typical somatic cells contain less than 0.1% of the cell's DNA but in fertilized and dividing egg cells this number is greater. mtDNA is much smaller, often containing fewer than 20,000 base pairs. The value for humans is 16,569 base pairs. The mtDNA is a circular duplex. mDNA codes for the mitochondrial tRNAs and rRNAs but only a fraction of the mitochondrial proteins. Over 95% of the mitochondrial proteins are encoded by nuclear DNA. The mitochondria divide when the cell divides.

The association of a particular disease with a particular gene or group of genes is rapidly increasing. A spot check of www.ncbi.nlm.nih.gov/omim, the online version of Mendelian

TABLE 10.4
Number of Chromosomes of Some Common Species

Organism	Chromosome Number*	Organism	Chromosome Number*
Bacteria	1	Mouse	20
Fruit fly	4	Rat	21
Pea	7	Rabbit	22
Frog	13	Human	23
Fox	17	Ape	24
Cat	19	Chicken	39

* The diploid chromosome number is double this number except for bacteria.

Inheritance in Man (OMIN), gives an ongoing updated progress report of this activity. Currently, about 1500 disease mutations have been entered. With the advent of the mapping come a number of shifts in thinking and activity. Thus, we will move from the so-called map-based gene discovery to looking at the particular activity of gene sequences; from association of particular gene-associated diseases to looking at tendency and susceptibility for given conditions and the variation with tendency or susceptibility between individuals; from looking at the activity of a single gene or gene location to investigating combined activities of several genes from varying locations; from genomics or the study of genes themselves to proteomics and the study of the interaction between the genes and proteins; from gene action to gene regulation; and from specific mutations to the mechanisms and causes of such mutations. Much of this is a guessing game—hopefully an educated and educating guessing game—and is currently very costly. As new techniques and strategies are developed, the cost should decrease.

As noted above, one of the important themes is that small, or seemingly small, changes in the genetic code can have profound effects. Many of the better-known diseases are named after their discoverers or unfortunate victim(s). The Wolf–Hirschhorn disease and Huntington's chorea are examples. They are wholly genetically based or, in their case, the result of a missing (Wolf–Hirschhorn) or mutated (Huntington's) gene. It is believed that the genetic origin of the disease is contained in chromosome 4. The coding that is responsible for Huntington's disease is the sequence CAG. This replication occurs several times. If this sequence occurs 35 times or less, you will not develop the disease. But if you have this sequence 39 times or more, you will develop the disease, with the onset noticeably beginning in midlife with a slight loss of balance. There begins a decline in mental capacity, and jerking of the limbs. This continues until death. It generally takes 15–30 years to run its course, but there is currently no cure. In general, the greater the number of repeat sequences, the earlier is the onset of the disease. If you have 40 repeat units, you will exhibit the disease at about 60; if you have 42, you will exhibit the disease by 40, progress well along the disease at 50, and most probably be dead by 60. Thus, the frequency of this sequence in this particular chromosome determines one's outcome with respect to the disease. While both diseases are rare, it is Huntington's disease that killed noted folk balladeer Woody Guthrie in 1967.

In Huntington's disease long repeat sequences of CAG appear. The CAG codon codes for glutamine, so that areas that emphasize the buildup of this amino acid appear to offer a greater incidence of certain neurological diseases possibly wherever they are found. This may be due to a buildup of glutamine over a time, with the glutamine-rich proteins being "sticky" and more apt to remain at the particular site rather than "moving on" to do what it was supposed to do. After some time this buildup becomes great enough to block the healthy activity of the gene, causing problems and possibly leading to death or noticeable loss of function of the cell. This buildup and death of a significant number of cells takes time and that is probably why these diseases take time to make themselves known. As an aside, it is interesting that some health potions emphasize the presence of glutamine, but it must be remembered that while the presence of some glutamine is essential to healthy lives, it is not the presence of glutamine that may cause these diseases, but rather the coding on the DNA.

Other repeat sequences also appear to offer problems. Many begin in C and end in G. Thus, we have large numbers of repeats of CCG and CGG (that code for proline, and arginine) that are believed to give a disposition to certain nerve degeneration–related diseases.

Another phenomenon is worth mentioning. There appears to be a tendency for such repeats to become longer through each replication cycle. This is called anticipation and is believed to be related to a very slight tendency for the replication cycle to "lose count" of the number of repeats as the number of exact repeats becomes large, say 30 or more. Again, this is a reason why some diseases take time to manifest themselves since it takes time for the number of replications to increase to a "dangerous" length.

The Huntington scenario paints a sad picture for our ability to "cure" those with the disease. Are we to modify each chromosome 4 in the billions of cells in our brain, and if so, how? It is not the sequence itself, but rather the length of the sequence, that is the problem. All of us have some of these repeat sequences and they are necessary for other essential activities.

While certain behavioral and nonbehavioral diseases are believed to be monogenic, diseases such as Huntington's, cystic fibrosis, Marfan, and Hirschsprung result in the specified disease, and the outward appearance or result (phenotype) of the disease varies between individuals. For instance, for Marfan syndrome, there is a level below which the mutant protein does not exhibit itself in an outward manner. Most of these diseases have modifier genes that cause modifications in the outward demonstration of the disease and play a key role in the clinical symptoms. Further, the particular metabolic pathways are often varied, with several of the steps being important and the importance of each mechanistic pathway may differ with every individual.

We are learning external ways to identify activities, or actions, that may be related to our genome makeup. One of these observations involves changes in the capacity of individuals to "learn" with age. It appears that the ability to learn language, especially grammar, decreases as we grow older and is most apparent in children. Thus, ability to learn a language appears to be gene-related. There are genetic conditions that are related to our linguistic ability. One is the Williams syndrome where affected children have very low general intelligence, but have a vivid and loquacious ability to use language, chattering on in long and elaborate sentences. Thus, they have a heightened ability to learn language. The Williams syndrome is caused by a change in a gene found on chromosome 11.

Another gene-related disease is known as specific language impairment (SLI) where individuals with general intelligence have lowered linguistic ability. SLI is believed to be related to a gene found on chromosome 7.

Genes are related to all aspects of our lives. Someone has said we are what we eat. We can extend this to say that we become what our genes do with what we eat. There is a group of genes called apolipoproteins or APO genes. There are four basis types of APO genes interestingly known as APOA, APOB, APOC, and APOE (no explanation for what happened to D). Here we will focus on a specific gene that appears on chromosome 19 known as APOE. As we eat, the various food parts are digested or broken down. Both fat and cholesterol are brought through our bloodstream by lipoproteins, of which some are very-low-density lipoproteins (VLDLs). The fat and cholesterol are brought to various parts of the body to act as fuel and building blocks. As some of the triglycerides are delivered, the proteins are now called simply low-density lipoprotein (LDL), known to many of us as "bad cholesterol." After delivering the cholesterol, the proteins become high-density lipoprotein (HDL), also known to us as "good cholesterol," and then returns to the liver to be replenished with cholesterol and fat. The APOE protein acts to affect the transfer between VLDL proteins and a receptor on a cell that needs some triglycerides. APOB serves a similar role, except in delivering cholesterol. Thus, the presence and effectiveness of genes that code for the APO genes helps control our weight and health, affecting such items as buildup on our arteries.

APOE is unusual in that it is polymorphic, i.e., having several versions. The three most common ones are E2, E3, and E4. E3, deemed the best variety of APOE, is the most common in Europeans, with about 80% having at least one copy and about 40% having two copies. But about 7% have two copies of the E4 gene, the worst variety, and are at high risk of early heart disease. These trends of APOE are geographical and correlate with the frequency of heart disease. Thus, the frequency of E4 is about three times higher in Sweden and Finland than it is in Italy and so is the frequency of coronary heart disease. On a race basis, Asians have the lowest frequency of E4 (about 15%), with American blacks, Africans, and Polynesians all having higher values of E4 (about 40%). Diet also contributes, so that while New Guineans have a high frequency of E4, their diet is low in fats and they have a low incidence of heart disease; but when they change their diet so that it is similar to ours, they become more susceptible to heart disease.

Our blood type is determined by a gene that is present on chromosome 9, near the end of the long arm. There are four general blood types: A, AB, B, and O. Some of these are "intermixable" while others are not. For instance, A blood from a person is compatible with A and AB; B with B and AB; AB with only AB; and O blood is compatible with all of the blood types—a person with type O is then a universal donor. These compatibility scenarios are not race-related. For all but the native Americans who have almost totally type O, the rest of us have about 40% type O; another 40% type A; 15% type B; and 5% type AB. (Some of the Eskimos are type AB or B and some Canadian tribes are type A.) A and B are codominant versions of the same gene and O is the "recessive" form of this gene.

The active codons of the blood-type gene are about 1000 base pairs long and are divided into six short and one longer sequence of exons. The difference between the type A and type B gene is seven letters of which three do not make any difference in the amino acid coded for. The four truly different bases are positioned at sites 523, 700, 793, and 800 and are C, G, C, G for type A and G, A, A, C for type B blood. Type O people have just a single change from the type A people with a deletion in the type A base at base pair 258, omitting the G base. While this appears to be very minor, it is significant in that it causes a reading or frame-shift mutation. These seemingly minor changes are sufficient to cause the body to have an immune response to different types of blood. Even so, while this causes a different type of blood, it appears to have little or nothing to do with other parts of the overall human genome so that tendencies toward cancer, ageing, etc. are not influenced by this change but it appears to have something to do with some general tendencies toward some diseases. For instance, those with AB blood are the most resistant toward cholera while those with type O blood are most susceptible. Those with two copies for the sickle-cell mutation generally contract sickle-cell anemia while those with one copy of the mutation are more susceptible to contracting sickle-cell anemia than the general public but they are more resistant to malaria. Some of these connections can be found in tracing the ancestry of individuals with the particular connections between blood type and susceptibility.

Recently we have been working on Parkinson's disease. This and other similar diseases are due to a depletion of dopamine in the corpus striatum. Direct addition of dopamine is not effective in the treatment presumably because it does not cross the blood–brain barrier. However, levodopa, the metabolic precursor of dopamine, does cross the blood–brain barrier and is believed to then be converted to dopamine in the basal ganglia.

On the short arm of chromosome 11 is a gene known as D4DR that manufactures the protein dopamine receptor. It is active in some parts of the brain and not active in other parts.

Dopamine is a neurotransmitter released from the end of neutrons by an electrical signal. When the dopamine receptor is exposed to dopamine, it also releases an electrical signal. In general, much of the brain activity is related to such stimulation of chemical reactions by electrical changes, and vice versa, electrical current calling for chemical reactions. Many of these exchanges occur essentially at the same time. Digressing for a moment, our brain is often compared to the operation of a computer. In some sense it is but in others it is not. In our brain "switches" are activated and closed, opened and shut, by not simply electrical charge, but rather by an electrical switch associated to a very sensitive, selective chemical site.

Brain sites that have an active D4DR are then part of the brain's dopamine-mediated system. A lower amount of dopamine causes this part of the brain's system to either shut down or be less than fully active, and in extreme cases results in Parkinson's and related diseases. Excess of dopamine may lead to schizophrenia. Some of the hallucinogenic drugs act to increase the amount of dopamine. Thus, there is a tight balance between good health and health problems.

D4DR has a variable repeat sequence throughout its length of about 48 base pairs. Most of us have between 4 and 7 such sequences. The larger the number of repeat units, the more ineffective is the dopamine receptor at capturing dopamine, while a low number of such repeat sequences mean the D4DR gene is highly responsive to dopamine. In some preliminary personality studies focusing on the number of these repeat sequences, it was found, in general, that those with only a few, like one or two, sequences appeared to be more adventurous than those with a larger number of repeat sequences. Again, here we are looking at tendencies that are greatly shaped by our individual circumstances. Behavior tendencies are also implicated by other monoamines such as norepinephrine and serotonin.

Such wholly caused gene diseases are at one end of the spectrum. More likely, gene composition declares tendencies, some of which are somewhat random and others are related to our lifestyles—both voluntary and involuntary. Thus, single genes that dictate aggression, are good-natured, intelligent, criminal, etc. are not present. Most of our tendencies are just those tendencies, and such tendencies are complex and involve the interaction of many genes and associated proteins as well as external forces and opportunities. Genes in such multiple-gene systems are called quantitative trait loci (QTLs), because they are apt to produce similar behaviors within different people.

Behavior-related illnesses and patterns, both the so-called healthy and nonhealthy, are complex and involve many factors including external ones that are both learned and simply exposed to. Two features emerge from this ongoing study. First, is a tendency (not certainty) for this trait to be inherited. This tendency is generally greater than is the tendency with respect to physical disease. Second, environment plays a role. Similar environments produce similar people and different environments for related people produce different people.

As noted earlier, there are probably few single gene–associated, or monogenic, diseases and most involve a number of genes. This latter group comprises complex or multifactorial diseases, which are called QTL disorders or diseases.

Similar animal studies are useful in examining such diseases in a similar animal. The term "similar animal" simply means an animal that contracts the same disease because of a similarity in the disease-causing gene complex. As similarity exists in the genes between varying species, similar animals should be available for many of the diseases.

Attention deficit hyperactivity disorder is believed to be related to genes associated with the dopamine system, namely DAT1, DRD4, and DRD5. Schizophrenia has been reported to be linked to genes on chromosomes 1, 5, 6, 10, 13, 15, and 22. As the human genome map is better understood such combinations will become more evident. Finding such QTLs is the initial step. Next comes identifying the particular interactions between the QTLs, and between the various proteins produced by them, and finally deciding what, if anything, can or should be done to correct or modify the situation.

The Huntington-related problems, while deadly, are visually simple in relation to some other gene-related problems. Asthma is a disease that has multiple causes and symptoms and appears to be the consequence of groups of genes acting in multiple ways, some of which may be positive and others may cause asthma. Asthma, allergy, anaphylaxis, and eczema are all caused by mast cells altered and triggered by immunoglobulin-E molecules. I am allergic to certain foods and used to be to allergic to certain plants like ragweed. I outgrew much of the ragweed-like allergies but retain the food allergies. This is typical: allergies can come and go, are of varying severities, and can vary with age, sex, and race. While there is evidence to link asthma to genes, the precise group of genes remains unknown and surely will be more complex than that of the Huntington-related diseases.

A brief review of the meiosis process is in order. In the first step, the chromosomes of a cell containing six chromosomes, i.e., three homologous pairs, are replicated and held together at their centromeres. Each replicated double-stranded DNA is called a chromatid or "sister chromatid." In the second step, the three homologous sets of chromatids align forming tetrads that are held together by covalent bonding at homologous junctions called chiasmata. Crossovers, or recombinations, occur such that the two tethered chromosomes segregate properly to opposite poles in the third step. This is followed by the homologous pairs separating and migrating toward opposite poles of the dividing cells. This first meiotic division gives two daughter cells, each with three pairs of chromatids. The homologous pairs again line up across the center or equator of the cell in preparation for separation of the chromatids, or chromosomes. The second meiotic division produces four haploid daughter cells that can act as gametes. Each cell has three chromosomes, half the number of the diploid cell. The chromosomes have resorted and recombined.

We have just considered mitosis in general. We can take a simplistic look at the determination of whether a given embryo is a male or female. Females have two X chromosomes while males have one X and one Y so that the ability of the X chromosome to overwhelm the Y chromosome and give only female embryos is favored on a statistical basis. On a size basis, the Y chromosome is the smallest of all the chromosomes while the X is among the largest. Further, the Y chromosome is largely composed of noncoding DNA, giving few targets for the X chromosome to interact with. The gene on the Y chromosome that makes men men is called the SRY gene. The SRY gene interacts with the DAX gene on the X chromosome. In some sense, these two genes are antagonistic to one another where two DAX genes overcome the single SRY gene but one SRY gene overcomes one DAX gene so that depending upon the particular course of evens the outcome is a male or female. The SRY gene, when activated, ignites a whole cascade of events that leads to the maculation of the embryo. The SRY gene is peculiar in that it is remarkably consistent between men with essentially no variations in the coding regardless of race. Further, the human SRY gene is very different from those of other primates.

For many species this XY battle greatly favors one sex, generally the female, over the other. For instance, in the butterfly *Acrea encedon*, 97% are female. But in humans the competition is such that the ratio of males to females is about 1:1.

We will look at another example where the "equal" splitting of chromosome information is not entirely true. Some families have members that exhibit two related diseases. Those with the Prader–Willi syndrome are characterized with small hands and feet, underdeveloped sex organs, are generally obese, and are also often mildly mentally retarded. Those with the Angelman syndrome are taut, thin, insomniac, and small-headed, move jerkily, have a happy disposition, are always smiling, are generally unable to speak, and are mentally retarded. In both cases a section of chromosome 15 is missing. In the Prader–Willi syndrome the missing part is from the father's chromosome but in the Angelman syndrome the missing part is from the mother's chromosome. Thus, the two diseases differ depending on whether they are transmitted through the male or female.

Related to this are recent attempts to produce unisex children, i.e., embryos that are from male–male and those from female–female as sources of the chromosomal material. In both cases the attempt failed. The ‘‘two-mother-derived’’ chromosomes could not make a placenta and the ‘‘two-father-derived’’ chromosomes could not make a discernible head so that chromosomes from both sexes are required to give a healthy successful embryo.

We now move to what makes a single egg–sperm combination grow into a child. It is a combination of special events of which we will look at only one aspect. The machinery to construct a person is found within our chromosomes. One cluster of these developmental genes is located in the middle of chromosome 12. Within these genes is a group of homeotic genes. These genes are called the Hox genes and affect parts of the body in the exact sequence that they appear in the fruit fly—mouth, face, top of head, neck, thorax, front half of abdomen, rear half of abdomen, and finally the other parts of the abdomen. Also, found in each of these homeotic genes is the same sequence of about 180 base pairs that is believed to act as a switch to turn on or off each gene and is referred to as the homeobox. Mice were examined and also found to have such homeotic genes and homeoboxes. Mice have 39 Hox genes in four clusters with some differences, but many similarities, with the fruit fly. Humans have the same Hox clusters as mice with one such cluster, cluster C, on chromosome 12. A practical implication is that all the work done with other species, such as the fruit fly, may be useful as we look at our own genome with at least such developmental genes.

The similarity of the embryo genes between humans and other species gives developmental scientists considerable data to sort out. It does not eliminate or confirm a so-called master designer, since one can argue about the simplicity and interrelatedness of the design as well as its origin, and the ability to design through ordinary evolution such complex organs as the human eye.

The imprinted region of chromosome 15 contains about 8 genes, one of which is responsible, when broken, for Angelman syndrome—a gene called UBE_3A. Beside this gene are the two top candidates for the Prader–Willi syndrome when broken: one called the SNRPN gene and the other called IPW.

While these diseases normally occur because of mutation of these genes, they may also occur from a pair of parental chromosomes failing to separate, with the egg ending up with two copies of the parental chromosome. After fertilization with a sperm, the embryo has three copies of that chromosome, two from the mother and one from the father. While the embryo generally dies, in some cases it persists. If it persists and if it is chromosome 21, the result is a Down syndrome child. But normally the body detects the mistake and ‘‘kills’’ one of them. It does so randomly so that there is about a one-third chance of eliminating the paternal-derived chromosome. Generally there is no problem but if the tripled chromosome is number 15, there are two copies of UBE_3A, the maternally imprinted gene, and no copies of SNRPN (or IPW) exist, resulting in a Prader–Willi syndrome child. Recently it has been found that UBE_3A is switched on in the brain. This leads us to another unfolding saga of imprinted genes being controlled ‘‘directly’’ by the brain. In mice, it is believed that much of the hypothalamus, found at the base of the brain, is built by imprinted genes derived from the father, while much of the forebrain is built by imprinted genes derived from the mother.

What is intelligence? There are different ‘‘kinds’’ of intelligence. The so-called IQ intelligence appears to be related to the ability to gain, understand, remember, and relate information, and it is believed that about one-half is in some ways related to our genes. So, unlike the Huntington-related diseases, while there is a genetic link it is not an absolute link. Several chromosomes and genes within these chromosomes are beginning to be identified as ‘‘smart’’ genes. One of these, called IGF_2R, is found on the long arm of chromosome 6. This gene was first linked to liver cancer so it shows the variety of capability that may be present within a single gene. IGF_2R is a large gene with the typical exons and introns. Among its varied activities is its involvement in the metabolism of sugar. One form of this gene is found more frequently in supposedly supersmart people than in average intelligence people. Thus, there appears to be a relationship between the occurrence of one form of this gene and intelligence. This is circumstantial evidence at best but it is a start. An interesting side light is the observation that people with high IQ are, on the average, more effective at metabolizing sugar, and that this gene is sometimes connected with insulin-related proteins and the ability to metabolize sugar.

We again must not believe that IQ-related intelligence irrevocably binds or propels us. Harvard did a study some time ago where they tried to relate intelligence to success (whatever success is) and came up with a relationship that success was related to intelligence times the square of effort.

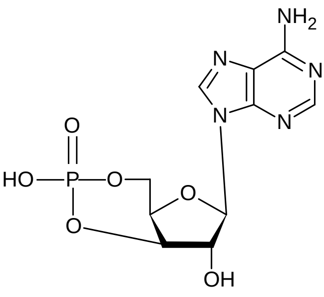
Learning is related to intelligence. In general, the more apt we are to learn, retain, integrate, and use information, the more intelligent we are. Since the brain is really limited in storage of information and for other reasons, intelligence requires an interesting mix of remembering and forgetting, a short-term memory and a long-term memory. Our input is also mixed. We have a system that filters out supposedly unwanted input, such as the constant ticking of a clock or constant hum of a fluorescent light.

One of the active agents is adenosine 3′,5′-monophosphate or cyclic AMP. A protein called CREB (for CRE binding protein, where CRE is simply a specific DNA unit that stands for the cyclic AMP response element) is activated, altering the shape and functioning of the synapse in our brain when exposed to cyclic AMP or some related compound in our brain. Genes that are activated are called CRE genes. CREB, when phosphorylated, binds to the CREs near certain genes, acting as a transcription factor and turning on, or activating, the genes. Animals without the CREB-producing gene are able to learn but do not possess long-term memory. It is believed by some that the CREB-related genes are in fact essential to our learning and memory and act as master switches in activating other genes necessary in our learning and memory process. The CREB gene is on chromosome 2. A related and essential gene that helps CREB perform is found on chromosome 16 and is given the name CREBBP.

Another essential "learning gene," related to alpha-integrin (integrins are proteins with two unlike units called alpha and beta that are anchored to the plasma membrane; they act as molecular adhesives and also as receptors and signal transducers), is also found on chromosome 16. This gene, called the volado (meaning "forgetful" in Chilean) gene, appears to be a player in memory and is not involved in the cyclic AMP sequence. The volado gene codes for one of the subunits of alpha-integrin. The volado gene appears to tighten connections between neurons as we learn.

We are aware of certain drugs that interfere with the activity of integrins by interfering with a process called long-term potentiation (LTP), which is an essential part of creating a memory. At the base of our brain is the hippocampus (Greek for "seahorse"). A part of the hippocampus is called the Ammon's horn (named after the Egyptian god associated with the ram). The Ammon's horn has a large number of pyramidal neurons that assemble the inputs of secondary neurons. Single inputs appear not to "fire" these neurons but when two or more inputs arrive at the same time, the neuron fires. Once fired, it is easier to fire again when one of the two original inputs arrive. Thus, in a real sense, memories are made in the hippocampus. In relation to the human genome, the brain is much more complex, and is controlled by a matrix of activities including our genome. It operates on a three-dimensional network rather than a one- or two-dimensional somewhat flat chromosome face. So artificial intelligence has a long way to go to mimic our brain.

It is then a group of genes found on several chromosomes that give us the ability to learn and retain information, and we are just beginning to discover the genome elements responsible for this wonderful ability.



(10.12)

Cyclic AMP

Only vertebrates show an immune response. If foreign objects, called antigens, gain entry into our bloodstream, a molecular-level protection system, called the immune response, comes into action. This response involves production of proteins capable of recognizing and destroying the antigen. It is normally mounted by certain white blood cells called the "B" and "T" cell lymphocytes and macrophages. B cells are called that because they mature in the bone marrow, and T cells mature in the thymus gland. Antibodies which "recognize" and bind antigens are immunoglobulin proteins secreted from B cells. Because the antigens can be quite different from the protein inserted by an insect bite, or by pollen, the number of proteins that can recognize and bind this variety of invaders must be quite large. Nature's answer to creating such a great host of antibodies is found in the organization of the immunoglobulin genes that are scattered among multiple gene segments in germline cells (sperm and eggs). During our development and the formation of B lymphocytes, these segments are brought together and assembled by DNA rearrangement (genetic recombination) into complete genes. DNA rearrangement, or gene reorganization, provides a mechanism for creating a variety of protein isoforms from a limited number of genes. DNA rearrangement occurs in only a few genes, those encoding the antigen-binding proteins of the immune response—the T cell receptors and the immunoglobulins. The gene segments encoding the amino-terminated part of the immunoglobulin proteins are also quite susceptible to mutation. The result is a collective population of B cells within most of us with the ability of producing the required large number of antibodies. Thus, gene variety is produced near to the event of our conception.

As noted earlier, a single gene may play several roles, or at least the proteins derived from them may. Several genes have been associated with the early onset of Alzheimer's disease: two on chromosome 14, one on chromosome 21, and interestingly one on chromosome 19, which is none other than APOE. It is not unexpected (many results are not unexpected after the fact) that a blood-lipid-related gene is associated with a brain disease. It has been found for some time that those with Alzheimer's disease had high cholesterol levels. Again, the bad actor is the E4 variety. For the families that are prone to Alzheimer's disease, those with no E4 gene have about a 20% chance of contracting the disease; those with one E4 gene have almost 50% chance, with a mean age of 75 for onset; and those with two E4 genes have a probability of over 90%, with a mean age of 68 for onset. Other genes also affect the incidence of Alzheimer's disease. For instance, the incidence of contracting the disease is much higher for whites with the same E4 amounts in comparison to blacks and Hispanics.

The difference between E4 and E3 is a signal base pair, the 334th base pair with the E4 having a G instead of an A.

The body is a marvelous "machine," growing and learning, and performing its own maintenance. Much of this maintenance is a sort of self-preservation or self-protection to maintain its own original molecular design. Involved in this are DNA repair enzymes that continuously monitor the genome to correct nucleotides and nucleotide sequences that are damaged through self-inflected mutations or through environmental factors such as exposure to various chemical agents and radiation. There are currently about 150 known human DNA repair genes whose function (or at least one function) is known along with their location within the genome and their particular sequence. The sequences for many of these have been known for several years but the specific location and proximity to other genes has only become known with the recent human genome project. These repair genes perform a number of functions. MSH2 and MSH3 found on chromosomes 2 and 5 are involved with mismatch and loop recognition repair; a group of genes known as fanconi anemia, or FAN genes, are found on chromosomes 3, 6, 9, 11, 16, etc., and are involved with repair of DNA cross-links. The overall shape of these DNA repair proteins is rapidly being uncovered and active sites identified.

Now let us look briefly at one aspect of aging. We are given, or so we are told in literature, our fourscore or 80 years. We are not able to describe why 80, but can comment on why this number is not much larger. The human genome is much longer-lived and its copying has occurred many times. Yet the cells in our body have only replicated a few times in comparison. Even the more active cells have replicated only several hundred times. Part of the answer resides on chromosome 14 in a gene called TEPI, which forms a protein that is part of the telomerase system. Lack of telomerase causes senescence. Addition of telomerase allows some cells a much longer lifetime. Telomeres, produced by telomerase, occur at the end of chromosomes. These telomeres are included in the so-called junk with a seemingly uncoded sequence, TTAGGG. This sequence is repeated many times, and is the same for all mammals and for most living species. Typically, each time the chromosome is reproduced, the number of "telomere sequences" decreases, at the average rate of about 30 base pairs a year, and may be partially responsible for the various cells "wearing out." By the time we reach our fourscore years, we have lost about 40% of the telomere sequences.

The telomerase contains RNA, which is used as the template for making telomeres, and a protein part that resembles reverse transcriptase, the enzyme responsible for the production of transposons and retroviruses. Telomerase acts to repair the ends of chromosomes re-lengthening the telomere ends. Thus, the lack of telomerase appears to cause the aging and eventual death of at least some of our cells. The relation to aging is much less certain, and surely more complicated. Thus, those with Werner syndrome, in which rapid aging occurs, start out with the same average length of telomeres, but the telomeres shorten more rapidly so that at least cell aging involves not only the length of telomeres but also the rate at which they become shorter. Recently, it was found that certain genes on chromosome 6 appear with differing versions for long-lived males, and other versions for long-lived females.

In the laboratory the immortal cell lines are those derived from cancer. The most famous is the HeLa cancer cells that many of us use as one of the cell lines tested against various anticancer agents. The name HeLa cells is derived from Henrietta Lacks, a black woman, who died from cervical cancer. The cells are so strong that they invade other cell lines, both healthy and other cancer cell lines, giving contaminated or mutated cell lines. HeLa cells have good telomerase levels. If antisense RNA is added to HeLa cells so that the RNA contains the opposite message to the ordinary RNA in the telomerase, the effect is that the telomerase is blocked and the HeLa cells are no longer immortal and die after about 25 replications.

It is estimated that about 700 genes are involved in the overall aging process and TEPI is only one of these.

It can be argued as to whether all cancers occur as a direct result of our genes, although there is a relationship between cancer and genes. We are aware that many chemical agents and high-energy radiation that result in cancer do so through damaging DNA. Oncoviruses are also known to cause cancer, and these oncoviruses are not viruses but are really genes. In general, cancer genes are genes that cause growth. Fortunately we have other genes that detect excessive growth and whose job it is to stop the growth. These genes are called tumor-suppressor genes as opposed to oncogenes. The malfunctioning of either can result in cancer.

Cancer occurs if the oncogenes are not switched off or if the tumor-suppressor genes are not permitted to work.

On the short arm of chromosome 17 is a gene called TP_{53}. This gene is a tumor-suppressor gene and it codes for the production of a protein called p53 that is being tested as an anticancer drug. TP_{53} is found to be broken in over 50% of tested human cancers and is found broken in 95% of those with lung cancer. The most resistant cancers such as melanoma, lung, colorectal, and bladder are those in which mutated TP_{53} is found. Further, when a patient initially responds to treatment, but then develops the so-called resistant cells, it is often found that the TP_{53} genes have mutated. (Thus, it should be possible to look at this gene to see if it has been mutated and if additional chemo may be useful in the treatment of a particular cancer.) Those born with one of the two TP_{53} genes broken have a 95% chance of developing cancer, and generally early in their lives. We can look at the progress of colorectal cancer. Here, cancer begins with a mutation of the tumor-suppressor gene APC. If the developing polyp then undergoes a second mutation causing an oncogen to operate without restraint, the polyp becomes an adenoma. If the adenoma in turn undergoes a third mutation of a tumor-suppressor gene, it continues to grow. If a fourth mutation occurs, now in the TP_{53} gene, it becomes a full-blown carcinoma. Many other cancers follow a similar scenario, often with TP_{53} as the final mutated tumor-suppressor gene. Thus, this gene appears to be important in the production of cancer and in the fight against it.

TP_{53} is about 1179 base pairs long and it encodes for the production of the protein p53. This protein is normally rapidly degraded by other enzymes with a half-life of only about 20 min. But when a certain signal occurs, protein production greatly increases and its degradation becomes less rapid. The signal appears to be caused by selective damage to DNA with the damaged parts calling for production of excess p53. The p53 protein then "takes over" the cell activating, essentially causing, the cell to either stop making DNA until repair is done, or signals to the cell to commit suicide. Another indicator for p53 is a shortage of cellular oxygen. Cancerous cells often outgrow their oxygen availability so that they send out new arteries to capture more oxygen for themselves. Some of the drugs being developed are aimed at preventing such adventurous artery formation.

Opposing forces operate in our bodies, often guided by our genes. These opposing forces or activities are important but become dangerous when not held in check. Thus, oncogenes cause cell growth that is necessary for injury repair and cell replacement. They are held in check by tumor-suppressor genes. Interestingly, some oncogenes, such as the MYC gene, also hold in their code cell death. The death code is held in check by chemical signals known as survival signals. Thus, if the MYC cell begins to operate in a cancer mode, the cell is signaled to kill itself. There are in fact three different oncogenes—MYC, RAS, and BCL-2—that appear to hold one another in balance. Normal cells can exist only if all three of these oncogenes are operating "correctly."

Mutations often occur but most have no long-term consequence. Some mutations are responsible for specific diseases and may cause tumor growth and cancer. Mutations are responsible for some of our diseases including gene-related diseases. Figure 10.15 shows the general location on the X chromosome of the genes where selected disease-related mutations have been found to occur. There are numerous kinds of mutations and many of them can be divided into two groups. Substitution mutations occur when one of the bases in a codon is changed from the intended base, creating a flaw in the gene. Deletion mutations occur when a base is deleted often causing the other bases to shift, altering the remaining codons. Knowing where such mutations occur allows scientists to better understand and treat them.

When we take the sum total of humanity, it is not our human genomes, but rather a complex group of events, that include our genome which actually make us what we are. In some cases, the genome casts boundaries, but more likely, it gives us probabilities, though some outcomes are so sure as to be nearly certainties. We are humans with moral, ethical, and

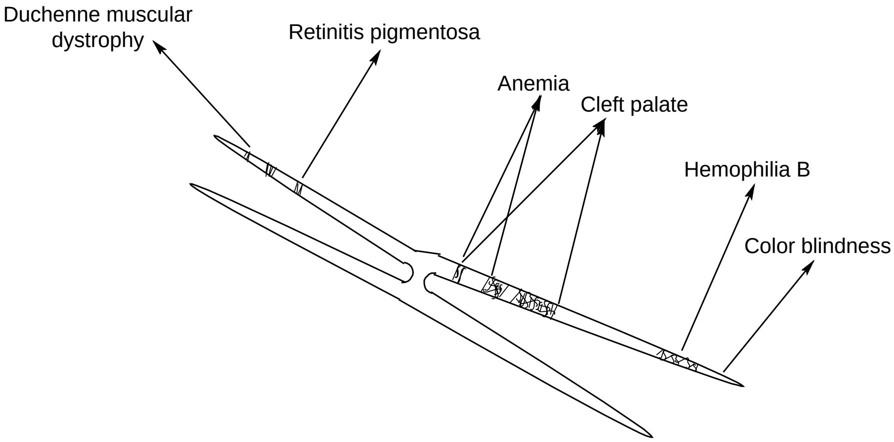


FIGURE 10.15 Selected mutations found in the X chromosome.

gene-driven tendencies and freedoms. We have just begun another trip where moral, ethical, and gene-driven aspects all play a role. We wish for good fortune and wisdom in this new adventure.

The secrets of the human genome are just beginning to be uncovered, discovered, understood, and finally utilized. It is an eventful, important trip that we are both witness to and have an essential stake in, and some of us may take an active part in. New genes are continually being discovered. So while we have decoded the human genome, we have not unlocked most of its secrets.

New information is being found daily. Some of this information may be intuitive and consistent with information gathered from other sources. For instance, it is found that certain genes behave differently in men and women. While men and women have the same genes, the information expressed by the genes varies based on gender. The differences are particularly apparent in the liver where the number of copies of a particular gene varies by gender, meaning that there is a general difference in how we metabolize drugs so that different doses of a drug are more suitable for one sex than the other. The difference is greater than previously suspected and is leading to different treatment strategies being developed based on sex.

(Some ideas for the chromosome section were taken from the timely, lively, interesting, and easy-to-read book, *Genome* (M. Ridley, HarperCollins, New York, 1999).)

10.12 PROTEOMICS

Identification of the protein target that interacts with a molecule is a bottleneck in drug discovery. Here we will deal with one branch of this important venture.

Probably for defensive reasons, because of the overwhelming amount of information, possibilities, and techniques required, subdivisions are present so that different groups focus on protein structures, DNA structures, the interaction between the two, target molecules or sites, and specific diseases and biological responses. One such subdivision has been named "proteomics," which deals with the interfacing or bridging between genomics or gene information and drug or target molecule activity. While we have uncovered over 75,000 sequences of the human genome, we have just begun to look at this "raw" information for actual active or target sites. We need to remember that we are looking at the master template, the DNA genome, its interactions with various proteins at each of the real and potential sites of action, and finally target sites and molecules to effect specific biological responses—this is polymer science in its truest form.

Almost three-quarters of the known proteins have no known cellular function but as we have learned in the past, nature seldom has true junk in its biological pile of macromolecules. In addition to identifying specific targets and target molecules, other discoveries are important such as new enzymes, signaling molecules, pathways, and finally mechanistic behaviors and factors. Identification of such factors will allow better drug discovery and activity downstream.

There are several factors that will be needed in this hunt. First, a more complete understanding of the behavior of particular proteins is needed. This includes seemingly pedestrian, but critical, activities such as providing pure and structurally and chemically unaltered proteins. This "unaltered" form includes conformational as well as configurational aspects. It is known that proteins and protein fragments may be misfolded when reproduced employing a variety of reproductive techniques. These wrong structures can cause incorrect test results and when present as part of a large data bank, may point scientists in the wrong direction, or alternately, not point them in the right direction.

Second, while each of us have over 100,000 proteins, only a fraction is expressed in any given cell type. Thus, it is a complex and puzzling problem to accurately match protein activity to some biological response. One emerging tool is to measure the relative abundance of mRNA in a cell because there is a not unexpected relationship between protein concentration and mRNA concentration. However, these correlations do not always follow, sometimes because the regulatory processes occur after transcription, so that caution must be exercised. Thus, the direct measure of the concentration of the particular protein is a better measure. Such protein determination is often achieved by traditional analytical tools such as coupling some chromatography technique such as electrophoresis with MALDI (mass spectrometry). Other biological techniques are employed and sometimes coupled with traditional analytical techniques.

Third, screens are developed that look at the many potentially active sites on each of the genome fragments. These screens often evaluate selected catalytic activity of the particular sites. As we look at the large proteins and DNA fragments we need to be aware that the presence or absence of small possibly important molecules is critical to the site activity. Again, knowing the precise identity of the site in question is critical. We also need to be aware that the particular site testing may be the wrong test and may not unlock the true site function or capabilities.

Fourth, because of the need for the involvement of diverse groups, common language problems will develop. This is true even between seemingly like medically related specialties. Thus, it is important that we define our terms as we work with other colleagues in related fields.

Fifth, we need to recognize important driving or overriding factors. Structure is one of these. It is found that structural similarities may be employed as one (notice only one) factor in determining site activity. Thus, it is important that precise three-dimensional site geometry is now including surrounding geometries. This is time- and instrument-intensive, and shortcuts are being developed, but as always caution must be exercised. Shared structural data banks are created. Computer modeling efforts are particularly useful in helping solve such structural problems.

Sixth, if the vast array of sites and site-important molecules is not enough, protein–protein interactions are part of most cellular processes including carbohydrate, lipid, protein, and nucleic acid metabolism, signal transduction, cellular architecture, and cell-cycle regulation. In fact, many of the major diseases are believed to involve a breakdown in such protein–protein interactions. These include some cancer, viral infections, and autoimmune disorders.

Techniques to discover the identity of such protein–protein interactions are evolving. One approach involves protein affinity chromatography. Here, the purified protein of interest is immobilized on a solid polymer support and proteins that associate with it are identified by electrophoresis and MALDI. There exist a wide number of modifications to the affinity chromatography approach. For instance, a number of proteins can be fixed to the support in such a manner to look at target molecule interactions as well as nucleic acid–protein interactions. You can also run through a variety of possible binders and select the ones that bind most strongly for further study. Thus, affinity chromatography is a powerful and versatile tool in this search.

Finally, a large sea of information is becoming available to us. How do we handle it? What sense does it make? Again, we will turn to two powerful tools: the computer and ourselves.

10.13 PROTEIN SITE ACTIVITY IDENTIFICATION

Scientists are developing a number of tools to look at the specific interactions that occur within proteins. As noted above, some deal with the interaction between proteins and genes while others are more general. Section 10.5 dealt with one such approach.

In general, protein target identification often employs genetic techniques such as expression cloning, expression profiling, screening of yeast mutations, and yeast three-hybrid assays. None of these techniques works for every situation.

Another approach to identifying the protein targets employs multicellular organisms. This approach is aimed at identifying the targets of small molecules. The notion of using genetics to identify small-molecule targets is not new but work with worms and zebrafish embryos is new and represents the first multicellular approaches. In the worm approach, tens of thousands of genetically modified worms are exposed to the test molecules. The worms are watched for changes in their shape. In this genetic suppressor screening, the genes of the affected and not affected worms are compared, identifying the particular gene, and hopefully the site on that gene, that is interacted with by the target molecule. With the knowledge of the activity of the particular affected site, the potential for that molecule to be active in treating an illness associated with that site is obtained. As a test, the worms are treated with a drug that is specific for that illness, and again the site of activity identified.

10.14 SUMMARY

1. Physically there is little difference in the behavior, study, or testing of natural and synthetic polymers. The fundamental principles that underpin the behavior of macromolecules apply equally to both synthetic and natural polymers. Both groupings contain members that exhibit characteristics that are unique to that grouping. Even so, differences within even these groupings are by degree rather than by kind, with the fundamental laws continuing to be applicable.
2. Contributions from studying both natural and synthetic polymers are being used to forward the science of both sets of macromolecules.
3. Organic polymers are responsible for the very life—both plant and animal—that exists. Their complexity allows for the variety that is necessary for life to occur, reproduce, and adapt.
   Structures of largely linear natural and synthetic polymers can be divided into primary structures, which are used to describe the particular sequence of (approximate) repeat units; secondary structures, which are used to describe the molecular shape or conformation of the polymer; tertiary structures, which describe the shaping or folding of macromolecules; and quaternary structures, which give the overall shape to groups of tertiary-structured macromolecules. The two basic secondary structures are the helix and the sheet.
4. Proteins are composed of 20 different alpha-amino acids and contain peptide linkages similar to those present in polyamides. With the exception of glycine, all the amino acids contain a chiral carbon. The geometrical shape and behavior of the giant proteins is a product of the various preferred geometries that allow the molecules to balance factors

such as preferred bond angle, secondary bonding forces, emphasizing hydrogen bonding, size, shape, hydrophobic and hydrophilic interactions, external and internal chemical environments, and cross-linking. Small chains of amino acids are referred to as peptides.

5. Secondary structures for proteins are generally fibrous and globular. Proteins such as keratins, collagen, and elastin are largely fibrous and have secondary structures of sheets and helices. Many of the globular proteins are composed of protein chains present in secondary structures approximating helices and sheets.
6. Enzymes are an important group of proteins. They serve as natural catalysts immobilizing various components that will be later joined or degraded.
7. The two major types of nucleic acids are DNA and RNA. Nucleic acids are polyphosphate esters containing the phosphate, sugar, and base moieties. Nucleic acids contain one of five purine or pyrimidine bases that are coupled within double-stranded helices. DNA, which is an essential part of the cell's chromosome, contains the information for the synthesis of protein molecules. For double-stranded nucleic acids, as the two strands separate, they act as a template for the construction of a complementary chain. The reproduction or duplication of the DNA chains is called replication. The DNA undergoes semiconservative replication where each of the two new strands contains one of the original strands.
8. The flow of biological genome knowledge is from DNA to RNA via transcription, and from RNA to direct protein synthesis via translation.
9. Genetic engineering is based on chemical manipulations that are exactly analogous to those carried out by chemists in basic chemistry laboratories, but it involves the use of biological agents.
10. Much that is occurring with genes, proteins, mutations, chain folding, and other important molecular biology–related efforts is polymer chemistry applied to natural systems, and we have much to offer to assist in these ventures.

GLOSSARY

active site Region of an enzyme or chromosome that binds the substrate molecule and catalytically transforms it.

alpha-helix Right-handed helical conformation of a chain, usually with maximal interchain hydrogen bonding; one of the most common natural structures.

AluI One of a family of restriction endonucleases that are site-specific endodeoxyribonucleases that cause cleavage of both strands of DNA within or near a specific site recognized by the enzyme; its recognition sequence is AG/CT.

antibody Defense protein synthesized by the immune system of vertebrates.

anticodon Specific sequence of three nucleotides in tRNA, complementary to a codon for an amino acid in mRNA.

antigen Molecules capable of eliciting the synthesis of a specific antibody.

attenuator RNA sequence involved in regulating the expression of certain genes; also functions as a transcription terminator.

base pair Two nucleotides in nucleic acid chains that are paired by hydrogen bonding of their bases; like Gee CAT representing the preferred pairing of G with C and A with T.

beta arrangement Pleated sheet-like conformation.

chromosome Single large DNA molecule and its associated proteins that contain many genes; it stores and transmits genetic information.

centromere Specialized site within a chromosome that serves as the attachment point for the mitotic or meiotic spindle during cell division, which allows proteins to link to the chromosome. This attachment is essential for the equal and orderly distribution of chromosome sets to daughter cells. It is about 130 base pairs in length and is rich in A–T pairs.

clones Descendants of a single cell.

cloning Production of large numbers of identical DNA molecules, cells, or organisms from a single ancestral DNA molecule, cell, or organism.

codon Sequence of three adjacent nucleotides in a nucleic acid that codes for a specific amino acid.

cofactor A coenzyme or other cofactor required for enzyme activity.

collagen Protein present in connective tissue.

complementary Molecular surfaces with chemical groups arranged to interact specifically with the chemical groupings on another molecular surface or molecule.

denaturation Change in conformation of a protein resulting from heat or chemicals.

denatured Partial or complete unfolding of the specific native conformation of a polypeptide, protein, or nucleic acid.

degenerate code Code where a single element in one language is specified by more than one element in a second language.

deoxyribonucleic acid (DNA) Nucleic acid in which deoxyribose units are present; composes the human genome.

diploid Having two sets of genetic imformation such as a cell having two chromosomes of each type.

DNA profiling Identification method based on variations between an individual's DNA.

domain Distinct structural unit of a polypeptide.

elastin Protein that is the major material of arterial blood vessels and ligaments which is noted for its flexibility.

enhancers DNA sequences that help the expression of a specific gene; may be located close to, or far from, the particular gene.

enzyme Molecule, protein or RNA, that catalyzes a particular chemical reaction.

engineering material Material that can be machined, cut, drilled, sawed, etc.; must have enough dimensional stability to allow these actions to be carried out on them.

eukaryote Unicellular or multicellular organism with cells having a membrane-bounded nucleus, several chromosomes, and internal organelles.

exon Segment of a eukaryotic gene that encodes a portion of the final product of the gene; part that remains after posttranscriptonal processing and is transcribed into a protein or incorporated into the structure of an RNA. See also **intron**.

fibrillar protein Hairlike, insoluble, intermolecularly hydrogen-bonded protein.

fibrils Threadlike strands or bundles of fibers.

gene Chromosomal segment that codes for a single functional polypeptide or RNA chain.

gene expression Transcription, and in proteins, translation, giving the product of a gene; a gene that is expressed within its biological product is present and active.

gene splicing Enzymatic attachment of one gene or part of a gene to another.

genetic code Set of triplet code words in DNA or mRNA coding for the specific amino acids of proteins.

genetic information Information contained in a sequence of nucleotide bases in chromosomal DNA or RNA.

genetic map Diagram showing the relative sequence and position of specific genes within a chromosome.

genome All of the genetic information encoded in a cell or virus.

genotype Genetic makeup of an organism as distinct from its physical characteristics.

globular proteins Proteins with an overall globular structure formed from contributions of secondary structures including sheets and helices.

glycine Simplest and only nonchiral alpha-amino acid.

immune response Ability of a vertebrate to create antibodies to an antigen, a molecule typically a macromolecule, foreign to the host.

inducer Signal molecule that, when attached to a regulatory protein, produces an increased expression of a specific gene.

intron Most genes are divided into two coding regins: one called exons or coding regions and the other called introns or noncoding regions.

in vitro Literally means "in glass," but today means outside the normal biological environment.

in vivo Means "in life" and generally within the normal biological environment.

isoelectric point pH at which an amino acid does not migrate to either the positive or negative pole in a cell.

ketatin Fibrillar protein.

latex Stable dispersion of polymer particles in water.

myosin Protein present in muscle.

N-terminal amino acid Amino acid with an amino end group.

nucleoside Contains a pentose and base.

nucleotide Contains a phosphate, pentose, and base.

oligosaccharide Low molecular weight polysaccharide.

phenotype The observable, physical characteristics of an organism.

plasmid Extrachromosomal, independently replicating, small circular DNA molecule often used in genetic engineering.

polynucleotide Nucleic acid.

polypeptide Protein; often used for low molecular weight proteins.

primer Oligomeric molecule to which an enzyme adds additional monomeric subunits.

probe Labeled fragment of a nucleic acid containing a nucleotide sequence complementary to a gene or genomic sequence that one wants to detect.

prokaryotic cell Bacteria single-celled organism with a single chromosome, no nuclear envelope and no membrane-bounded organelles.

primary structure Term used to describe the primary configuration present in a protein chain.

prosthetic group Nonprotenious group conjugated (connected) to a protein.

protein Polyamide in which the building blocks are alpha-amino acids joined by peptide (amide) linkages.

purine base Compounds consisting of two fused heterocyclic rings: a pyrimidine and an imidazole ring; essential part of nucleic acids.

pyrimidine 1,3-diazine; essential part of nucleic acids.

recombination Enzymatic process whereby the linear arrangement of nucleic acid sequences in a chromosome is altered by cleavage and rejoining.

recycling codes Designations that allow easy, quick identification of a number of plastics used in the manufacture of containers.

replication Term used to describe duplication such as the duplication of DNA.

repressor Molecule, protein, that binds to the regulatory sequence or operator for a gene, blocking its transcription.

ribosomal RNA (rRNA) Class of RNA that serves as components of ribosomes.

ribosome Very large complex of rRNAs and proteins; site of protein synthesis.

ribonucleic acid (RNA) Nucleic acid in which ribose units are present; essential units of life and replication.

secondary structure Term used to describe the conformation of a protein molecule such as a helix.

silent mutation Mutation in a gene that causes no delectable change in the biological functioning of the gene.

somatic cells All body cells except germ-line cells, which develop into gametes, i.e., egg or sperm cells.

sticky ends Two DNA ends in the same or different DNA with short overhanging single-stranded segments that are complementary to one another helping to join the two sites.

structural gene Gene coding for a protein or RNA as distinct from regulatory genes.

template Pattern or surface upon which mirror-image replication can occur.

tertiary structure Term used to describe the shape or folding of a protein.

transcription Enzymatic process where genetic information contained in one strand of DNA is employed to make a complementary sequence of bases in an mRNA.

transfer RNA (tRNA) Class of RNAs each of which combines covalently with a specific amino acid as the initial step in protein synthesis.

translation Process where the genetic information present in mRNA specifies the sequence of amino acids within a protein synthesis.

transposons Segments of DNA, found in almost all cells, that move or “hop” from one place on a chromosome to another on the same or different chromosome.

transposition Movement of one gene or set of genes forms one site in the genome to another site.

transcription Term used to describe the transfer of information from DNA to RNA.

translation Term used to describe the transfer of information from RNA to protein synthesis.

virus Self-replicating nucleic acid–protein complex that requires an intact host cell for replication; its genome can be either DNA or RNA.

zwitterion Dipolar ion of an amino acid.

EXERCISES

1. Define a protein in polymer science language.
2. Which alpha-amino acid does not belong to the L-series of amino acids?
3. To which pole will an amino acid migrate at a pH above its isoelectric point?
4. Why is collagen stronger than albumin?
5. What are the requirements for a strong fiber?
6. Which protein would be more apt to be present in a helical conformation: (a) a linear polyamide with small pendant groups or (b) a linear polyamide with bulky pendant groups?
7. What is the difference between the molecular weight of (a) ribose and (b) deoxyribose?
8. What is the repeating unit in the polymer DNA?
9. Which is more acidic: (a) a nucleoside or (b) a nucleotide?
10. What base found in DNA is not present in RNA?
11. Why would you predict helical conformations for RNA and DNA?
12. If the sequence of one chain of a double helix of DNA is ATTACGTCAT, what is the sequence of the adjacent chain?
13. Why is it essential to have trinucleotides rather than dinucleotides as codons for directing protein synthesis?
14. Why is *E. coli* most often used in gene splicing?
15. A protein that is rich in glutamic acid and aspartic acid will be rich in what kind of functional groups present as substituents on the alpha-carbon? Will it be attracted, in electrophoresis, to the positive or negative side? What is this kind of protein polymer called?
16. The inclusion of which amino acids into proteins is responsible for the sulfur found in coal? What is the consequence of the presence of this sulfur?
17. Which of the amino acids contribute to the formation of nitrogen oxides? What is the consequence of the presence of this nitrogen to our atmospheric air?
18. What is the general shape of our enzymes? Why do they take this shape? What are they composed of?
19. What are essential amino acids?
20. Sulfur is contained in some amino acids. What else is sulfur utilized for in our bodies?
21. Since much of a protein is not active and is at times referred to as junk, why is it there?
22. Describe briefly the typical flow of biological information.
23. What role do "chaperonins" play in protein formation?
24. Why are the active sites of proteins found either as a cleft in the macromolecule or shallow depression on its surface and not thrust out where there is little hindrance for entry of the molecules?
25. Select a particular disease or illness and using the web find out what is known about its molecular biology including gene location.
26. What is the probability of a match if three tests were positive with the following probabilities: 1 in 100; 1 in 1000, and 1 in 250?

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11 Organometallic and Inorganic–Organic Polymers

11.1 INTRODUCTION

Classical polymer chemistry emphasizes materials derived from about a dozen elements (including C, H, O, N, S, P, Cl, and F). Chapters 11 and 12 deal with polymers containing additional elements. The present chapter focuses on inorganic and metal-containing polymers containing organic units.

Elements such as silicon, sulfur, and phosphorus catenate similar to the way carbon does, but such catenation generally does not lead to (homo) chains with high degrees of polymerization. Further, such products might be expected to offer lower thermal stabilities and possibly lower strengths than carbon-based polymers since their bond energies are generally lower (Table 11.1). The alternative of using heteroatomed backbones is attractive since the resultant products can exhibit greater bond energies (Table 11.1).

One common misconception concerns the type of bonding that can occur between inorganic and organic atoms. With the exception of the clearly ionic bonding, many of the inorganic–organic bonding is of the same general nature as that present in organic compounds. The percentage contribution of the organic–inorganic bonding due to covalent contributions is typically well within that found in organic acids, alcohols, and thio and nitro moieties (e.g., the usual limits are about 5% ionic character for the B–C bond to 55% ionic for the Sn–O and both are clearly directional bonding in character). Thus, the same spacial, geometrical rules apply to these polymers as to the more classical polymers such as PE, PS, nylons, polyesters, and PP. The exception is the ionomers where the metals are bonded through ionic bonding to the oxygen atoms.

The number of potential inorganic–organic polymers is great. The inorganic portions can exist as oxides and salts in different oxidation states, different geometries, etc. The importance of these inorganic–organic polymers can be appreciated by considering the following. First, photosynthesis, the conversion of carbon dioxide and water to sugars by sunlight, is based on a metal-containing polymer—chlorophyll. Also, a number of critical enzymes, such as hemoglobin, contain a metal site as the key site for activity (Section 16.7). Second, the inorganic–organic polymers produced thus far exhibit a wide range of properties not common to most organic polymers, including electrical conductivity, specific catalytic operations, wide operating temperatures, greater strengths, and greater thermal stabilities (Table 11.2). Third, inorganic–organic polymers form the basis for many insulators and building materials. Fourth, inorganic elements are present in high abundances in the earth's crust (Table 11.3).

The topic of metal- and metalloid-containing polymers can be divided by many means. Here, the topic will be divided according to the type of reaction employed to incorporate the inorganic atom into the polymer chain. While many other types of reactions have been employed to produce metal- and metalloid-containing polymers including redox, coupling,

TABLE 11.1
General Magnitude of Bonds

Bond	General Bond Energy (kJ/mol)	Ionic Character[a] (%)	Bond	General Bond Energy (kJ/mol)	Ionic Character (%)
Al–O	560	60	P–O	400	40
B–C	360	5	P–S	320	5
B–N	440	20	S–S	240	0
B–O	460	45	Si–Si	220	0
Be–O	500	65	Si–C	300	10
C–C	340	0	Si–N	420	30
C–H	400	5	Si–O	440	50
C–N	300	5	Si–S	240	10
C–O	340	20	Sn–Sn	160	0
C–S	260	5	Sn–O	520	55
P–P	200	0	Ti–O	640	60
P–N	560	20			

[a] Based on Pauling electronegativity values. The percentage of ionic bonding should be less where pi-bonding occurs. Given to nearest 5%.

and ring-opening polymerizations, the present will focus on addition, condensation, and coordination reactions. Emphasis is given to unifying factors.

11.2 INORGANIC REACTION MECHANISMS

Many of the polymerizations and monomer syntheses are simply extensions of known inorganic, organometallic, and organic reactions. The types and language used to describe inorganic–organic reaction mechanisms are more diversified than those employed by classical organic chemists.

The majority of inorganic reactions can be placed into one of two broad classes: (1) oxidation–reduction (redox) reactions including atom and electron transfer reactions and (2) substitution reactions. Terms such as inner sphere, outer sphere, and photo-related reactions are employed to describe redox reactions. Such reactions are important in the synthesis of polymers and monomers and in the use of metal-containing polymers as catalysts and in applications involving transfer of heat, electricity, and light. They will not be dealt with to any appreciable extent in this chapter.

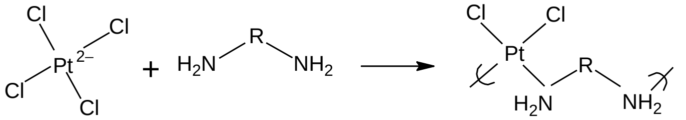
TABLE 11.2
Actual and Potential Applications for Organometallic and Metalloid Polymers

Biological	Anticancer, antiviral, treatment of arthritis, antibacterial, antifungal, antifouling, treatment of Cooley's anemia, algicides, molluscicides, contrast agents, radiology agents
Electrical/optical	Nonlinear optics, lithography, conductors, semiconductors, piezoelectronic, pyroelectronic, solar energy conversion, electrodes, computer chip circuitry
Analytical, catalytic, building	UV absorption, smart materials, nanocomposites, laser, sealants, paints, caulks, lubricants, gaskets

TABLE 11.3
Relative Abundances of Selected Elements in the Earth's Upper (10 miles) Crust

Element	Weight %	Element	Weight %
Oxygen	50	Titanium	0.4
Silicon	26	Fluorine	0.3
Aluminum	7.3	Chlorine	0.2
Iron	4.2	Carbon	0.2
Calcium	3.2	Sulfur	0.1
Sodium	2.4	Phosphorus	0.1
Potassium	2.3	Barium	0.1
Magnesium	2.1	Manganese	0.1
Hydrogen	0.4		

Terms such as liability, inertness, ligand, associative, interchange, and dissociative are important when discussing substitution reactions. The ligand is simply (typically) the Lewis base that is substituted for and is also the agent of substitution. Thus, in the reaction between tetrachloroplatinate and diamines forming the anticancer and antiviral platinum II polyamines, the chloride is the leaving group or departing ligand, while the amine-functional group is the ligand that is the agent of substitution:



(11.1)

There is a difference between the thermodynamic terms “stable and unstable” and the kinetic terms “labile and inert.” Furthermore, the differences between the terms stable and unstable, and labile and inert are relative. Thus, $Ni(CN)_4^{-2}$ and $Cr(CN)_6^{-3}$ are both thermodynamically stable in aqueous solution, yet kinetically the rate of exchange of radiocarbon-labeled cyanide is quite different. The half-life for exchange is about 30 sec for the nickel complex and 1 month for the chromium complex. Taube has suggested that those complexes that react completely within about 60 sec at 25°C be considered labile, while those that take a longer time be called inert. This rule of thumb is often given in texts, but is not in general use in the literature. Actual rates and conditions are superior tools for the evaluation of the kinetic and thermodynamic stability of complexes.

The term “D mechanism” (dissociation) is loosely comparable to S_N 1-type reaction mechanisms, but it does not imply an observed rate law. Here, a transient intermediate is assumed to live long enough to be able to differentiate between various ligands, including the one just lost, and between solvent molecules. Thus, the overall rate expression may be dependent on the nature of LL′, solvents, or some combination as pictured below where S is the solvent, L is the leaving ligand, and L′ is the incoming ligand.

$$ML_4 \leftrightarrows ML_3 + L \tag{11.2}$$

$$ML_3 + L' \rightarrow ML_3L' \tag{11.3}$$

$$ML_3 + S \leftrightarrows ML_3S \tag{11.4}$$

In the I_d mechanism, dissociative interchange, the transition state involves extensive elongation of the M–L bond, but not rupture.

$$ML_4 + L' \rightarrow [L\cdot\cdot ML_3\cdot\cdot L'] \rightarrow ML_3L' + L \tag{11.5}$$

The ML_3L' species is often called an outer sphere complex, or, if ML_4 is a cation and L an anion, the couple is called an ion pair.

For the I_a mechanism, associative interchange, the interaction between M and L′ is more advanced in the transition state than in the case of the I_d. The M–L′ bonding is important in defining the activated complex. Both of these interchange mechanisms are loosely connected to the S_N 2-type mechanism.

For the A mechanism, associative, there is a fully formed intermediate complex ML_4L', which then dissociates, being roughly analogous to the E_1-type reaction mechanism.

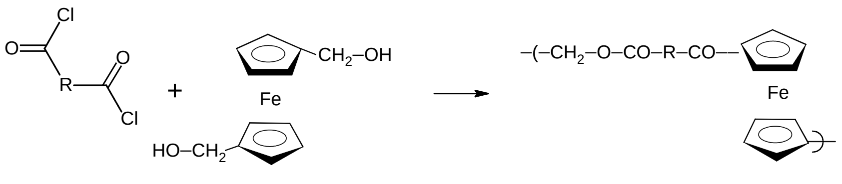
It is important to remember that the same electronic, steric, mechanistic, kinetic, and thermodynamic factors that operate in regard to smaller molecules are in operation during a polymerization process.

11.3 CONDENSATION ORGANOMETALLIC POLYMERS

Condensation reactions exhibit several characteristics such as (typically) expulsion of a smaller molecule on reaction leading to a repeat unit containing fewer atoms than the sum of the two reactants, and most reactions can be considered in terms of polar (Lewis acid–base; nucleophilic–electrophilic) mechanisms. The reaction site can be at the metal atom (that is adjacent to the atom)

$$R_2MX_2 + H_2N-R-NH_2 \rightarrow -(-MR_2-NH-R-NH-)- + HX \tag{11.6}$$

or it can be somewhat removed from the metal site.



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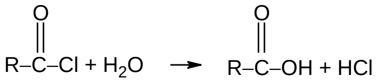
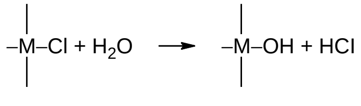
Research involving condensation organometallic polymers was catalyzed by the observation that many organometallic halides possess a high degree of covalent character within their composite structure and that they can behave as organic acid chlorides in many reactions, such as hydrolysis

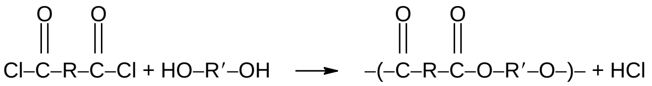


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2O \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HCl \tag{11.8}$$

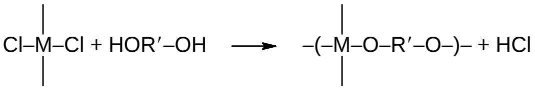


$$-\overset{|}{\underset{|}{M}}-Cl + H_2O \longrightarrow -\overset{|}{\underset{|}{M}}-OH + HCl \tag{11.9}$$

and polyesterfication.



$$Cl{-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}Cl + HO{-}R'{-}OH \longrightarrow {-}({-}\overset{O}{\overset{\|}{C}}{-}R{-}\overset{O}{\overset{\|}{C}}{-}O{-}R'{-}O{-}){-} + HCl \qquad (11.10)$$



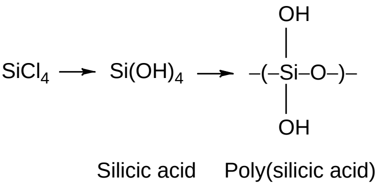
$$Cl{-}\underset{|}{\overset{|}{M}}{-}Cl + HOR'{-}OH \longrightarrow {-}({-}\underset{|}{\overset{|}{M}}{-}O{-}R'{-}O{-}){-} + HCl \qquad (11.11)$$

Thus, many of the metal-containing polycondensations can be considered extensions of organic polyesterfications, polyaminations, etc.

11.3.1 POLYSILOXANES

The most important organometalloid polymers are the polysiloxanes based on the siloxane Si–O linkage found in glass and quartz (Chapter 12). The polysiloxanes were incorrectly named silicones by Kipping in the 1920s, but this name continues to be widely used.

The production of silicate glass is believed to be a transcondensation of the siloxane linkages in silica. A comparable poly(silicic acid) is produced when silicon tetrachloride is hydrolyzed.



$$SiCl_4 \longrightarrow Si(OH)_4 \longrightarrow {-}({-}\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}{-}O{-}){-} \qquad (11.12)$$

Silicic acid Poly(silicic acid)

The poly(silicic acid) further condenses producing a cross-linked gel. This cross-linking can be prevented by replacing the hydroxyl groups in silicic acid with alkyl groups. Ladenburg prepared the first silicone polymer in the 19th century by the hydrolysis of diethyldiethoxysilane. Kipping, in the early 1940s, recognized that these siloxanes could also be produced by the hydrolysis of dialkyldichlorosilanes giving a poly(silicic acid)-like structure where the hydroxyl groups are replaced by alkyl groups.

In 1945, Rochow discovered that a silicon–copper alloy reacted with organic chlorides forming a new class of compounds called organosilanes.

$$CH_3Cl + Si(Cu) \longrightarrow (CH_3)_2SiCl_2 + Cu \qquad (11.13)$$

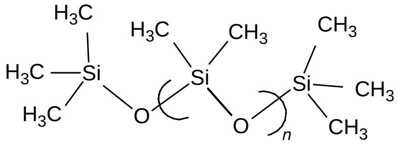
Dimethyldichlorosilane

These compounds react with water forming dihydroxylsilanes,

$$(CH_3)_2SiCl_2 + H_2O \longrightarrow (CH_3)_2Si(OH)_2 + HCl \qquad (11.14)$$

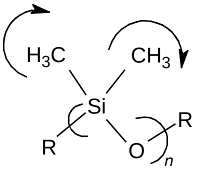
and eventually dimeric, oligomeric, and finally polysiloxanes.

Polysiloxanes, also called silicones, are characterized by combinations of chemical, mechanical, and electrical properties which taken together are not common to any other commercially available class of polymers. They exhibit relatively high thermal and oxidative stability, low power loss, high dielectric strength, and unique rheological properties, and are relatively inert to most of the ionic reagents. Almost all of the commercially utilized siloxanes are based on polydimethylsiloxane with trimethylsiloxy end groups. They have the widest use temperature range for commercial polymers, suitable for outdoor applications from the winter of Nome, Alaska to the summer of south Florida (about −80°F to 100°F; –60°C to 40°C). The first footprints on the moon were made with polysiloxane elastomeric boots.



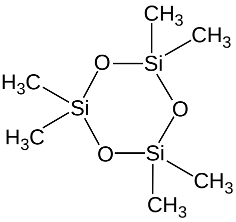
(11.15)

The reason for the low-temperature flexibility is a very low T_g, about −120°C, which is the result of the methyl groups attached to the silicon atoms being free to rotate causing the oxygen and other surrounding atoms to "stay away" creating a flexible chain.

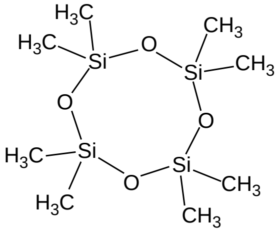


(11.16)

Polysiloxanes degrade by an unzipping mechanism forming six- and eight-membered rings. They also form the same rings when polymerized forming what is referred to as "wasted loops" because they must be removed before the polysiloxane is useful. This tendency to form six- and eight-membered rings is based on the good stability of such siloxane rings.



Six-membered loop (11.17)



Eight-membered loop (11.18)

The viscosity or resistance to flow increases as the number of repeat units increases, but physical properties, such as surface tension and density, remain about the same after a DP of about 25. The liquid surface tension is lower than the critical surface tension of wetting, resulting in the polymer spreading over its own absorbed films. The forces of attraction between polysiloxane films are low resulting in the formation of porous films that allow oxygen and nitrogen to readily pass though, but not water. Thus, semipermeable membranes, films, have been developed that allow divers to "breath air under water" for short periods.

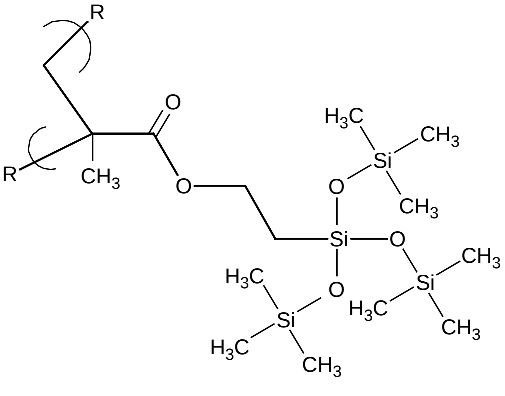
As noted above, viscosity increases with DP allowing many of the uses to be grouped according to chain length. Low-viscosity fluids with DPs of 2–30 are used as antifoams and in the flow control of coatings applications. These applications are the direct consequence of the low attractions between polysiloxane chains which, in turn, is responsible for their low surface tension. Thus, they encourage a coatings material to flow across the surface-filling voids, corners, and crevices. Their good thermal conductivity and fluidicity at low temperatures allow their use as low-temperature heat exchangers and in low-temperature baths and thermostats.

Viscous fluids correspond to a DP range of about 50–400. These materials are employed as mold release agents for glass, plastic, and rubber parts. They are good lubricants for most metal to nonmetal contacts. They are used as dielectric fluids (liquids) in a variety of electrical applications including transformers and capacitors: (1) as hydraulic fluids in vacuum and hydraulic pumps; (2) in delicate timing and photographic devices; (3) as antifoam agents; (4) components in protective hand creams; (5) toners in photocopiers; (6) in oil formulations when mixed with thickeners; and (7) in inertial guidance systems. High-performance greases are formed by mixing the polysiloxane fluids with polytetrafluoroethylene or molybdenum disulfide. Brake fluids are formulated from polydimethylsiloxane fluids with DPs of about 50. High-viscosity fluids with DPs about 700–6000 are used as damping fluids for weighting meters at truck stops. They act as liquid springs in shock absorbers. The longer chained fluids are used as impact modifiers for thermoplastic resins and as stationary phases in gas chromatography.

As with the alkanes, even longer chains form the basis for solid polysiloxanes that, according to design, can be classified as thermoplastics, engineering thermoplastics, elastomers, and when cross-linked as thermosets. Solid polysiloxanes are used in a variety of applications including as sealants, thermostripping, caulking, dampening, O-rings, and window gaskets. Weather stripping on cooling units, trucks, and automobiles is often made of polysiloxanes.

Room temperature-vulcanizing (RTV), silicon rubbers make use of the room temperature reaction of certain groups that can be placed on polydimethylsiloxanes, which react with water. When exposed to water, such as that normally present in the atmosphere, cross-links are formed creating an elastomeric product.

The first contact lenses were based on poly(methyl methacrylate). Although they could be polished and machined, they did not permit gas exchange and were rigid. By early 1970s, these were replaced by soft contact lenses containing cross-linked poly(2-hydroxyethyl methacrylate) (HEMA). These so-called disposable lenses do permit gas exchange. More recently, Salamone and coworkers developed contact lenses based on the presence of siloxane units. Polysiloxanes have good gas permeability. These polymers are referred to as Tris materials and are generally copolymers containing units as shown in the following structure.



(11.19)

Polysiloxanes are widely employed as biomaterials. Artificial skin can be fabricated from a bilayer fabricated from a cross-linked mixture of bovine hide, collagen, and chondroitin sulfate derived from shark cartilage with a thin top layer of polysiloxane. The polysiloxane acts as a moisture and oxygen-permeable support and protects the lower layer from the "outer world." A number of drug delivery systems use polysiloxanes because of the flexibility and porous nature of the material.

The first Silly Putty™ was made over 50 years ago by mixing together silicone oil with boric acid. The original formula has changed little though colorants have been added giving the material brighter colors and some the ability to "glow-in-the-dark." Silly Putty is a dilatant material (Chapter 14) which means that it has an inverse thioxotropy (a thioxotropic liquid is one whose viscosity decreases with time). In essence, the resistance of flow increases faster than the increases in the rate of low. Thus, under short interaction times (Chapter 14) it behaves as a solid where the various molecular components resist ready movement, acting as a solid and under sharp impact, like hitting it with a hammer or rapidly "snapping" it, it will act as a brittle material. Under a relatively long interaction time the molecular chains are able to yield and the material acts as a liquid. Under moderate interaction times there is segmental movement and the material acts as a rubber.

James Wright, a researcher for General Electric, first discovered Silly Putty in 1943 during a search for synthetic rubber during World War II. Initially no practical use was found. By 1949, it was found in a local toy store as a novelty item. Despite its good sales, the store dropped it after 1 year. The next year, Peter Hodson began packaging it in the now-familiar plastic egg. Today, it sells for about the same price it did in 1950. Silly Putty sells at a rate of about 6 million eggs, or 90 t, yearly.

11.3.2 ORGANOTIN AND RELATED CONDENSATION POLYMERS

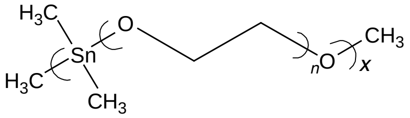
Carraher and coworkers have produced a wide variety of organometallic condensation polymers based on the Lewis acid–base concept. Polymers have been produced from Lewis bases containing amine, alcohol, acid, thiol, and related units including a number of drugs such as ciprofloxacin and acyclovir. Lewis acids containing such metals and metalloids as Ti, Zr, Hf, V, Nb, Si, Ge, Sn, Pb, As, Sb, Bi, Mn, Ru, P, Co, Fe, and S have been employed. These compounds have potential uses in the biomedical arena as antifungal, antibacterial, anticancer, Parkinson's treatment, and antiviral drugs. These polymers show promise in a wide variety of other areas including electrical, catalytic, and solar energy conversion. Polymers referred to as polydyes, because of the presence of dye moieties in the polymer backbones, have impregnated paper products, plastics, rubber, fibers, coatings, and caulks giving the impregnated material color (often) added biological resistance, and special photo properties. Some of the polymers, including the metallocene-containing products, show the ability to control laser radiation. Depending on the range of radiation, laser energy can be focused allowing the material to be cut readily or it can be dispersed imparting to the material containing the polymer added stability toward the radiation.

A number of these polymers exhibit a phenomenon called "anomalous fiber formation," reminiscent of "metallic whiskers."

There are more organometallic compounds containing tin than for any other metal. Further, the volume of organotin compounds employed commercially is greater than for any other organometallic. Worldwide, the production of organotin compounds, about 120 million pounds yearly, accounts for about 7% of the entire tin usage. Tin has been included into polymers for a variety of reasons. The two major reasons are its biological activities known for about 100 years and its ability to help stabilize PVC. The second behavior accounts for about 70% by weight of the organotin compounds used commercially. These materials are employed to improve the heat stability of PVC as it is formed into piping. Today, because polymers leach much slower than small molecules, organotin polymers initially synthesized by Carraher and coworkers are being used as heat stabilizers in PVC piping.

The emphasis on organotin-containing polymers is the results of several factors. The first one involves the early discovery of their biological activity and more recently that these organotin compounds generally degrade to nontoxic inorganic compounds so that they are "environmentally friendly." The second reason is the commercial availability of a wide variety of organotin compounds that are suitable as monomers. Thirdly, because of the biological activity of organotin compounds they were found to inhibit the growth of desirable species, in particular, in aquatic surroundings. This brought about federal laws that prohibited the use of leachable, monomeric organotin compounds in a variety of coatings and protective applications. The result was a move to polymeric materials that did not suffer the same leachability and which were allowed by law.

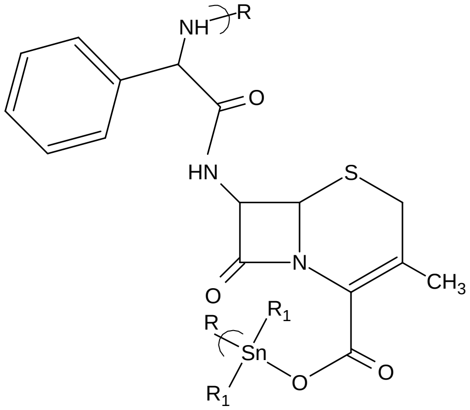
Much of the recent activity with organotin compounds, including polymers, involves their use to inhibit a wide variety of microorganisms at low concentrations. These microorganisms include a variety of cancers, bacteria, yeasts, and viruses. Carraher, Roner, Barot, and coworkers have found that some simple organotin polyethers based on hydroxyl-terminated poly(ethylene glycols) inhibit a wide variety of cancers including the ones associated with bone, lung, prostate, breast, and colon cancers.



(11.20)

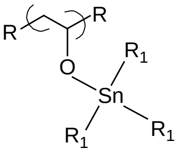
Two measures are typically employed to measure the ability of cancer cell growth. The first is the concentration needed to inhibit 50% growth of the cell line, GI_{50}. Some of these polymers have GI_{50} values well below that of cisplatin, the most widely used anticancer drug. The second measure is the chemotherapeutic index, CI, which is the concentration of the compound that inhibits the growth of the tumor cell by 50% divided by the concentration of the compound that inhibits the growth of the normal cell by 50%. Larger values are desired since they indicate that a larger concentration is required to inhibit the healthy cells in comparison with the cancer cells or stated in another way, larger values indicate some preference for inhibiting the cancer cells in preference to the normal cells. Some of these polymers have CI values in hundreds allowing healthy cells to reproduce at concentrations where cancer cell lines are inhibited. Of additional interest is that some of these organotin polymers are water soluble allowing for medical applications utilizing the material in simple pills.

A wide variety of organotin compounds developed by Carraher, Sabir, Roner, and others based on known antiviral drugs such as acyclovir and known antibacterial agents such as ciprofloxacin, norfloxacin, cephalexin (structure 11.21), and ampicillin inhibit a wide variety of viruses including ones responsible for many of the common colds, chicken pox, small pox, shingles, and herpes simplex.



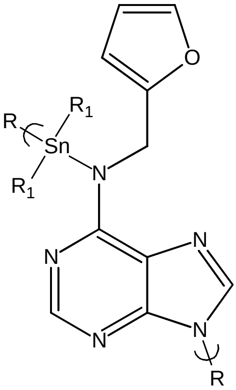
(11.21)

Some of the organotin-containing polymers inhibit *Candias albicans*, the yeast responsible for infections in humans better than commercially available applications while leaving the normal flora unharmed. Others inhibit methicillin-resistant *Staphylococcus aureus* (MRSA) (structure 11.22), preferentially.



(11.22)

Organotin polyamines containing the plant growth hormone kinetin (Equation 11.23) increase the germination of damaged seeds and thus may help in providing food in Third World countries. It also increases the germination rate of saw grass seed from about 0% to over 50% and is an important agent in replacing the "sea of grass" (actually saw grass) in the Everglades.



(11.23)

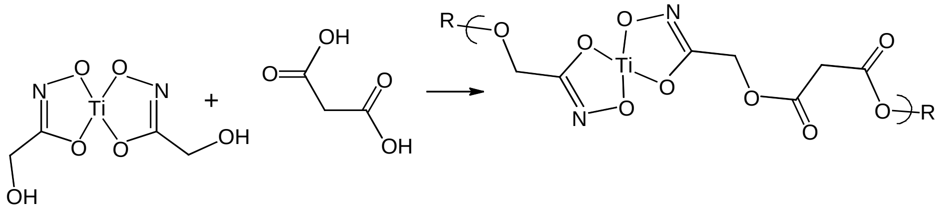
11.4 COORDINATION POLYMERS

Coordination polymers have served humankind since before recorded history. The tanning of leather and generation of selected colored pigments depend on the coordination of metal ions. A number of biological agents, including plants and animals, owe their existence to coordinated polymers such as hemoglobin. Many of these coordination polymers have unknown and/or irregular structures.

The drive for the synthesis and characterization of synthetic coordination polymers was catalyzed by work supported and conducted by the U.S. Air Force in a search for materials which exhibited high thermal stabilities. Attempts to prepare highly stable, tractable coordination polymers were disappointing. Typically, only oligomeric products were formed and the monomeric versions were often more stable than the polymeric versions.

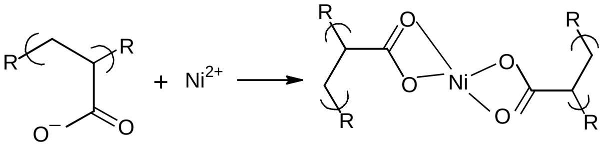
Bailar listed a number of principles that can be considered in designing coordination polymers as follows: (1) Little flexibility is imparted by the metal ion or within its immediate environment; thus, flexibility must arise from the organic moiety. Flexibility increases as the covalent nature of metal–ligand bond increases. (2) Metal ions only stabilize ligands in their immediate vicinity; thus, the chelates should be strong and close to the metal ions. (3) Thermal, oxidative, and hydrolytic stabilities are not directly related; polymers must be designed specifically for the properties desired. (4) Metal–ligand bonds have sufficient ionic character to permit them to rearrange more readily than typical "organic bonds." (5) Polymer structure (e.g., square planar, octahedral, linear, and network) is dictated by the coordination number and stereochemistry of the metal ion or chelating agent. (6) Employed solvents should not form strong complexes with the metal or chelating agent or they will be incorporated into the polymer structure and/or prevent reaction.

Coordination polymers can be prepared by a number of routes, among which the three most common being (1) preformed coordination metal complexes polymerized through functional groups where the actual polymer-forming step may be a condensation or addition reaction;



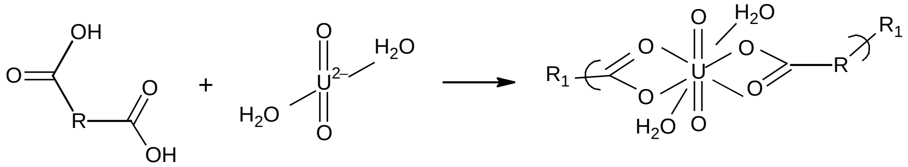
(11.24)

(2) reaction with polymer-containing ligands; or



(11.25)

(3) polymer formation through chelation



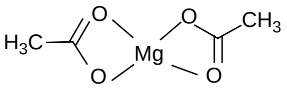
(11.26)

Carraher and coworkers employed the last two processes to recover the uranyl ion. The uranyl ion is the natural water-soluble form of uranium oxide. It is also toxic, acting as a heavy metal toxin. Through the use of salts of dicarboxylic acids and poly(acrylic acid), the uranyl ion was removed to 10^{-5} M with the resulting product much less toxic and convertible to uranium oxide by heating.

Many of the organometallic polymers are semiconductors with bulk resistivities in the range of 10^3–10^{10} Ω-cm suitable for specific semiconductor use. Further, some exhibit interesting photo properties.

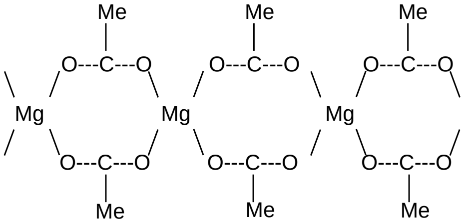
Simple chelation polymers are all around us, but they are not always recognized as such. During winter, the north experiences freezing temperatures and associated ice. Sodium chloride and calcium chloride are the most widely used freezing point-lowering agents. They are inexpensive and readily available. On the negative side, they adversely affect surrounding plant life and must be reapplied generally after each rain–ice cycle.

Recently, magnesium acetate has been used for application in particularly dangerous sites such as bridges. The acetate can be either internally bridged (structure 11.27), where it is not polymeric,



(11.27)

or it can be bridged forming a complex linear polymeric material.

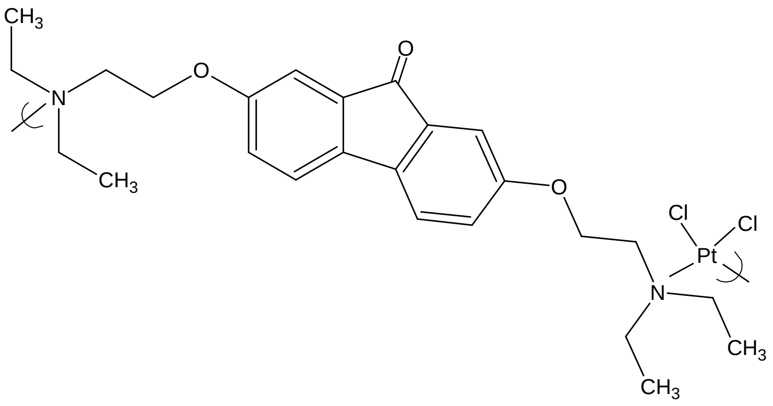


(11.28)

Hellmuth believes that the polymeric material forms. If magnesium acetate is simply the internally chelated material, then it should be quickly washed away. The combination of calcium and magnesium acetates is known as CMA. CMA is more expensive than sodium chloride or calcium chloride, but it does not damage plant life and it has a much longer effective life. The polymer seeks the cracks and crevices in and around the pavement and remains until needed again to lower the freezing point of water. Often, one application of CMA is sufficient for a winter season.

11.4.1 PLATINUM-CONTAINING POLYMERS

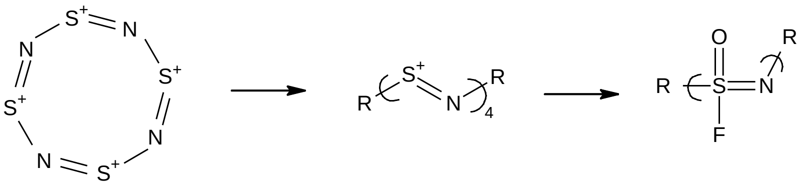
In 1964, Rosenberg and coworkers found that bacteria failed to divide but continued to grow. After much effort they found that the cause of this anomalous growth was a broken electrode and eventually identified the chemical as *cis*-dichlorodiamineplatinum II. This compound is now licensed under the name Platinol and is also known as cisplatin. Cisplatin is the most widely used anticancer drug. Carraher, Rosenberg, Allcock, Neuse, and others have reduced the toxic effects of cisplatin through placement of the platinum moiety into various coordination platinum polymers. Some of these polymers inhibit various cancer growths with much less toxic effects. Carraher and coworkers also found that many of these are also very active antiviral agents and some are able to prevent the onset of virally related juvenile diabetes in test animals. Recently, Carraher and Roner found that cisplatin derivatives formed from the reaction of tetrachloroplatinum II and methotrexate inhibited a wide range of viruses in the nanograms/milliliter range. Similar results were found for the analogous product formed from reaction with tilorone.



(11.29)

11.5 ADDITION POLYMERS

Sulfur nitride polymers [–(–S = N–)–], which have optical and electrical properties similar to those of metals, were first synthesized in 1910. These crystalline polymers, which are superconducive at 0.25 K, may be produced at room temperature using the solid state polymerization of the dimer (S_2N_2). A dark blue-black amorphous paramagnetic form of poly(sulfur nitride) (structure 11.30) is produced by quenching the gaseous tetramer in liquid nitrogen. The polymer is produced on heating the tetramer to about 300°C.

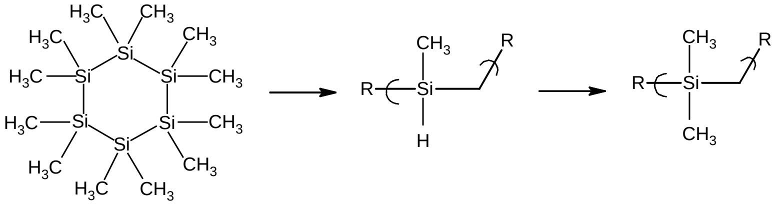


(11.30)

Much of the interest in the polysilanes, polygermanes, and polystannanes involves their sigma delocalization and their sigma–pi delocalization when coupled with arenes or acetylenes. This is not unexpected since silicon exists as a covalent network similar to diamond. In exhibiting electrical conductivity, germanium and tin show more typical "metallic" bonding. Some polystannanes have been referred to as "molecular metals."

Because of the interesting electronic and physical properties of polysilanes, a number of potential uses have been suggested including precursors of beta–SiC fibers, impregnation of ceramics, polymerization initiators, photoconductors for electrophotography, contrast enhancement layers in photolithography, deep ultraviolet (UV)-sensitive photoresists, nonlinear optical (NLO) materials, and self-developing by excimer laser for deep UV exposure. The unusual absorption spectra of polysilanes have indicated potential use in a number of conducting areas.

One area of active interest in ceramics is the formation of ceramics that may contain some fiber structure. Currently, ceramics, while very strong, are very brittle. Introduction of thermally stable fiber-like materials might allow the ceramics some flexibility before cleavage. Such materials might be considered as ceramic composites, where the matrix is the ceramic portion and the fibers are thermally stable. Introduction of fibers during the ceramic-forming step is a major obstacle that must be overcome. Carbon fibers have been investigated as having other high-temperature materials such as the polysilanes. Polysilanes are formed from the six-membered ring through extended heating at 400°C.



(11.31)

Further heating gives silicon carbide.

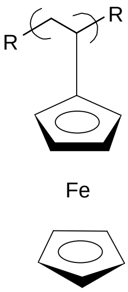
Table 11.4 lists a number of nonoxide ceramics that have been produced from the pyrolysis of polymers.

TABLE 11.4
Nonoxide Ceramics Produced from the Pyrolysis of Polymeric Materials

Polymer(s)	Resultant Ceramic
Poly(phosphonitric chlorides)	PN
Polysilanes, polycarbosilanes	SiC
Polyphenylborazole	BN
Polytitanocarbosilanes	Si–Ti–C
Polysilazanes	Si_3N_4, Si–C–N

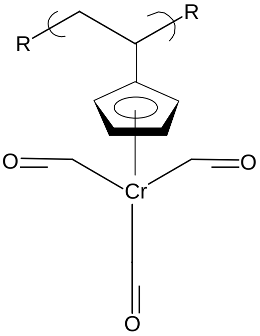
11.5.1 FERROCENE-CONTAINING AND RELATED POLYMERS

The landmark discovery of ferrocene by Kealy and Paulson in 1951 marked the beginning of modern organometallic chemistry. The first organometallic addition polymer was polyvinylferrocene synthesized by Arimoto and Haven in 1955. While polyvinylferrocene (structure 11.32) had been synthesized it was about another decade until the work of Pittman, Hayes, and George, and Baldwin and Johnson allowed a launch of ferrocene-containing polymers.



(11.32)

A large number of vinyl organometallic monomers have been prepared, homopolymerized, and copolymerized with classic vinyl monomers by Pittman and others. These include polymers containing Mo, W, Fe, Cr (structure 11.33), Ir, Ru, Ti (structure 11.34), Rh (structure 11.35), and Co.



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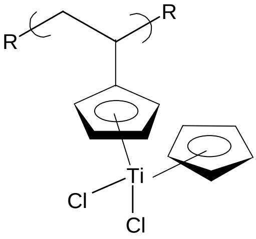

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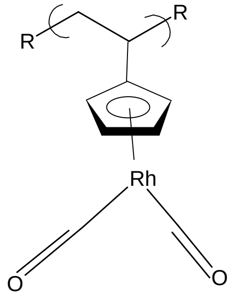
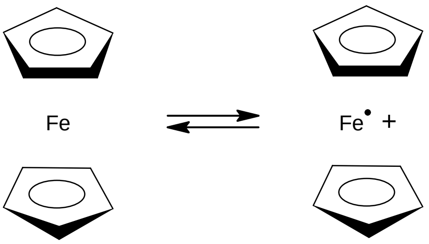


(11.35)

The effect that the presence of the organometallic function exerts in vinyl polymerizations is beginning to be fully understood. A transition metal may be expected, with its various readily available oxidation states and large steric bulk, to exert unusual electronic and steric effects during polymerization. The polymerization of vinyl ferrocene will be employed as an example. Its homopolymerization has been initiated by radical, cationic, coordination, and Ziegler–Natta initiators. Unlike the classic organic monomer styrene, vinylferrocene undergoes oxidation at the iron atom when peroxide initiators are employed. Thus, azo initiators (e.g., AIBN) are typically used. Here, we see one difference between an organic and an organometallic monomer in the presence of peroxide initiators. The stability of the ferricinium ion makes ferrocene readily oxidizable by peroxides, whereas styrene, for example, undergoes polymerization in their presence. Unlike most vinyl monomers, the molecular weight of polyvinylferrocene does not increase with a decrease in initiator concentration because of the unusually high chain-transfer constant for vinylferrocene. Finally, the rate law for vinylferrocene homopolymerization is first order in initiator in benzene. Thus, intramolecular termination occurs. Mossbauer studies support a mechanism involving electron transfer from iron to the growing chain radical giving a zwitterion that terminates polymerization.

The high electron richness of vinylferrocene as a monomer is illustrated in its copolymerization with maleic anhydride, where 1:1 alternation copolymers are formed over a wide range of monomer feed ratios and $r_1r_2 = 0.003$. Subsequently, a large number of detailed copolymerization studies have been undertaken using metal-containing vinyl monomers.

Neuse acted as an early catalyst in the development of metal-containing polymers including the use of ferrocene-containing polymers to fight cancer. One key feature of ferrocene is its ability to donate an electron from a nonbonding high-energy MO resulting in the transformation of a neutral, diamagnetic site to the positive paramagnetic ferricenium ion radical (structure 11.36). This formation occurs within a typical chemical environment and selected biological environments.

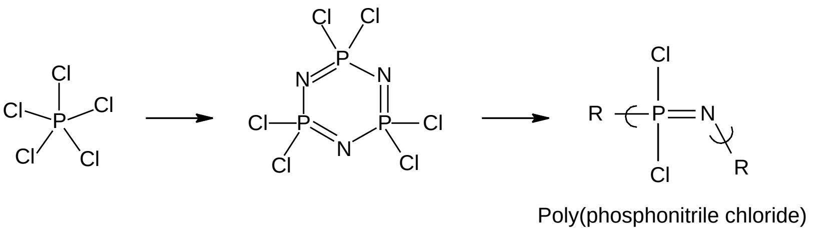


(11.36)

This ferricenium ion radical, as do other free radicals, readily reacts with other free radicals through recombination. Neuse and others have had good results at successfully inhibiting a wide variety of cancers using ferrocene-containing polymers. Often, the employed compounds are elaborately designed with specially designed backbones and employing a ferrocene-containing unit as a tether dangling from the polymer backbone.

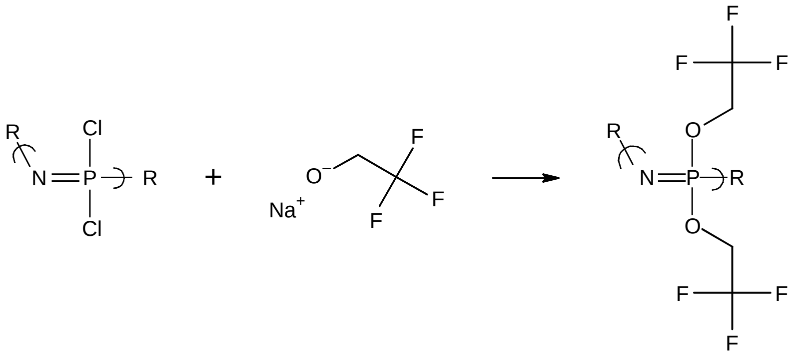
11.5.2 POLYPHOSPHAZENES AND RELATED POLYMERS

Other inorganic and metal-containing polymers have been formed using the addition approach. These include polyphosphazenes, polyphosphonitriles, and poly(sulfur nitride). Phosphonitrilic polymers have been known for many years, but since they lacked resistance to water they were not of interest as commercial polymers. However, when the pendant chlorine groups are replaced by fluorine atoms, amino, alkoxy, or phenoxy groups, these polymers are more resistant to hydrolysis. Allcock and coworkers have pioneered these efforts. Phosphonitrile fluoroelastomers are useful throughout a temperature range of −56°C to 180°C. Phosphazenes are produced by the thermal cleavage of a cyclic trimer obtained from the reaction of phosphorus pentachloride and ammonium chloride.



(11.37)

Amorphous elastomers are obtained when phosphazene is refluxed with nucleophiles, such as sodium trifluoroethoxide or sodium cresylate, and secondary amines. Difunctional reactants such as dihydroxybenzenes (hydroquinone) produce cross-linked phosphazenes.



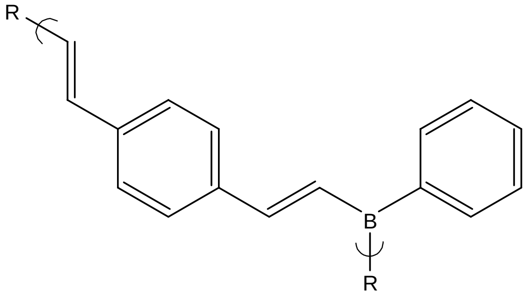
(11.38)

Polyphosphazenes generally exhibit very low T_g values consistent with the barriers to internal rotation being low and indicate the potential of these polymers for elastomer applications. In fact, theoretical calculations based on a rotational isomeric model assuming localized pi-bonding predict the lowest (400 J/mol repeating unit) known polymer barrier to rotation for the skeletal bonds for polydifluorophosphazene. Temperature intervals between T_g and T_m are unusually small and generally fall outside the frequently cited relationship. This behavior may be related to complications in the first-order transition generally found for organosubstituted phosphazenes and not common to other semicrystalline polymers. Two first-order transitions are generally observed for organosubstituted phosphazenes with a temperature interval from about 150°C to 200°C. The lower first-order transition can be detected using distributed control system (DCS), differential thermal analysis (DTA), and thermomechanical analysis (TMA). Examination by optical microscopy reveals that the crystalline structure is not entirely lost, but persists throughout the extended temperature range to a higher temperature transition, which appears to be T_m, the true melting temperature. The nature of this transitional behavior resembles the transformation to a mesomorphic state similar to that observed in nematic liquid crystals. It appears from the relationship between the equilibrium melting temperature (heat and entropy of fusion; $T_m = H_m/S_m$) and the low value of H_m at T_m compared with the lower transition temperature that the upper transition, T_m, is characterized by a very small entropy change. This may be due to an onset of chain motion between the two transitions leading to the small additional gain in conformational entropy at T_m. The lower transition is believed to correspond to the T_g.

Allcock and coworkers have employed polyphosphazenes in a variety of uses including the broad areas of biomedical and electrical applications. From a practical point of view, polyphosphazenes are usually soft, just above the lower transition so that compression molding of films can be carried out. This suggests that the lower transition temperature represents the upper temperature for most useful engineering applications of polyphosphazenes in unmodified forms.

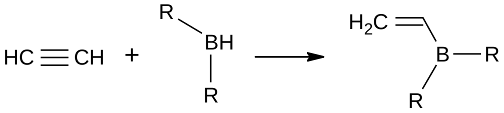
11.5.3 BORON-CONTAINING POLYMERS

Organoboron has been incorporated into polymers employing a variety of techniques. Stock, in the 1920s, first created a boron hydride polymer during his work on boron hydrides. Much of the current interest in boron-containing polymers is a consequence of three factors. First, the presence of a "low-lying" (meaning low energy) vacant "p" orbital allows its use in moving electrons in a conjugated system. This is being taken advantage through the synthesis of various pi-conjugated systems and their use in optical and sensing applications. This includes use in light-emitting diodes (LEDs), NLO systems, energy storage in batteries, and the construction of sensing devices. One such polymer structure is given in the following structure.



(11.39)

These polymers are mainly synthesized employing the hydroboration reaction which is simply the addition of hydrogen from a boron hydride to a double or triple bond.



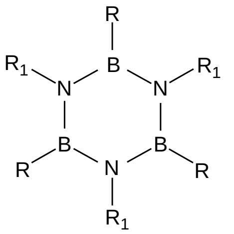
(11.40)

This low-lying vacant p orbital also allows boron-containing polymers to be luminescent again signaling potential optical applications. Many of these luminescent materials are NLO materials.

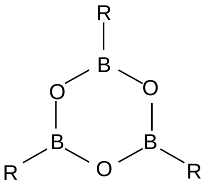
The second reason for interest in boron polymers involves their use as catalysts. While the boron atom can be used as the site of catalytic activity, more effort has been involved in the use of boron-containing materials as blocking and protecting agents, and as cocatalysts. They are increasingly being used in catalytic asymmetric syntheses.

The third reason involves the ability of many boron compounds to form cocoons about objects allowing a ready method for coating wires and fibers. Thus boron-containing polymers and monomers have been employed to form a surface layer of intumescent protective char that acts as a barrier to oxygen protecting the wires and fibers from ready oxidation. These coatings also provide flame retardancy to the coated materials. Recently, boron-containing units have been incorporated into polymers resulting in materials that have added flame resistance through char formation. Somewhat related to this is the use of boron-containing polymers in forming high-strength fibers and whiskers for use in composites. Finally, boron has a high capture ability of neutrons; so effort had gone into using this nuclear characteristic.

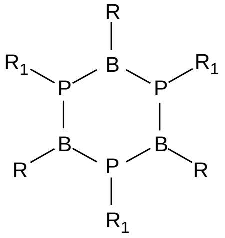
Today, there exist a wide variety of boron-containing polymers including ring systems such as borazines (structure 11.41), boroxines (structure 11.42), and triphosphatoborins (structure 11.43),


Borazine

(11.41)


Boroxine

(11.42)


Triphosphatoborin

(11.43)

as well as metal, metalloid, ferrocene, etc. containing polymers, each offering their own potential for exhibiting desired properties.

11.6 ION-EXCHANGE RESINS

Just as calcium ions, for an insoluble compound, form a complex through reaction with the carbonate ion (calcium carbonate), it also forms complex with a carbonyl functional group on a polymer. This concept forms the basis for many analyses, separations, and concentration techniques. Many of these techniques are based on organic resins, silicon dioxide-intense compounds such as the zeolites, and on carbohydrate-related compounds such as dextran-based resins. The functional groups include typically fully charged sulfates, sulfonates, and acids and noncharged groups such as amines, imines, and hydroxyls. The functional groups are normally located on the surface of somewhat spherical beads. The use of negatively charged functional groups to preferentially capture cations is referred to as cation exchange. Amines are often protonated forming cations that attract anions and are called anion-exchange resins. The combinations of reactions generally are simple Lewis acid–base reactions.

While acid groups attract cations the neutralized acid groups, salts, are more effective. The tendency of coordination is related to the size of the cation and charge on the cation. In general, multiple-charged cations such as Ca^{+2}, Mg^{+2}, and $Fe^{+3,+2}$ are more strongly coordinated than single-charged cations as Na^{+1} and K^{+1}. This difference in tendency to coordinate is widely used in ion-exchange resin applications.

When two or more coordinations occur with a single cation, it is called chelation after the Greek word for the claw of a crab.

Applications of cation and anion resins are varied and include purification of sugar, identification of drugs and biomacromolecules, concentration of uranium, calcium therapy to help increase the amount of calcium in our bones (i.e., increase the bone density), and use as therapeutic agents for the control of bile acid and gastric acidity. In the latter use, a solid polyamide (Colestid) is diluted and taken with orange juice, which facilitates removal of bile acids from the body. This removal helps the body to produce more bile acid from cholesterol, thus effectively reducing the cholesterol level.

The Merrifield protein synthesis (employing chloromethylated polystyrene as the substrate) makes use of ion-exchange resins like many of our industrial and home water purifiers. Water containing dissolved Ca^{+2}, Mg^{+2}, Fe^{+2}, and Fe^{+3} is called hard water. These ions act to reduce the effectiveness of detergents and soaps by coordinating with them, producing solid scum. The precipitates may also be deposited in pipes and water heaters forming boiler scale. In bathtubs they form the ring that must be scrubbed to remove it. The ions are generally from natural sources such as the passing of water over and through limestone ($CaCO_3$).

Most home water softeners are based on ion-exchange resins. The first ion-exchange materials used in softening water were naturally occurring polymeric aluminum silicates called zeolites. At present, synthetic zeolites are also used for this purpose. Today, most ion-exchange resins are based on styrene and divinylbenzene (vinylstyrene) resins that are then sulfonated. When the resin is ready for use, sodium ions generated from rock salt (simple sodium chloride) is passed through the resin bed replacing the hydrogen ion (protons). The sulfonate functional groups have a greater affinity for multiple-charged cations than for the single-charged sodium ion, and the multivalent metal ions replace the sodium ions resulting in the water having a lower concentration of the ions responsible for the water being hard. Eventually, the sulfonate sites on the resin become filled and the resin bed must be recharged by adding large amounts of dissolved sodium ions (derived from sodium chloride), which displace the more tightly bound but overwhelmingly outnumbered "hard ions." After the system is flushed free of these "hard ions" the resin bed is again ready to give "soft water" for our use. This sequence is described in Figure 11.1.

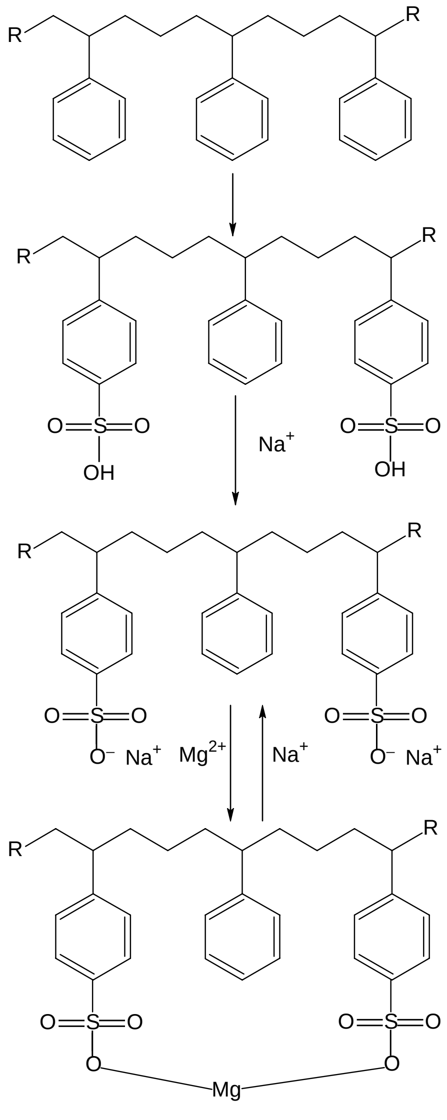


FIGURE 11.1 The ion-exchange cycle from top to bottom: sulfonation of some of the phenyl rings; formation of the sodium form; and metal chelation and regeneration.

11.7 SUMMARY

1. There are a wide variety of inorganic and metal-containing polymers. The potential uses are many and include the broad areas of biomedical, electrical, optical, analytical, catalytic, building, and photochemical applications.
2. The bond strength from any combinations is higher than for many traditional polymers with many having superior thermal stabilities.
3. Metal and inorganic polymers can be formed through a variety of reaction types including condensation, coordination, and addition reactions.
4. The majority of the condensation polymerizations can be considered extensions of typical Lewis acid–base reactions.
5. Polysiloxanes (silicons) offer a good combination of properties not found in organic polymers. Silicons are employed in a number of applications including antifoaming agents, lubricants, caulks, sealants, gaskets, and as biomaterials.
6. Polyphosphazenes offer unique thermal properties and have shown a number of uses in the field of electronics and medicine.
7. The number and variety of organometallic polymers and potential applications for organometallic polymers is great. Because of the high cost of production of many of these materials, uses will often be limited to applications employing minute quantities of the polymers. This is not true for many polymers containing silicon, tin, and main group materials since these are available in large quantities at reasonable cost.

GLOSSARY

borazoles Molecules composed of boron and nitrogen atoms.
capping Protecting end groups.
carboranes Molecules composed of carbon and boron atoms.
coordination polymers Polymers based on coordination complexes.
metallocenes Sandwich or distorted sandwich-like molecules containing generally two cyclopentadienes and a metal atom bonded to them.
polyphosphonitrile Polymer with a repeat unit of $-P=N-$.
RTV Room temperature vulcanization.
siloxanes and silicones Polymers containing –Si–O– backbones.

EXERCISES

1. What is meant by "lost loops" in the production of silicones?
2. How could you produce a silicone with a low DP?
3. What would you estimate the solubility parameters of silicones to be?
4. Sodium silicate is water soluble (forming water glass), but silicones are water repellents. Explain the difference.
5. How would you polymerize an aqueous solution of sodium silicate?
6. How would you explain the good thermal stability of silicones?
7. Show the repeat unit for polydiethylsiloxane.
8. What are the reactants used to make phosphazenes?
9. Why would you predict that the chloro groups in phosphonitrilic polymers would be attacked by water?
10. Which phosphazene would be more flexible one made by reaction of poly(phosphonitrilic chloride) with (a) sodium trifluoroethoxide or (b) sodium trifluorobutoxide?
11. Show the structure of borazole.
12. Since tin-containing organometallic polymers are used in marine antifouling coatings, what would you predict about their water resistance?

13. In addition to high cost, name another disadvantage of coordination polymers.
14. What is the ceiling temperature of sulfur nitride polymers?
15. What are the main uses of tin-containing polymers?
16. What is the basis for many of the electrical and optical applications of boron-containing polymers?
17. Why is there interest in the synthesis and study of metal-containing polymers?
18. What are some attractive features of polysiloxanes?
19. Name two biological polymers that contain metals and which are important to life.
20. What is the main difference between ionic and covalent bonds remembering that most bonds have both characteristics involved in them?

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12 Inorganic Polymers

12.1 INTRODUCTION

Just as polymers abound in the world of organics, they also abound in the world of inorganics. Inorganic polymers are the major components of soil, mountains, and sand. They are also extensively employed as abrasives and cutting materials (diamond, boron carbide, silicon carbide [carborundum], aluminum oxide), coatings, flame retardants, building and construction materials (window glass, stone, Portland cement, brick, tiles), and lubricants and catalysts (zinc oxide, nickel oxide, carbon black, graphite, silica gel, alumina, aluminum silicate, chromium oxides, clays).

The first man-made, semisynthetic polymer was probably inorganic in nature. Alkaline silicate glass was used in the Badarian period in Egypt (about 12,000 B.C.) as a glaze, which was applied to steatite after it had been carved into various shapes. Frience, a composite containing powered quartz or steatite core covered with a layer of opaque glass, was employed from around 9000 B.C. to make decorative objects. The earliest known piece of regular (modern day-type) glass, dated to 3000 B.C., is a lion's amulet found at Thebes and now housed in the British Museum. This is a blue opaque glass partially covered with a dark green glass. Transparent glass appeared around 1500 B.C. Several fine pieces of glass jewelry were found in Tutankhamen's tomb (~1300 B.C.) including two bird heads of light blue glass incorporated into the gold pectoral worn by the Pharaoh.

Because of the wide variety and great number of inorganic polymers, this chapter will focus on only a few of the more well-known inorganic polymers. Table 12.1 contains a partial listing of common inorganic polymers.

12.2 PORTLAND CEMENT

Portland cement is the least expensive, most widely used synthetic inorganic polymer. It is employed as the basic nonmetallic, nonwoody material of construction. Concrete highways and streets span our countryside and concrete skyscrapers silhouette the urban skyline. Less spectacular uses are found in everyday life as sidewalks, fence posts, and parking bumpers.

The name "Portland" is derived from the cement having the same color as the natural stone quarried on the Isle of Portland, a peninsula on the south of Great Britain. The word cement comes from the Latin *caementum*, which means "pieces of rough, uncut stone." Concrete comes from the Latin *concretus*, meaning "to grow together."

Common (dry) cement consists of anhydrous crystalline calcium silicates (the major ones being tricalcium silicate, Ca_3SiO_5, and β-dicalcium silicate, Ca_2SiO_4), lime (CaO, 60%), and alumina (a complex aluminum silicate, 5%). While cement is widely used and has been studied in good detail, its structure and the process whereby it is formed are not completely known. This is due to at least two factors. First, its three-dimensional arrangement of various

TABLE 12.1
Important Inorganic Polymers

Agate
Alumina
Aluminum oxide
Amphiboles
Anthophylite
Arsenic selenide
Arsenic sulfide
Asbestos
Berlinite
Beryllium oxide
Boron nitride
Boron oxides
Boron phosphate
Calcite
Carbon black
Chabazite
Chett
Chrysotile
Concrete
Cristobalite
Crocidolite
Diamond
Dickite
Epistilbite
Feldspars
Flint
Fuller's earth
Garnet
Germanium selenide
Gibbsite
Glasses (many kinds)
Graphite
Imogolite
Jasperite
Kaolinite
Mesolite
Mica
Montmorillonite
Muscovite
Phosphorus oxynitride
Polyphosphates (many)
Quartz
Rhodonite
Serpentine
Silicon dioxides (many)
Silicon carbide
Spodumene
Stilbite
Stishorite
Sulfur nitride
Talc
Thomsonite
Tremolite
Tridymite
Valentinite
Vermiculite
Wollastonite
Xonotlite
Ziolites
Zirconia

atoms has a somewhat ordered array when a small (molecular level) portion is studied, but as larger portions are viewed, less order is observed giving only an average overall structure. This arrangement is referred to as short-range order and long-range disorder and is a good description of many three-dimensional, amorphous inorganic and organic polymers. Thus, there exists only an average structure for the cement, which varies with amount of water and other components added, time after application (i.e., age of the cement), and source of concrete mix and location (surface or internal). Second, three-dimensional materials are insoluble in all liquids; therefore, tools of characterization and identification that require materials to be in solution cannot be employed to assist in the structural identification of cement.

When anhydrous cement mix is added to water, the silicates react, forming hydrates and calcium hydroxide. Hardened Portland cement contains about 70% cross-linked calcium silicate hydrate and 20% crystalline calcium hydroxide.

$$2Ca_3SiO_5 + 6H_2O \rightarrow Ca_3Si_2O_7 \bullet 3H_2O + 3Ca(OH)_2 \tag{12.1}$$

$$2CaSiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7 \bullet 3H_2O + Ca(OH)_2 \tag{12.2}$$

A typical cement paste contains about 60%–75% water by volume and only about 40%–25% solids. The hardening occurs through at least two major steps (Figure 12.1). First, a gelatinous layer is formed on the surface of the calcium silicate particles, which consists mainly of water with some calcium hydroxide. After about 2 h, the gel layer sprouts fibrillar outgrowths that radiate from each calcium silicate particle. The fibrillar tentacles increase in number and length, becoming enmeshed and integrated. The length-wise growth slows, with the fibrils now joining up sideways, forming striated sheets that contain tunnels and holes. During this time, calcium ions are washed away from the solid silicate polymeric structures by water molecules and react further, forming additional calcium hydroxide. As particular local sites become saturated with calcium hydroxide, calcium hydroxide itself begins to crystallize, occupying once vacant sites and carrying on the process of interconnecting about and with the silicate "jungle."

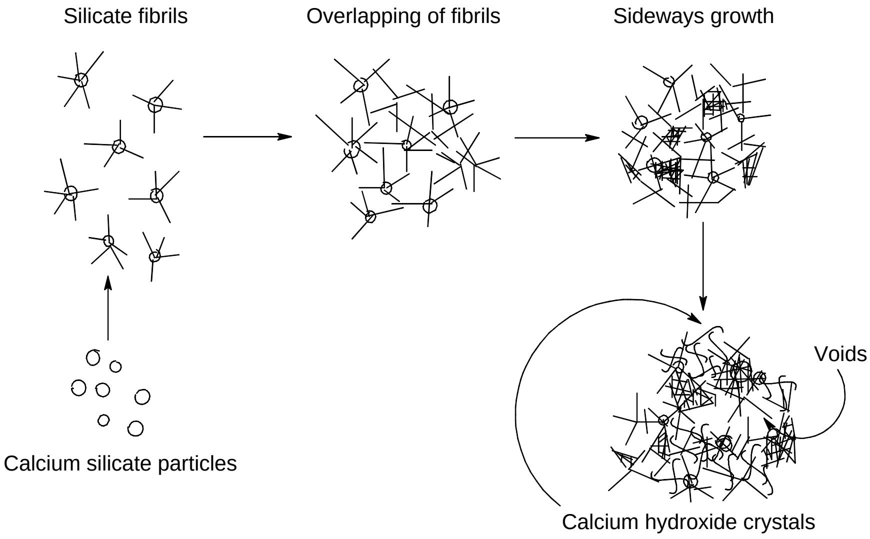


FIGURE 12.1 Steps in the hardening of Portland cement.

In spite of attempts by the silicate and calcium hydroxide to occupy all the space, voids are formed, probably from the shrinkage of the calcium hydroxide as it forms a crystalline matrix. (Generally crystalline materials have higher densities than amorphous materials; thus, a given amount will occupy less volume, leaving some unfilled sites.) Just as a chain is no stronger than its weakest link, so also is cement no stronger than its weakest sites, i.e., its voids. Much current research concerns attempts to generate stronger cement with the focus on filling these voids. Interestingly, two of the more successful cement-void-fillers are also polymers—dextran, a polysaccharide, and polymeric sulfur.

Table 12.2 shows a typical concrete mix. The exact amounts may vary by as much as 50% depending on the intended use and preference of the concrete maker.

The manufacture of Portland concrete consists of three basic steps—crushing, burning, and finish grinding. As noted earlier, Portland cement contains about 60% lime, 25% silicates, and 5% alumina with the remainder being iron oxides and gypsum. Most cement plants are located near limestone ($CaCO_3$) quarries since this is the major source of lime. Lime may also come from oyster shells, chalk, and a type of clay called marl. The silicates and alumina are derived from clay, silicon sand, shale, and blast-furnace slag.

TABLE 12.2
Sample Concrete Mix

	Amount	
Material	**By Volume**	**By Weight**
Portland cement	90–100 lb (1 cu. ft)	90–100 lb (40–50 kg)
Water	5.5 gal	45 lb (20 kg)
Sand	2 cu. ft	200 lb (90 kg)
Gravel (small rocks)	3 cu. ft	250 lb (120 kg)

12.3 OTHER CEMENTS

There are a number of cements specially formulated for specific uses. *Air-entrained concrete* contains small air bubbles formed by the addition of soaplike resinous materials to the cement or to the concrete when it is mixed. The bubbles permit the concrete to expand and contract (as temperature changes) without breaking (since the resistance of air to changes in the concrete volumes is small). *Lightweight concrete* may be made through the use of lightweight fillers such as clays and pumice in place of sand and rocks or through the addition of chemical foaming agents that produce air pockets as the concrete hardens. These air pockets are typically much larger than those found in air-entrained concrete.

Reinforced concrete is made by casting concrete around steel bars or rods. Most large cement-intense structures such as bridges and skyscrapers employ reinforced concrete. *Prestressed concrete* is typically made by casting concrete around steel cables stretched by jacks. After the concrete hardens, the tension is released, resulting in the entrapped cables compressing the concrete. Steel is stronger when tensed, and concrete is stronger when compressed. Thus, prestressed concrete takes advantage of both of these factors. Archways and bridge connections are often made from prestressed concrete.

Concrete masonry is simply the name given to the cement building blocks employed in the construction of many homes, and it is simply a precast block of cement, usually with lots of voids. *Precast concrete* is concrete that is cast and hardened before it is taken to the site of construction. Concrete sewer pipe, wall panels, beams, grinders, and spillways are all examples of precast cements.

The cements cited above are all typically derived from Portland cement. Following are non-Portland cements.

Calcium–aluminate cement has a much higher percentage of alumina than does Portland cement. Furthermore, the active ingredients are lime (CaO) and alumina. In Europe it is called melted or fused cement. In the United States, it is manufactured under the trade name Lumnite. Its major advantage is its rapidity of hardening, developing high strength within a day or two.

Magnesia cement is largely composed of magnesium oxide (MgO). In practice, the MgO is mixed with fillers and rocks and an aqueous solution of magnesium chloride. This cement sets up (hardens) within 2–8 h and is employed for flooring in special circumstances.

Gypsum, or hydrated calcium sulfate ($CaSO_4 \bullet 2H_2O$), serves as the basis of a number of products including plaster of Paris (also known as molding plaster, wall plaster, and finishing plaster). The ease with which plaster of Paris and other gypsum cements can be mixed and cast (applied) and the rapidity with which they harden contribute to their importance in the construction field as a major component for plaster wall boards. Plaster of Paris' lack of shrinkage in hardening accounts for its use in casts. It is also employed as a dental plaster, pottery plaster, and as molds for decorative figures. Unlike Portland cement, plaster of Paris requires only about 20% water and dries to the touch in 30–60 min giving maximum strength after 2–3 days. Portland cement requires several weeks to reach maximum strength.

12.4 SILICATES

Silicon is the most abundant metal-like element in the earth's crust. It is seldom present in pure elemental form, but is rather found in a large number of polymers based largely on the polycondensation of the orthosilicate anion, SiO_4^{-4}, as illustrated in the following equations:

$$\underset{(1)}{\mathrm{Si\,O}_4^{-4}} \rightleftharpoons \underset{(2)}{\mathrm{Si_2O}_7^{-6}} + \mathrm{O}^{-2} \tag{12.3}$$

$$\mathrm{Si_2O}_7^{-6} + \mathrm{SiO}_4^{-4} \rightleftharpoons \underset{(3)}{\mathrm{Si_3O}_9^{-6}} + 2\mathrm{O}^{-2} \tag{12.4}$$

$$2Si_2O_7^{-6} \rightleftharpoons \underset{(4)}{Si_4O_{10}^{-4}} + 4O^{-2} \tag{12.5}$$

$$2Si_2O_7^{-6} \rightleftharpoons \underset{(5)}{Si_4O_{11}^{-6}} + 3O^{-2} \tag{12.6}$$

$$2Si_2O_7^{-6} \rightleftharpoons \underset{(6)}{Si_4O_{12}^{-8}} + 2O^{-2} \tag{12.7}$$

$$3Si_2O_7^{-6} \rightleftharpoons \underset{(7)}{Si_6O_{18}^{-12}} + 3O^{-2} \tag{12.8}$$

$$SiO_4^{-4} \rightarrow\rightarrow\rightarrow \underset{(8)}{SiO_2} \tag{12.9}$$

The number listed with each product corresponds with the "Geometric ID number" and the "Structural geometry" given in Table 12.3 and is depicted in Figure 12.2.

Each of these steps is based on a tetrahedral silicon atom attached to four oxygen atoms. The complexity and variety of naturally occurring silicates is due to two major factors. First, the ability of the tetrahedral SiO_4^{-4} unit to be linked together often giving polymeric structures. Second, the substitution of different metal atoms of approximately the same size as that of Si often occurs giving many different materials.

In the structures cited in Table 12.3, except for pure silicon dioxide, metal ions are required for overall electrical neutrality. These metal ions are positioned in tetrahedral, octahedral, etc. positions in the silicate-like lattice. Sometimes they replace the silicon atom. Kaolinite asbestos has aluminum substituted for silicon in the Gibbosite sheet. Further, sites for additional anions, such as the hydroxyl anion, are available. In ring, chain, and sheet structures neighboring rings,

TABLE 12.3
Inorganic Polymeric Silicates as a Function of Common Geometry

Geometric ID Number (Text)	Basic Geometric Unit	Structural Geometry (Figure 12.2)	General Silicate Formula[a]	Examples[a]
1	Tetrahedran	A	SiO_4^{-4}	Granite olivine—$(Mg,Fe)_2SiO_4$ Fosterite—Mg_2SiO_4 Topez
2	Double tetrahedran	B	$Si_2O_7^{-6}$	Akermanite—$Ca_2MgSi_2O_7$
3	Triple ring	C	$Si_3O_9^{-6}$	Wollastonite
4	Tetra ring	D	$Si_4O_{12}^{-8}$	Neptunite
5	Six ring	E	$Si_6O_{18}^{-12}$	Beryl—$Al_2Be_3Si_6O_{18}$
6a	Linear chain	F	$Si_4O_{12}^{-8}$	Augite, Enstatite—$MgSiO_3$ Diopside—$CaMg(SiO_3)_2$ Chrysotile—$Mg_6Si_4O_{11}(OH)_6$
6b	Double stranded ladder	G	$Si_4O_{11}^{-6}$	Hornblende
7	Parquet (layered)	H	$Si_4O_{10}^{-4}$	Talc—$Mg_3Si_4O_{10}(OH)_2$ Mica—$KAl_3Si_3O_{10}(OH)_2$ Kaolinite—$Al_2Si_2O_5(OH)_4$ (Condensed) Silicic acid—$H_2Si_2O_5$
8	Network	I	SiO_2	Quartz, Feldspar (Orthoclase)—$KAlSi_3O_8$

[a] The formulas given are for the most part simplified.

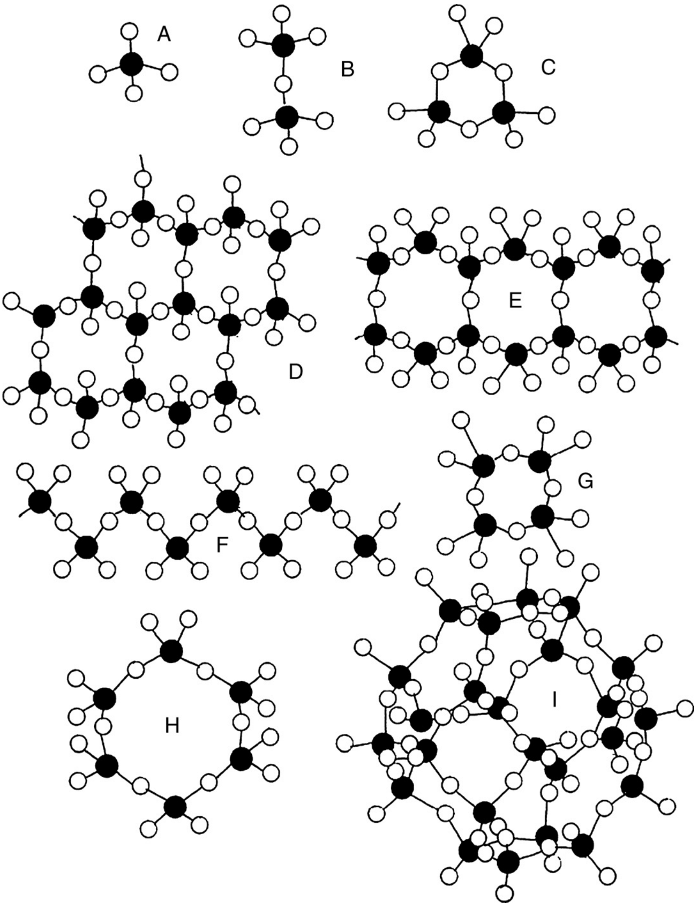


FIGURE 12.2 General silicate structures.

chains, and sheets are often bonded together by metal ions held between the rings. In vermiculite asbestos, the silicate sheets are held together by nonsilicon cations.

For sheet-layered compounds, the forces holding together the various sheets can be substantially less than the forces within the individual sheets. Similar to graphite, such structures may be easily cleaved parallel to the sheets. Examples of such materials are mica, kaolinite, and talc.

Bonding occurs through a combination of ionic and covalent contributions just as are present in organic polymers except that the ionic character is a little higher. ‘‘Back-bonding’’ from electrons associated with the oxygen to vacant orbitals in the silicon (or other tetrahedral metal atom) occurs giving the silicon–oxygen linkages some double or pi-bond character.

As noted earlier, cations other than silicon may occupy the tetrahedral centers. A major factor in predicting which cations will be found to substitute for silicon is ionic size. In general, cations whose size is about 0.03–0.1 nm are the best candidates. Si^{+4} has an ionic radius of about 0.041 nm. Cations such as Fe^{+2} (ionic radius = 0.07 nm), Al^{+3} (0.05 nm), Ca^{+2} (0.1 nm), and Mg^{+2} (0.065 nm) are often found in silicate-like structures and meet this requirement.

Most silicate-like polymers can be divided into three major classes—the network structures based on a three-dimensional tetrahedral geometry (such as quartz), layered geometries with stronger bonding occurring within the ‘‘two-dimensional’’ layer (such as talc), and linear structures.

12.4.1 NETWORK

Quartz is an important network silicate (Section 12.10). A number of additional tetrahedral silicate-like materials possess some AlO_4 tetrahedra substituted for the SiO_4 tetrahedra. Such structures offer a little larger "hole" in comparison to the entirely SiO_4 structures allowing alkali and alkaline-earth cations to be introduced. Feldspar (orthoclase) is one such mineral. The alumino–silicate networks are almost as hard as quartz. For feldspar and other tetrahedral networks the number of oxygen atoms is twice the summation of silicon and other MO_4 cations.

The feldspars are widely distributed and comprise almost two-thirds of all igneous rocks. Orthoclase and albite ($NaAlSi_3O_8$) are feldspars in which one-fourth of the silicon atoms are replaced by aluminum and anorthite ($CaAl_2Si_2O_8$) and has one-half of the silicon atoms replaced by aluminum. Because the ionic radius of Na^+ (0.095 nm) and Ca^{+2} (0.1 nm) are the same, solid solutions are often formed between albite and anorthite. Good stones of albite and orthoclase are known as moonstones.

Some of the network structures exhibit a framework sufficiently "open" to permit ions to move in and out. The zeolite minerals used for softening water are of this type.

Ultramarines are three-dimensional cage-like structures. They differ from feldspars and zeolites because of the large spaces within the structures that can contain cations and anions but not water, illustrating a natural "buckeyball-like" structure and cavity, and a diversity of environment between the internal and external cages. Ultramarines can act as ion-exchangers for both anions and cations. The blue color of ultramarines is due to the presence of the S_3^- ion although a yellow ion S_2^- also exists in the same structure.

12.4.2 LAYER

Layered structures typically conform to the approximate composition $S_4O_{10}^{-4}$ or $Si_3O_5^{-2}$. For most of these, three of the oxygen atoms of each tetrahedron are shared by other tetrahedra, and the fourth oxygen is present on one side of the sheet.

In talc and kaolinite the layers are neutral. Thus, the layers slide over one another easily imparting to these minerals a softness and ease in cleavage. In other minerals the layers are charged and held together by cations. In mica, the alumino–silicate layers are negatively charged and cations, generally K^+, are present between the layers giving electronic neutrality to the entire system of layers. The ionic attractive forces between the layers result in mica being much harder than talc and kaolinite. Even so, these intersheet bonding forces are less than the "within-the-sheet" bonding forces permitting relatively easy and clean cleavage of mica, which is used as an insulator for furnaces and electric equipment. Montmorillonite is an important ingredient in soils and is employed industrially as a catalyst in the conversion of straight-chain hydrocarbons to more branched hydrocarbons and more recently as a sheet or clad material in the manufacture of tires.

Vermiculites are formed by the decomposition of mica. They contain layers of water and magnesium ions in place the potassium ions. When heated to 800°C–1100°C, vermiculite expands because of the conversion of the water to gas. The expanded vermiculite has a low thermal conductivity and density, and is used as a thermal and sound barrier as well as an aggregate in lightweight concrete. It is also used as a moisture-retaining soil conditioner in planting.

A number of clays are layered silicate-like materials. Most clays contain finely divided quartz, micas, and feldspars. Iron oxide-rich clays are employed to make pottery and terracotta articles. Clays containing iron oxide and sand are used to make bricks and tiles. Clays rich in calcium and magnesium carbonate are known as marls and are used in the cement industry (Section 12.2).

Kaolinite is the main constituent in china clay used to make porcelain. The layers are largely held together by van der Waals forces. Bentonite is used in cosmetics, as a filler for soaps, and as a plasticizer, and it is used in drilling-muds as a suspension stabilizer. Bentonite and kaolinite clays are used, after treatment with sulfuric acid to create acidic surface sites, as petroleum cracking catalysts. Asbestos also has a layered structure (Section 12.13).

12.4.3 CHAIN

Both single- and double-stranded chains are found. The most important members of single chains are the pyroxenes including diopside. The most important double-chained minerals are the amphiboles. Some of these contain hydroxyl and fluoride ions, bonded directly to the metal cation and not to the silicon atom.

Jade, which has been valued in carving by eastern Asians for centuries, is generally one of two minerals—pyroxene or jadeite ($NaAl(SiO_3)_2$) and the amphibole nephrite, $Ca_2(Fe^{+2})_5$ and/or $Ca_2(Mg^{+2})_5(Si_4O_{11})_2(OH)_2$. X-ray diffraction has shown the presence of triple chains in nephrite.

Because the interchain bonding is weaker than the Si–O backbone bonding, these chain structures can generally be easily cleaved between the chains.

Several amphiboles are fibrous and fibers from them can be processed to give heat-insulating materials. Among these are tremolite and crocidolite. These minerals are also used as fibers in composites.

12.5 SILICON DIOXIDE (AMORPHOUS)

Silicon dioxide (SiO_2) is the major repeating general formula for the vast majority of rock, sand, and dirt around us and for the material we refer to as glass. The term glass can refer to many materials, but here we will use the ASTM definition that glass is an inorganic product of fusion that has been cooled to a rigid condition without crystallization. In this section silicate glasses, the common glasses for electric light bulbs, window glass, drinking glasses, glass bottles, glass test tubes and beakers, and glass cookware, will be emphasized. Figure 12.3 contains a segment of an amorphous silicon dioxide structure. For some of the structure there is a general distorted octahedral ring structure where each octahedral contains four silicon and four oxygen atoms. There is also a number of "dangling" hydroxyl groups. This amorphous structure allows the glass to be melted and some, but not much, flexibility.

Glass has many useful properties, as listed in Table 12.4. It ages (changes chemical composition and physical property) slowly, typically retaining its fine optical and hardness-related properties for centuries. Glass is referred to as a supercooled liquid or a very viscous liquid. Indeed, it is a slow-moving liquid as attested to by sensitive measurements carried out in many laboratories. Concurrent with this is the observation that the old stained glass windows adorning European cathedrals are a little thicker at the bottom of each small, individual piece than at the top. For most purposes though, glass can be treated as a brittle solid that shatters on sharp impact.

Glass is mainly silica sand (SiO_2) and is made by heating silica sand and powdered additives together in a specified manner and proportion much as a cake is baked, following a recipe that describes the items to be included, amounts, mixing procedure (including sequence), oven temperature, and heating time. The amounts, nature of additives, etc., all affect the physical properties of the final glass.

Typically cullet, recycled or waste glass (5%–40%), is added along with the principle raw materials (mostly SiO_2). The mixture is thoroughly mixed and then added to a furnace where the mixture is heated to near 1500°C to form a viscous, syruplike liquid. The size and nature

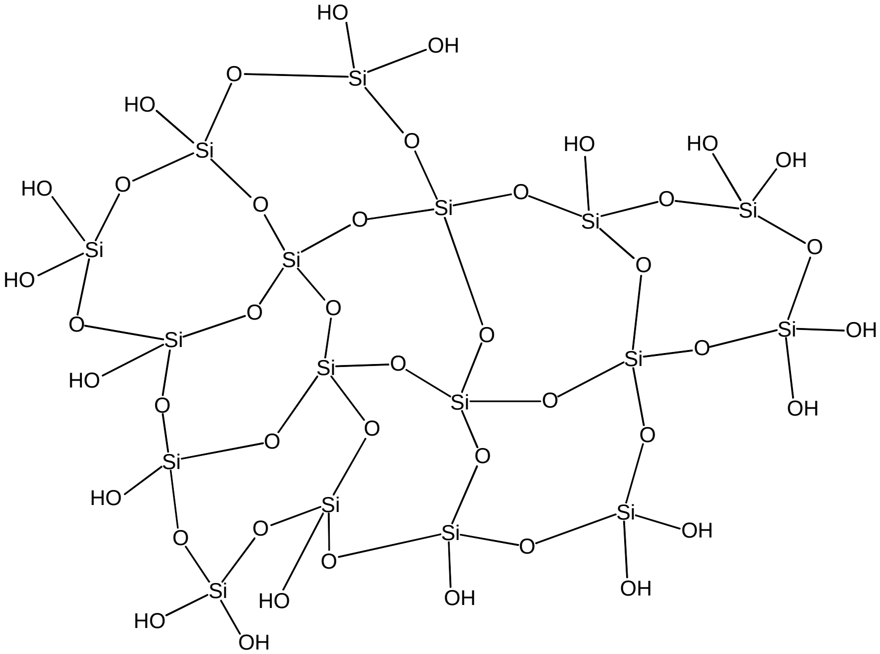


FIGURE 12.3 Segment of amorphous silicon dioxide (SiO_2) structure.

of the furnace corresponds to the glasses' intended uses. For small, individual items the mixture may be heated in a small clay (refractory) pot.

Most glass is melted in large (continuous) tanks that can melt 400–600 t a day for production of other glass products. The process is continuous with the raw materials fed into one end as molten glass is removed from the other end. Once the process (called a campaign) is begun it is continued indefinitely, night and day, often for several years until the demand is met or the furnace breaks down.

A typical window glass will contain 95%–99% silica sand with the remainder being soda ash (Na_2CO_3), limestone ($CaCO_3$), feldspar, and borax or boric acid along with the appropriate coloring and decolorizing agents, oxidizing agents, etc. As noted earlier, 5%–40% by weight of crushed cullet is also added. The soda ash, limestone, feldspar, and borax or boric acid all form oxides as they are heated, which is integrated into the silicon structure:

$$\begin{array}{l} Na_2CO_3 \rightarrow Na_2O + CO_2 \\ \text{Soda ash} \\ \text{(Sodium Carbonate)} \end{array} \tag{12.10}$$

TABLE 12.4
General Properties of Silicate Glasses

High transparency to light	Permanent (long-term) transparency
Hard	Scratch-resistant
Chemically inert	Low thermal expansion coefficient
Good electrical insulator	High sparkle
Good luster	Low porosity
Good ease of reforming	Easily recyclable
Relatively inexpensive	Available in large amounts

$$\underset{\text{Limestone}}{CaCO_3} \rightarrow CaO + CO_2 \tag{12.11}$$

$$\underset{\text{Feldspar}}{R_2OAl_2O_3 \bullet 6H_2O} \rightarrow R_2O + \underset{\text{Alumina}}{Al_2O_3} + 6SiO_2 \tag{12.12}$$

$$\underset{\text{Boric Acid}}{H_3BO_4} \rightarrow B_2O_3 \tag{12.13}$$

The exact structure varies according to the ingredients and actual processing conditions. As in the case of Portland cement, glass is a three-dimensional array that offers short-range order and long-range disorder—it is amorphous offering little or no areas of crystallinity. The structure is based on the silicon atoms existing in a tetrahedral geometry with each silicon atom attached to four oxygen atoms, generating a three-dimensional array of inexact tetrahedra. Thus, structural defects occur, due in part to the presence of impurities such as Al, B, and Ca, intentionally or unintentionally introduced. These impurities encourage the glass to cool to an amorphous structure, since the different-sized impurity metal ions, etc., disrupt the rigorous space requirement necessary to allow crystal formation.

Processing includes shaping and retreatments of the glass. Since shaping may create undue sites of amorphous structure, most glass objects are again heated to near their melting point. This process is called *annealing*. Since many materials tend to form more ordered structures when heated and recooled slowly, the effect of annealing is to "heal" sites of major dissymmetry. It is important to heal these sites since they represent preferential locations for chemical and physical attack, such as fracture.

Four main methods are employed for shaping glass—drawing, pressing, casting, and blowing. Drawing is employed for shaping flat glass, glass tubing, and for creating fibrous glass. Most flat glass is shaped by drawing a sheet of molten glass (heated so it can be shaped but not so it freely flows) onto a tank of molten tin. Since the glass literally floats on the tin, it is called "float glass." The temperature is carefully controlled. The glass from the float bath typically has both sides quite smooth with a brilliant finish that requires no polishing.

Glass tubing is made through drawing molten glass around a rotating cylinder of the appropriate shape and size. Air is blown through the cylinder creating the hollow tubing. Fibrous glass is made by forcing molten glass through tiny holes and drawing the resulting fibers helping to align the chain on a molecular level.

Pressing is accomplished by simply dropping molten glass into a form and then applying pressure to ensure the glass takes the form of the mold. Lenses, glass blocks, baking dishes, and ashtrays are examples of press-processed glass objects.

Casting involves filling molds with molten glass in much the same manner as cement and plaster of Paris–molded objects. Art glass objects are often made by casting.

Glass blowing is one of the oldest arts known to man. The objects are constructed or repaired by a skilled worker who blows into a pipe intruded into the molten glass. The glass temperature must be maintained to allow it to be moldable but not so it freely flows. Mass produced materials are manufactured employing mechanical blowers often employing a combination of glass blowing and molding to form the desired product.

As noted above, annealing encourages the removal of sites of stress and strain. Slow cooling results in a glass with more crystallinity that is stronger but more brittle. *Tempering* is the name given when the glass is rapidly cooled, resulting in an amorphous glass that is weaker but less brittle. The correlation between crystallinity, rate of cooling, and brittleness is demonstrated by noting that an older window glass exposed to sun for years is more brittle and more easily shattered since the sunlight raises the temperature sufficiently to permit small molecular movements (though even in full sunlight the glass is not near the temperature required for ready movement) and over the years gives a glass with small regions of greater order.

Silicon-based glasses account for almost all of the glasses manufactured; silica is finely ground silica sand. Yet most sand is unsuitable for general glass making due to the presence of excessive impurities. Thus, while sand is plentiful, sand that is useful for the production of glass is less common. In fact, the scarcity of large deposits of glass sand is one major reason for the need to recycle glass items. The second major reason is associated with the lowered energy requirements for glass to be made molten again for reshaping compared with a virgin glass mixture, i.e., culled glass becomes molten at lower temperatures than virgin glass.

12.6 KINDS OF AMORPHOUS GLASS

The types and properties of glass can be readily varied by changing the relative amounts and nature of ingredients. *Soda-lime glass* is the most common of all glasses accounting for about 90% of glass made. Window glass, glass for bottles, etc., are all soda-lime glass (75% silica, 15% soda (sodium oxide), 9% lime (calcium oxide), and the remaining 4% minor ingredients), which has a relatively low softening temperature and low thermal shock resistance limiting its high-temperature applications.

Vycor, or 96% silicon glass, is made using silicon and boron oxide. Initially the alkali–borosilicate mixture is melted and shaped using conventional procedures. The article is then heat-treated, resulting in the formation of two separate phases—one that is high in alkalis and boron oxide, and the other containing 96% silica and 3% boron oxide. The alkali–boron oxide phase is soluble in strong acids and is leached away by immersion in hot acid. The remaining silica–boron oxide phase is quite porous. The porous glass is again heated to about 1200°C, resulting in a 14% shrinkage due to the remaining portions filling the porous voids. The best variety is "crystal" clear and called *fused quartz*. The 96% silica glasses are more stable and exhibit higher melting points (1500°C) than soda-lime glass. Crucibles, UV filters, range burner plates, induction furnace linings, optically clear filters and cells, and super heat-resistant laboratory-ware are often 96% silicon glass.

Borosilicate glass contains about 80% silica, 13% boric oxide, 4% alkali, and 2% alumina. It is more heat-shock-resistant than most glasses due to its unusually small coefficient of thermal expansion (typically between 2 and 5×10^{-6} $cm^2/°C$; for soda-lime glass it is 8 to 9×10^{-6} $cm^2/°C$). It is better known by such trade names as Kimax and Pyrex. Bakeware and glass pipelines are often borosilicate glass.

Lead glasses (often called heavy glasses) are made by replacing some or all of the calcium oxide by lead oxide (PbO). Very high amounts of lead oxide can be incorporated—up to 80%. Lead glasses are more expensive than soda-lime glasses, and are easier to melt and work with. They are more easily cut and engraved, giving a product with high sparkle and luster (due to the high refractive indexes). Fine glass and tableware are often lead glass.

Silicon glass is made by fusing pure quartz crystals or glass sand (impure crystals), and it is typically about 99.8% silicon dioxide. It is high-melting and difficult to fabricate.

Colored or *stained glass* has been made for thousands of years, first by Egyptians and later by Romans. Color is typically introduced by addition of transition metals and oxides. Table 12.5 contains selected inorganic colorants and the resulting colors. Because of the high

TABLE 12.5
Colorants for Stained Glass

Colorant	Color	Colorant	Color
Nickel (II) oxide	Yellow to purple	Calcium fluoride	Milky white
Cobalt (II) oxide	Blue	Iron (II) compounds	Green
Iron (III) compounds	Yellow	Copper (I) oxide	Red, blue, or green
Tin (IV) oxide	Opaque	Manganese (IV) oxide	Violet
Gold (III) oxide	Red		

TABLE 12.6
Leading U.S. Glass Companies

Owen-Illinois, Inc.	PPG Industries, Inc.
Corning Glass Works	Owens-Corning Fiberglass Corporation
Libbery-Owens-Ford Company	

clarity of glass, a small amount of coloring agent goes a long way. One part of cobalt oxide in 10,000 parts of glass gives an intense blue glass. The most well-known use for colored glass is the construction of stain-glass windows. In fact, there are many other uses such as industrial color filters and lenses.

Glazes are thin, transparent coatings (colored or colorless) fused on ceramic materials. *Vitreous enamels* are thin, normally opaque or semiopaque, colored coatings fused on metals, glasses, or ceramic materials. Both are special glasses but can contain little silica. They have typically low melting points and are often not easily mixed in with more traditional glasses.

Optical fibers can be glass fibers that are coated with a highly refractive polymer coating such that light entering one end of the filer is transmitted through the fiber (even around corners as within a person's stomach), emerging from the other end with little loss of energy. These optical fibers can also be made to transmit sound and serve as the basis for transmission of television and telephone signals over great distances through cables (Section 12.12).

There are many silica-intensive fibers lumped together as *fibrous glass* or *fiberglass*. A general purpose fiberglass may contain silica (72%), calcium oxide (9.5%), magnesium oxide (3.5%), aluminum oxide (2%), and sodium oxide (13%). The fibers are produced by melting the "glass mixture" with the molten glass drawn through an orifice. The filaments are passed through a pan containing sizing solution onto a winding drum. The take-up rate of the filament is more rapid than the exit rate from the orifice acting to align the molecules and draw the fibers into thinner filaments. Thus, a fiber forced through a 0.1 cm orifice may result in filaments of 0.0005 cm diameter. This drawing increases the strength and flexibility of the fiberglass. Applications of fiberglass include insulation and use in composites.

Table 12.6 contains a listing of major glass-producing companies in the United States. Optical glass for eyeglass lenses and camera lenses is typically soda-lime glass that is highly purified so that it is highly transmissive of light. Today, there exists many other special glass that are important in today's society as laser glasses, photosensitive glass, photochromic windows and eyeglass glass, invisible glasses, radiation absorbing glass, etc. (see Section 12.8).

12.7 SAFETY GLASS

Safety glass is defined as "glass" that diminishes the threat of injuries and robberies as a result of impacts, distortion, or fire.

In 1905, British inventor John C. Wood was working with cellulose and developed a method to adhere glass panes using celluloid as the adhesive. Wood's version of shatter-resistant glass was produced under the band name Triplex since it consisted of outer layers of glass with an inner layer of celluloid polymer.

At about the same time, Edouard Benedictus, a French chemist, was climbing a ladder to get chemicals from a shelf and accidentally (another discovery due to an accident) knocked a glass flask onto the floor. He heard the flask shatter but when he looked at the broken flask, the broken pieces hung together instead of breaking into many pieces and scattering over the floor. Benedictus learned from his assistant that the flask had recently held a solution of cellulose nitrate. The solution of cellulose nitrate dried to give a thin film that was transparent, so the flask was set aside as a "cleaned" flask. It was this thin film that held together the broken glass pieces. The film was formed on evaporation of cellulose nitrate prepared from cellulose and nitric acid.

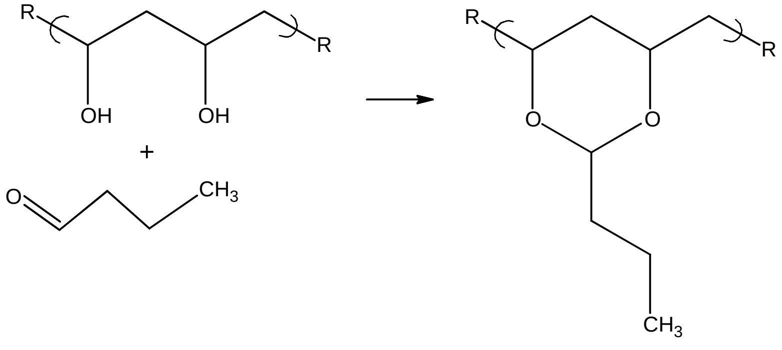
Shortly after the laboratory accident, he read about a girl who had been badly cut from flying glass resulting from an automobile accident. Later he read about other people being cut by flying glass in automobile accidents. He remembered the flask that did not splinter into small pieces when broken because of the cellulose nitrate coating. He experimented with placing cellulose nitrate between sheets of glass and applying pressure to help adhere the glass with the cellulose nitrate. By 1909 Benedictus had patented the material.

Before its use in windshields, safety glass found its initial major application as the lenses for gas masks during World War I. Manufacturers found it easy to work with so that the technology and ability to manufacture safety glass windshields came easily.

As automobiles became more common, so did the hazards of mud, rocks, etc., so that by 1904 windshields were introduced. These first windshields could be folded and removed if they were blocked by excessive mud. While the usefulness of the windshield was abundantly obvious, drivers found that they were dangerous during a wreck cutting passengers, drivers, and passers-by alike. Because the drivers were primarily believed to be responsible for automobile safety, most manufactures were slow to adopt safety glass. In 1919, Henry Ford addressed the windshield problem by having safety glass windshields on his automobiles.

This safety glass turned yellow after several years of exposure to light. The bonding layer was replaced in 1933 by cellulose acetate, made from the reaction of cotton with acetic acid. By 1939 this was replaced by poly(vinyl butyral) (PVB), which is still in use today as the adhesive placed between sheets of glass to produce laminated safety glass. This is one of a very few modern-use materials that has retained the same basic materials for over 60 years.

PVB is made from PVA, which is made from PVAc because the monomer vinyl alcohol does not exist.



(12.14)

Today, safety glass is divided into three general categories: laminated safety glass, tempered safety glass, and armed glass. *Tempered safety glass* is made by heating the glass to its melting point, about 700°C, and then cooling it rapidly by blowing cold air onto its surfaces. The effect is similar to the production of stressed concrete where the concrete is allowed to harden under stress giving a stronger concrete. In the case of glass, when it is rapidly cooled, a structure is locked in that produces extra stress on the glass structure making it stronger. As the glass is cooled, the surfaces harden first locking in the overall glass volume. As the center cools, it forces the surfaces and edges into compression. With appropriate rapid cooling, the glass is not only stronger, but when shattered, produces granulates rather than sharp cutting shards. The typical force necessary to break tempered glass is about four times that required to shatter ordinary glass of the same thickness.

While the windshield is made of safety glass, the remainder of the automotive glass windows are generally made from tempered glass. This glass is also used for commercial building doors and windows, sidelights, patio-door assemblies, storm doors, shower and tub enclosures, refrigerator, oven, stove shelves, and fireplace screens.

Armed glass is most commonly used as roofing on factory buildings. This type of glass has a built-in metal grill that strengthens it. The metal grill is often like chicken-wire in appearance. The glass breaks similar to regular glass, but the wire mesh helps hold it into place. The visibility is reduced because of the presence of the metal mesh.

Laminated glass is used in automobiles and often used for added protection in windows, balconies, or sloping glass roofs. The laminated glass resists breakage in comparison with ordinary glass because the PVB inner layer(s) helps dampen sharp blows. Even so, laminated glass more easily cracks than tempered glass. But, it is harder to pierce than tempered glass because of the PVB inner layer(s). Another difference is that laminated glass can be cut, sawn, or drilled whereas tempered glass cannot. The PVB film also has UV-screening properties reducing discoloration of objects placed behind the safety glass. It also acts to dampen sound for additional soundproofing.

Laminated safety glass is available in different thicknesses depending on the number of PVB–glass layers. *Bullet-resistant glass* is one use of thick, multilayer laminated safety glass. The laminated construction allows the multilayer assembly to have some additional flexibility with the multiple layers allowing the PVB layers to absorb some of the energy of the bullet. The plastic layers help hold the shattered glass fragments together aiding in retaining a restraining barrier. Such glass is used in bank teller windows, and in windshields for aircraft, tanks, and special automobiles and trucks.

The ability to resist bullets and blasts is enhanced by increasing the number of layers of laminated safety glass. This increases glass thickness and weight. So there is a trade-off between expected abuse and practicality.

12.8 LENSES

Around A.D. 1000 reading stones came into use. These were segments of a glass sphere that were used to magnify letters. The reading stones were placed directly on the letters. By A.D. 1350, reading stones were hung with ribbons and strings near the eyes allowing the "wearer" to magnify objects within their "sight." In 1730, a London optician, Edward Scarlett, developed rigid sidepieces that rested on the ears of the user. These were the first modern reading and seeing glasses. The first bifocals were developed by Benjamin Franklin by cutting two lenses in half and placing one above the other. Until recently, glasses fitting was largely trial-and-error with the person wearing the glasses responsible for determining the correct lenses. Even today, we can go to certain stores and select a pair of inexpensive glasses from a group of general eyeglasses through this same process.

Below is a general menu between properties and type of reading glasses that best demonstrate this property:

- Strongest (hardest to break)—polycarbonate
- Lightest—polycarbonate and plastic
- Greatest resistance to scratching—glass
- Clearest vision—glass and plastic
- Most responsive photochromic lens—glass

- Lightest photochromic lens—plastic
- Most resistant to heat and common household chemicals—glass
- Most resistant to flying objects—polycarbonate

In general, polycarbonate lenses are best for people

- Active in sports
- Who use power tools
- With good vision in only one eye
- With refractive surgery

Plastic lenses are best when lightweight and clear vision are important. They offer the widest range of bifocal designs.

Glass lenses are best for people

- Who work in a dusty environment
- Leave glasses in the car
- Wear sunglasses on the beach
- Want the best photochromic performance
- Who often take off and on their glasses

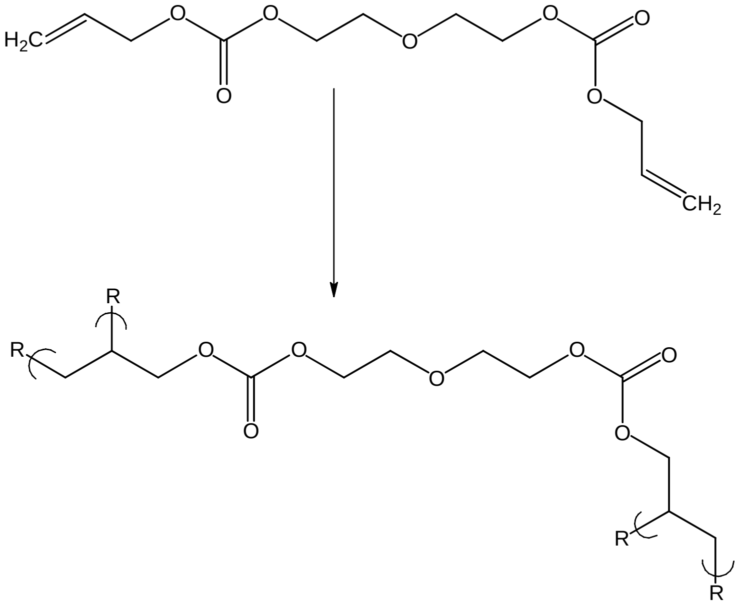
Reading glasses must pass a number of standard tests outlined in LCO993. Several of these are described below. The impact resistance test is described by the Federal Regulation on Impact Resistant Lenses (21 CFR 80.410) where a $^5\!/_8$ in. diameter steel ball weighing 0.56 oz. is dropped from a height of 50 in. onto the horizontal upper, convex surface of the lens. To pass, the lens must not fracture. The flammability test is passed when no evidence of ignition is found when the glasses assembly is placed in a preheated oven set to 200°C for 15 min.

The most common material for decent safety glasses is polycarbonate. Those glasses referred to as high impact must pass the American National Standards Institute (ANSI) test for high velocity impact. The requirements are that the lenses should withstand an impact from a 6.35 mm ($^1\!/_4$ in.) diameter steel ball traveling at a velocity of 45.7 mps (150 fps). From a sample size of 20, none should shatter or the lenses fail the test.

Glass lenses can be made finished from a mold or the general shape made in a mold and later worked providing the finished lens.

In the late 1960s Pittsburgh Plate Glass Company (PPG) introduced a new lens material that is today known simply as "plastic lenses." In comparison to crown glass, this material was lighter, produced thinner lenses, offered greater impact resistance, and was more flexible. While the new material is referred to by the sales people at eyeglasses outlets as simply "plastic" its name is CR-39. The "CR" stands for Columbia Resin and the 39 is the batch or formula made by the Columbia Laboratories in Ohio. CR-39 is made from allyl diglycol carbonate (or diethylene glycol bis[allyl carbonate]) monomer. On heating, the two vinyl groups open up forming a cross-linked thermoset plastic that cannot be resoftened on heating. By comparison, polycarbonate is a linear plastic that is a thermoplastic, which can be resoftened and recycled on addition of heat and pressure. The lenses are formed by melting polycarbonate pellets and injecting them into a mold. Lenses from CR-39 are made by casting the monomer into appropriate molds followed by polymerization creating the lens either as a finished product or further working the solid lens material creating the finished lens.

Initially, there was a problem casting lenses from CR-39 because there is typically shrinkage, with the polymer denser than the liquid monomer, when vinyl monomers are polymerized. In this case there was 14% shrinkage. This was not a problem when casting flat lenses since the resulting lens dimensions were simply a little less. Further, the shrinkage was different creating optical distortions. Robert Graham, working with others for the Armorlite Company, overcame this problem by casting thick blanks where the back curve matched the finished front curve. The lenses are then ground and polished to the required thickness and curve. CR-39 Monomer (12.15) polymerized forming CR-39 polymer (12.16)



(12.15)

(12.16)

There still remained the problem of scratching. The CR-39 lenses have less scratch resistance than polycarbonate lenses. In the 1970s, the 3M (Minnesota Mining and Manufacturing Company) had a research group that was an expert in coatings, including lenses. One problem was the need, for some materials, to have them particularly free from dust to achieve scratch-free-coated surfaces. By the mid-1970s they created a production facility that reduced airborne particles sufficiently to allow materials to be successfully coated. In 1979, 3M purchased the Armorlite Company and transferred their scratch-resistant coating technology to be used for the CR-39 lenses. In 1981, American Optical introduced photolite photochromic lenses that change color with exposure to light. PPG, in 1983, discovered a new family of photochromics, the blue pyridobenzoxanines and by 1984 formed a joint venture with Intercast Europe to manufacture and sell photochromic sunglasses called Attiva, which were made from CR-39. Many other companies have contributed to the presence of today's plastic lenses. The story illustrates how companies applied their interests and strengths to achieve the products we have today.

There are now new "high index lenses," made from a variety of polymers that are thinner than CR-39 and polycarbonate lenses.

12.9 SOL–GEL

In the sol–gel process, ceramic polymer precursors are formed in solution at ambient temperature; shaped by casting, film formation, or fiber drawing; and then consolidated to furnish dense glasses or polycrystalline ceramics. The most common sol–gel procedures involve alkoxides of silicon, boron, titanium, and aluminum. In alcohol–water solution, the alkoxide groups are removed stepwise by hydrolysis under acidic or basic catalysis and replaced by hydroxyl groups, which then form M–O–M (metal–oxygen–metal) linkages. Branched polymer chains grow and interconnect forming a network that can span the entire solution volume. At this point, the gel point, the viscosity, and elastic modulus rapidly increase.

The gel is a viscoelastic material composed of interpenetrating liquid and solid phases. The network retards the escape of the liquid and prevents structural collapse. The shapes formed by casting, drawing of fibers, or film formation are locked in by the gel formation. Some gels are oriented by drawing or shearing. The gel is dried by evaporation forming a xerogel or by supercritical fluid extraction giving an aerogel. Consolidation to dense glasses or ceramics is carried out by thermal treatment and sintering.

Since both aerogels and xerogels have high surface areas and small pore diameters they are used as ultrafiltration media, antireflective coatings, and catalysts supports. Final densification is carried out by viscous sintering.

The rate of silicate sol and gel formation is pH and water–alcohol-sensitive as is the solubility of the amorphous silica that is formed. Silica networks are based on $(SiO_4)^{-4}$ tetrahedra modified by (O_3 Si-O^-, M^+) units and often addition of boron oxide, aluminum oxide, titanium IV oxide, or zirconium IV oxide.

The nature of the reactants can be varied giving various silicate-like products. Equation 12.17 describes the formation of borosilicate glasses using the sol–gel approach.

$$\mathrm{NaOR + B(OR)_3 + Si(OR)_4 + H_2O \rightarrow NaOH + B(OH)_3 + Si(OH)_4 + ROH} \tag{12.17}$$

$$\mathrm{NaOH + B(OH)_3 + Si(OH)_4 \rightarrow Na_2O \bullet B_2O_3 \bullet SiO_2 \bullet H_2O \rightarrow Na_2O \bullet B_2O_3 \bullet SiO_2 + H_2O} \tag{12.18}$$

The use of organically modified silicates (ceramers) gives a wide range of products with a variety of structures and properties. Such ceramers have been used as adhesives for glass surfaces, protective coating for medieval stained glass, and as scratch-resistant coatings for plastic eyeglass lenses. They have also been used in the reinforcement of plastics and elastomers, and their nanoscale pores allow their use as porous supports, and as selective absorbents.

Sol–gel preparations of tetraethoxysilane can be spun into fibers once the appropriate viscosity has been achieved. These fibers are only slightly weaker than silica–glass fibers.

Hybrid materials have been made by incorporating end-capped poly(tetramethylene oxide) blocks to tetramethoxysilane sol–gel glasses. These materials have high extensibility with interdispersed organic and inorganic regions.

12.9.1 AEROGELS

Aerogels are highly porous materials where the pore sizes are truly on a molecular level, less than 50 nm in diameter. This gives a material with the highest known internal surface area per unit weight. The surface area of 1 oz. is equal to 10 football fields, over 1000 m^2 in 1 g.

Porous materials can be either open-pored such as a common sponge, or closed-pored such as the bubble-wrap packaging. Aerogels are open-pored materials such that unbonded material can move from one pore to another.

Although in the gel state the preaerogel has some flexibility, as a solid, aerogels behave like a fragile glass. It may be very strong in comparison to its weight, but it is very light. Aerogels are more durable when under compression, which can be simple such as sealing the aerogel sample in a typical food sealer packing. Aerogels are best cut using a diamond-coated saw similar to that used by rock cutters to slice rocks.

When handled, aerogel samples will initially appear to exhibit some flexibility but then burst into millions of pieces. For large arrays of atoms, such as solid metals and polymers below their glass transition temperature, energy can be absorbed through bond flexing or bending. For polymers between their glass transition and melting points, kinetic energy can also be absorbed through segmental movement. Silica aerogel, being an inorganic polymer in the glassy state at room temperature, is a brittle material. As force is applied, there is very little bond flexing, so that the applied kinetic energy results in the collapse of the network with the force of impact spread over a large part of the aerogel and over a time because of the time required to transfer this energy from one cell to another within the aerogel matrix. Because the aerogel is open-pored, gas contained within the solid is forced outwards as collapse occurs. The frictional forces caused by the gas passing through a restricted opening are indirectly proportional to the square of the pore diameter. Because the pore sizes are small, the rapidly moving gas also absorbs a lot of the energy. Thus, energy is absorbed by the aerogel through both collapse of the solid network structure and release of the gas within the aerogel.

Aerogels that are about 2–5 nm in diameter have large surface/volume ratios on the order of $10^9\ m^{-1}$ and high specific surface areas approaching 1000 m^2/g. Such large surface/volume ratios make the surface particularly active and potential materials as catalysts, absorbents, and catalyst substrates.

The precise chemical makeup of the surface depends on the materials used to make the aerogel and method of processing. Typical aerogel sequences give products whose surfaces are rich in hydroxyl groups. Because of the high surface area, –Si–OH groups act as weak acids and are reactive in typical Lewis acid–base reactions. As noted earlier, aerogels have many hydrogen-bonding hydroxyls at their surface making aerogels extremely hygroscopic. Dry aerogel materials will increase their weight by 20% through uptake of moisture from the air. This absorption is reversible and appears to have little or no effect on the aerogel. Water is removed through heating to 100°C–120°C.

Although adsorption of water vapor has little effect on aerogels, contact with liquid water has devastating effects. When water enters the nanometer-size pores, the surface tension of the water exerts capillary forces sufficient to fracture the silica backbone resulting in a collapse of the complex matrix structure. This tendency to be attacked by water is overcome through conversion of the surface polar –OH groups to nonpolar –OR groups. The "R" is typically a trimethylsilyl group though any aliphatic group would work. Conversion can be accomplished within the wet stage (preaerogel) or after the supercritical drying. These treatments result in an aerogel that is called "hydrophobic" aerogel, which is stable in water.

The pore size of aerogels varies. The International Union of Pure and Applied Chemistry classifies materials with pore sizes of less than 2 nm as "micropores," 2–50 nm are called "mesopores," and those greater than 50 nm in diameter are called "macropores." While aerogels have some pores that fall within the micropore region, the majority of pores are in the mesopore region.

Most of the aerogels produced today are described as being transparent. While it might be assumed that since aerogels are made of the same material as window glass and quartz (SiO_2) that they would be transparent, this is not necessarily the case. Transparency requires a number of factors. Thus, the so-called smokey and white quartz are colored because of the presence of impurities. Mixtures of amorphous and crystalline silicon dioxide can be made that are not transparent. The size and distribution of reflecting and refractive sites are important factors in determining if a material is transparent with the theme of "sameness" contributing to making a material transparent.

The majority of light we see is scattered light, i.e., light that reaches our eyes in an indirect manner. The scattering phenomenon is what gives us blue skies, white to gray clouds, and poor visibility in fog. This scattering is not simply reflecting but results from the interaction of light with an inhomogeneous site. Light scattering photometry is used to determine the size of polymers. Scattering is most effective when the scattering particle size is about that of the wavelength of the light. For visible light, this occurs with scattering sites that are about

400–700 nm. Scattering centers that are much less in size than the incoming light wavelength are much less effective at scattering the light. Since the particle sizes in an aerogel are much smaller than the individual sites they are ineffective scattering sites. Similar to classical polymer chains, where the entire chain or segments act as a scattering site, clusters of individual sites within the aerogel act as scattering sites. Most of these scattering sites are again smaller than the wavelength of visible light, but some are within the range to scatter visible light so that a soft reflected light results. The different-sized scattering sites and variable wavelengths present in visible light cause a reddening of the transmitted light (red light has a longer wavelength and is scattered less by small clusters present in the aerogel) resulting in the blue appearance of the reflected light from the aerogel.

The good visible light transmission and insulting power make aerogel, materials of interest in window manufacturing. The visible transmission spectra of light show little absorption in the range of about 300–2700 nm giving aerogels a good visible light "window" making them attractive for day-lighting applications. Aerogels provide about 40-fold more insulation than does fiberglass. While such aerogels may eventually be used as the entire window component, for the present time they may act as the material sandwiched between two pairs of clear plastic or glass. Thermoglass is generally simply glass sheets that are separated by a vacuum. The seals on such thermoglass often spring small leaks causing diminished insulation properties. Aerogel inner cores will not suffer from this problem. Currently, about 40%–50% of a house's heating bill literally goes out of the window because of lost heat or cold through windows. A single 1 in. thick glass pane of aerogel offers the insulation equivalent to over 30 windowpanes of R-20 insulation-rated glass.

Another commercial area that is being considered is the use of aerogels as nanocomposite materials. Approaches are varied. In one approach, material is added to the silica sol before gelation. The material can be inorganic, organic, polymeric, bulk fibers, woven cloths, etc. The additional material must be able to withstand the subsequent processing steps including carbon dioxide drying. The added material must be present in a homogeneous manner throughout the system. Gentle agitation appears to be sufficient to give a product with decent homogeneity. Aerogels may be good materials for optical sensors. They have good visible transparency, high surface area, good temperature and chemical stabilities, and facile transport of gases through their pores.

12.10 SILICON DIOXIDE (CRYSTALLINE FORMS)—QUARTZ FORMS

Just as silicon dioxide forms the basis of glass, so also does it form the basis of many of the rocks, grains of sand, and dirt particles that compose the earth's crust. Most rocks are inorganic polymers, but here we will deal with only a few of these containing significant amounts of silicon.

Silicon oxide crystallizes in mainly three forms—quartz, tridymite, and cristobalite. After feldspar, quartz is the most abundant material in the earth's crust, being a major component of igneous rocks and one of the most common sedimentary materials, in the form of sandstone and sand. Quartz can occur as large (several pounds) single crystals, but is normally present as granular materials. The structure of quartz (Figure 12.4) is a three-dimensional network of six-membered Si–O rings (three SiO_4 tetrahedra) connected such that every six rings enclose a 12-membered Si–O (six SiO_4 tetrahedra) ring.

Quartz is found in several forms in all three major kinds of rocks—igneous, metamorphic, and sedimentary. It is one of the hardest minerals known. Geologist often divides quartz into two main groupings—course crystalline and cryptocrystalline quartz. Course crystalline quartz includes six-sided quartz crystals and massive granular clumps. Some colored varieties of coarse crystalline quartz crystals, amethyst and citrine, are cut into gem stones.

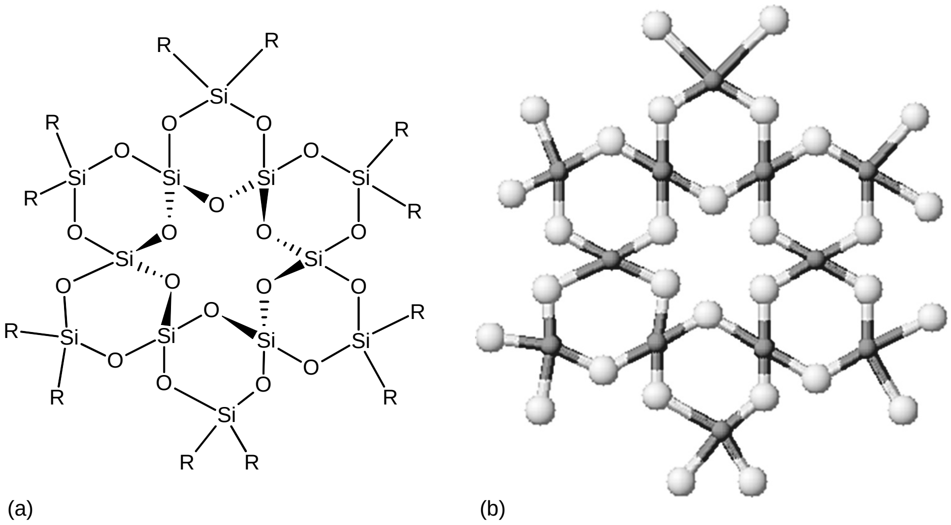


FIGURE 12.4 Structure of crystalline silicon dioxide (SiO_2) tetrahedra found in quartz (a) structural formula and (b) ball and stick model of one unit cell.

Others include pink (rose), purple, and milky quartz, but most coarse crystalline quartz is colorless and transparent. Sandstone is a ready example of granular quartz. Color is a result of the presence of small amounts of metal cations such as calcium, iron, magnesium, and aluminum.

Cryptocrystalline forms contain microscopic quartz crystals and include the chalcedony grouping of rocks such as chert, agate, jasper, and flint.

Quartz exhibits an important property that allows the piezoelectric effect. When pressure is applied to a slice of quartz, it develops a net positive charge on one side and a negative charge on the other. This phenomenon is the piezoelectric generation of a voltage difference across the two sides of the quartz crystal. Furthermore, the same effect is found when pressure is applied, not mechanically, but through application of an alternating electrical field with only certain frequencies allowed to pass through the crystal. The frequencies allowed to pass vary with the crystal shape and thickness. Such crystals are used in radios, televisions, and radar. This effect also forms the basis for quartz watches and clocks. Voltage applied to a quartz crystal causes it to expand and contract at a set rate, producing vibrations, which are then translated into a uniform measure of time.

Although quartz crystals are suitable for the production of optical lenses, most lenses are manufactured from synthetically produced quartz due to the scarcity of good-grade large quartz crystals.

Feldspars are the most abundant minerals in the earth's crust, accounting for about 60% of all igneous rocks. They are derivatives of silica in which about one-half or one-quarter of the silicon atoms have been replaced by aluminum. Feldspar is used in the manufacture of certain types of glass and pottery. Some feldspar crystals, such as moonstone (white perthilte), Amazon stone (green microcline), and multicolored labradorite, are used as gem stones and in architectural decorations. Some are used as a coating and filler in the production of paper.

Granite is a hard crystalline rock chiefly composed of quartz and feldspar. It is used in building bridges and building where great strength is needed. It is also employed in the construction of monuments and gravestones since it can be polished giving a lasting luster and because of its ability to withstand ware and tear by the natural elements.

Sand is loose grains of minerals or rocks, larger than silt but smaller than gravel. Soil contains mineral (often in the form of small sand granules) and organic matter.

Micas are also composed of Si–O tetrahedra. The anionic charge on the silicate sheet is the result of the replacement of silicon by aluminum. Cations such as potassium are interspaced between these negatively charged sheets. Some micas are used in construction and electrical engineering applications. Synthetic mica is manufactured on a large scale for industrial consumption in coatings, as fillers, etc. Micas are one of the many layered Si–O-intense materials found in nature.

12.11 SILICON DIOXIDE IN ELECTRONIC CHIPS

Silicon dioxide plays a critical role in the electronics industry. The silicon used to produce silicon chips is derived from silicon dioxide. Semipure silicon dioxide (to about 99%) is prepared from the reaction of silicon dioxide with coke (a poor grade of graphite) using high temperature and an electronic arc.

$$SiO_2 + C \rightarrow Si + CO_2 \tag{12.19}$$

Even so, this level of purity falls far short of that needed to produce chips used in computers. The purity required is about 99.9999996 or a level of impurity of about one part in a billion. This is achieved through multistep processes. One of these requires the silicon to be heated with HCl at high temperatures forming the desirable volatile trichlorosilane. The vapor is condensed, then purified using distillation and absorption columns. The trichlorosilane is reacted with hydrogen gas at about 1200°C depositing polycrystalline chip-grade silicon. The other product of this reaction is HCl, which can be again used to create more trichlorosilane, thus eliminating the production of unwanted by-products.

$$Si + HCl \rightarrow HSiCl_3 \tag{12.20}$$

$$HSiCl_3 + H_2 \rightarrow Si + HCl \tag{12.21}$$

Silicon dioxide is also used to insulate regions of the integrated circuit. Here silicon dioxide is grown on the silicon surface by heating it to about 1000°C in the presence of oxygen.

$$Si + O_2 \rightarrow SiO_2 \tag{12.22}$$

An alternate approach employs heating gaseous tetraethoxysilane to form layers of silicon dioxide.

$$Si(OC_2H_5)_4 \rightarrow SiO_2 + 2H_2O + C_2H_4 \tag{12.23}$$

12.12 SILICON DIOXIDE IN OPTICAL FIBERS

Today, almost all telecommunication occurs via optical fibers rather than metallic wires. Signal transmission with metallic wires was via electrons, while transmission through optical fibers is via photons. For a rough comparison, two small optical fibers can transmit the equivalent of over 25,000 telephone calls simultaneously or in one second the information equivalent to about 2 h of TV shows. On a weight basis, 1 g of optical fiber has the transmission capability of about 300,000 g of copper wire. The signal loss must be small. For a typical system the loss over a 10-mile distance is around that found for the transmission of light through an ordinary pane of window glass.

The optical fibers connect the two longest links of a typical optical fiber communications system. In brief, an input signal enters an encoder generally in an electrical form with the encoder transforming it into digitized bits of 1's and 0's. This electrical signal is then converted into an optical message in an electrical–optical converter. This converter is often a semiconductor laser that emits monochromatic coherent light. The message then travels through optical fibers to its target destination. Where the distance is large, such as between countries, repeater devices are employed that amplify the signal. Finally, at its destination, the message, in photonic form, is reconverted to an electric signal and then decoded.

The optical fiber is formed from a combination of polymeric materials. It typically consists of a core, cladding, and coating. The core does the actual transmission of the photons; the cladding constrains the light so it will travel within the core with little signal power loss and little pulse distortion; and the coating helps protect the inner material from damage and external pressures. There is a variety of materials that can be used in the construction of the optical fiber. Based on the core–cladding combination, there are three types of optical systems—the step index, graded index, and single mode fibers.

Most of the "long-distance" systems use high purity silica glass as the core material. These fibers are thin with a thickness of the order of 5–100 mm. Containment and retention of the signal is made possible because of the use of laser light and its total reflectance as it travels through the fiber. This containment is accomplished by using cladding and coating materials differing in refractive indexes from the core material. In the step-index approach, the index of refraction of the cladding is slightly less than that of the core. Here the output pulse is a little broader than the input because the light travels slightly different paths as they travel through the fiber. This is overcome by the use of graded index materials where impurities such as boron oxide or germanium dioxide are added to the silica glass so that the index of refraction varies parabolically across the cross-section of the optical fiber core. Thus, the velocity of light varies according to where it is within the core, being greater at the periphery and less at the center. Thus, light that must travel a longer pathway through the outer periphery travel faster than those close to the center balancing themselves to minimize distortion.

Organic core optical materials are also in use. Such materials, in comparison to the silica-cored materials, are lighter in weight, offer better ductility, have larger core diameters, and are less sensitive to vibrational stresses. They are often considered for shorter distances. For the step-index approach, where the refractive index of the cladding material should be a little less than that of the core material, a number of materials are possible. Two common combinations are PS core with poly(methyl methacrylate) cladding and a poly(methyl methacrylate) core with fluorinated polymers as the cladding. Since the fiber core is to be optically clear, amorphous organic polymers are used. Moreover, to avoid unwanted scattering, the polymer must be of high purity since impurities will cause sites of differing refractive indexes and the associated difference in the speed of propagation of the signal. The organic fibers are generally made by melt spinning with the core–cladding structure formed by extrusion.

The types of optical loss for both silica glass-cored fibers and organic-cored fibers are similar, but do differ in relative importance. In the visible wavelength region there are both absorption and scattering losses. Absorption losses include higher harmonic molecular vibration modes in the infrared region and electronic transitional absorption in the UV region. Scattering losses include Rayleigh scattering and loss due to imperfections in the waveguide structure, mismatching of the core–cladding boundary interface, and birefringence due to fiber drawing as the fiber was formed.

12.13 ASBESTOS

Asbestos has been known and used for over 2000 years. Egyptians used asbestos cloth to prepare bodies for burial. The Romans called it *aminatus* and used it as a cremation cloth and for lamp wicks. Marco Polo described its use in the preparation of fire-resistant textiles in the

13th century. Asbestos is not a single mineral but rather a grouping of materials that give soft, threadlike fibers. These materials will serve as an example of two-dimensional sheet polymers containing two-dimensional silicate $(Si_4O_{10})^{-4}$ anions bound on either or both sides by a layer of aluminum hydroxide ($Al(OH)_3$; gibbsite) or magnesium hydroxide ($Mg(OH)_2$; brucite). Aluminum and magnesium are present as positively charged ions. These cations can also contain varying amounts of water molecules associated with them as hydrates. The spacing between silicate layers varies with the nature of the cation and amount of its hydration.

Due to its fibrous nature and ability to resist elevated temperatures (compared with most organic-based fabrics) it is used to make fabrics for the production of fire-resistant fabric including laboratory glove-wear. Shorter fibers were used in electrical insulation, building insulation, and in automotive brake linings. Though asbestos has been known for thousands of years, it has only recently become known that asbestos can be dangerous. For instance, asbestos miners and manufacturing personnel who worked with it for 20 years or longer are 10 times more likely to contract asbestosis. Families of these workers and those living near the mines also have a greater than average chance of getting asbestosis. Asbestosis is a disease that blocks the lungs with thick fibrous tissue, causing shortness of breath, and swollen fingers and toes. Bronchogenic cancer (cancer of the bronchial tubes) is prevalent among asbestos workers who also smoke. Asbestos also causes mesothelioma, a fatal cancer of the lining of the abdomen or chest. These diseases may lay dormant for many years after exposure. It is believed that these diseases are caused by asbestos particles (whether asbestos or other sharp particles) about 5–20 μm in length corresponding to the approximate sizes of the mucous openings in the lungs. Thus, they were trapped in the mucous openings. Because they are sharp, they cut the lining when people cough. Scar tissue and the repeated healing process cause scar tissue build up and the opportunity for the commencement of mutations.

12.14 POLYMERIC CARBON—DIAMOND

Just as carbon serves as the basic building element for organic materials, so also does it form a building block in the world of inorganic materials. Elemental carbon exists in many different forms including the two longest known—diamond and graphite. Graphite is the more stable allotrope of carbon, with graphite readily formed by heating diamonds.

Natural diamonds (Figure 12.5) are believed to have been formed millions of years ago when concentrations of pure carbon were subjected by the earth's mantle to great pressures and heat. They are the hardest known natural material. The majority of diamonds (nongem) are now man-made. Most of the synthetic diamonds are no larger than a grain of common sand. The major use of synthetic diamonds is as industrial shaping and cutting agents to cut, grind, and bore (drill). By 1970 General Electric was manufacturing diamonds of gem quality and size through compressing pure carbon under extreme pressure and heat. It was found that addition of small amounts of boron to diamonds causes them to become semiconductors. Today, such doped diamonds are used to make transistors.

Although diamonds can be cut, shaping is done by trained gem cutters striking the rough diamond on one of its cleavage plates, which are called faces and represent sites of preferential cleavage and reflection of light. This balance between strength and flexibility, crystalline and amorphous regions, is demonstrated to one extreme by diamonds that are very crystalline resulting in a strong, inflexible, and brittle material.

12.15 POLYMERIC CARBON—GRAPHITE

While diamond is the hardest naturally occurring material, the most common form of crystalline carbon is the much softer and flexible graphite. Graphite occurs as sheets of

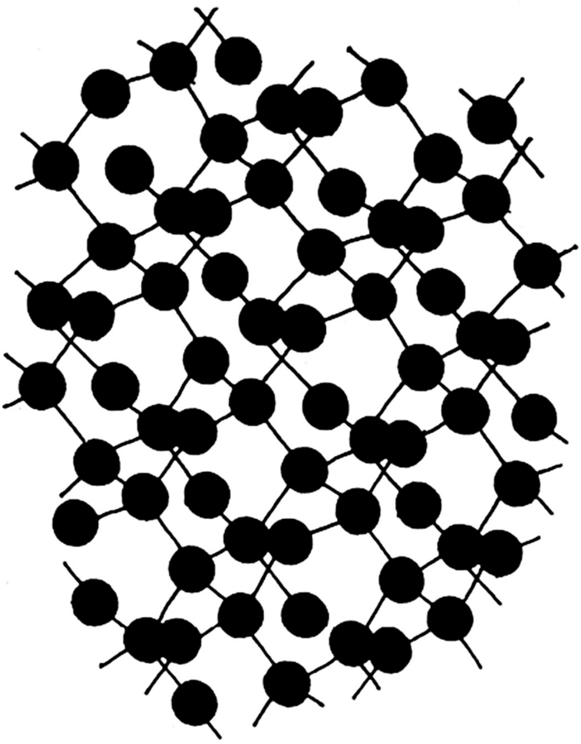


FIGURE 12.5 Representation of diamond where each carbon is at the center of a tetrahedron composed of four other carbon atoms.

hexagonally fused benzene rings (Figure 12.6) or "hexachicken wire." The bonds holding the fused hexagons together are traditional covalent bonds. The bonds holding the sheets together are weaker than the bonding within the sheets consisting of a weak overlapping of pi-electron orbitals. Thus, graphite exhibits many properties that are dependent on the angle at which they are measured. They show some strength when measured along the sheet, but very little strength if the layers are allowed to slide past one another. This sliding allows the graphite its flexibility, much like the bending of bundles of proteins sliding past one another allowing our hair flexibility. The fused hexagons are situated such that the atoms in each layer lie opposite to the centers of the six-membered rings in the next layer. This arrangement further weakens the overlapping of the pi-electrons between layers such that the magnitude of layer-to-layer attraction is on the order of ordinary secondary van der Waals forces. The "slipperiness" of the layers accounts for graphite's ability to be a good lubricant.

The variance of property with angle of applied force, light, magnetism, etc., is called anisotropic behavior. Calcite is anisotropic in its crystal structure, resulting in a dependency of its interaction with light on the angle of incidence of the light.

As with diamond, graphite's discovery and initial usage is lost in antiquity. It was long confused with other minerals such as molybdenite (MoS_2). At one time it was known as plumbago (like lead), crayon noir, silver lead, black lead, and *carbo mineralis*. Werner in 1789 first named it *graphit*, meaning (in Greek) "to write."

The Acheson process for graphite production begins by heating a mixture of charcoal, or coke, and sand. The silica is believed to be reduced to silicon that combines with carbon forming silicon carbide, which subsequently dissociates into carbon and silicon. The silicon vaporizes and the carbon condenses forming graphite. Graphite is also produced using other techniques.

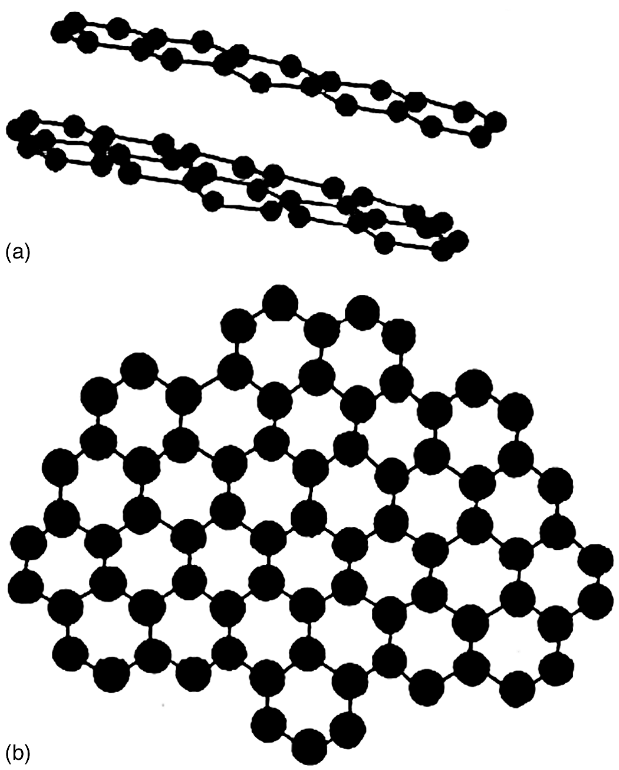


FIGURE 12.6 Representations of graphite emphasizing the layered (a) and sheet (b) nature of graphite.

Today, graphite is mixed with clay to form the “lead” in pencils. It conducts electricity and is not easily burned, so many industrial electrical contact points (electrodes) are made of this material. Graphite is a good conductor of heat and is chemically inert, even at high temperatures. Thus, many crucibles for melting metals are graphite-lined. It has good stability to even strong acids and is thus employed to coat acid tanks. It is also effective at slowing down neutrons, and so composite bricks and rods (often called carbon rods) are used in some nuclear generators to regulate the progress of the nuclear reaction. Graphite’s slipperiness allows its use as a lubricant for clocks, door locks, and hand-held tools. It is also the major starting material for the synthesis of synthetic diamonds and is sometimes used as a component of industrial coatings. Dry cells and some types of alkali storage batteries also employ graphite. Graphite fibers are used for the reinforcement of certain composites.

12.16 INTERNAL CYCLIZATION—CARBON FIBERS AND RELATED MATERIALS

There are a number of important polymers that are formed through internal cyclization. In almost all cases these are five- and six-membered rings with the vast majority being six-membered. The tendency to form six-membered rings is related to a statistical feature. In studying the most probable distances from the beginning point using random statistics for units with a bond angle of about 109.5° (for a tetrahedral), the most probable distance for a chain of six units long is back at the starting point. The number of units required before the most probable distance is the starting point is dependent upon the bond angle and is called the *Kuhn element*. As noted earlier, the Kuhn element for connected methylenes is six. The Kuhn

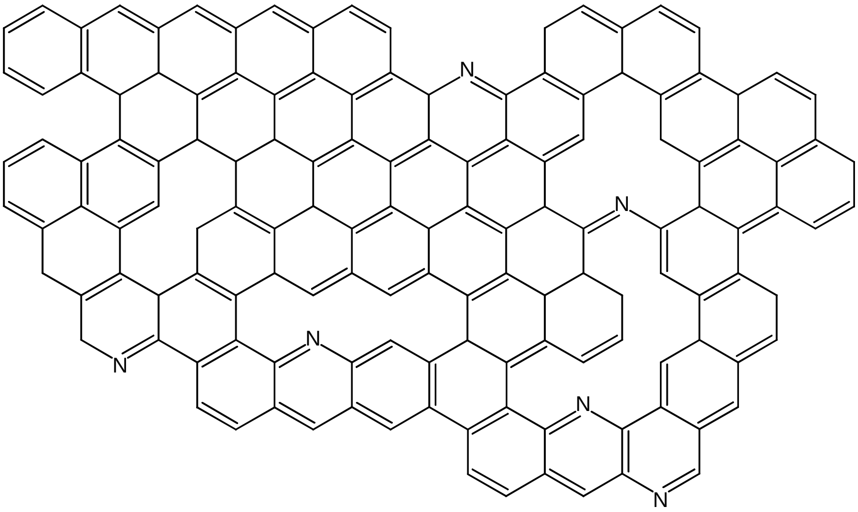


FIGURE 12.7 Idealized structure of “black orlon.”

element for sp^2 geometry is not six, but in this case, the driving force is the formation of six-membered rings with three alternating pi bonds, i.e., the formation of the aromatic structure.

Often these internal cyclizations are incomplete giving products with mixed moieties. Even so, such internal cyclization is the source of a number of interesting and important polymers. A number of ladderlike structures have been synthesized from the internal cyclization of polymers. Following are several examples that illustrate this. The most important commercial products are those utilized to form the so-called carbon fibers.

Carbon fibers, and associated composite materials, are the result of internal cyclization. Polyacrylonitrile, when heated, undergoes internal addition forming condensed polycyclic material called “black orlon.” Further heating to about 1000°C removes the hydrogen atoms and most of the nitrogens giving a polyaromatic structure containing about 95% carbon (Figure 12.7). Further heating to about 2800°C gives a product with almost 99% carbon. These products can be forced through tiny holes to form tiny fiber-like materials, fibrals, that are combined to give fibrous materials that can finally be woven together to give fabrics. The fibrals, fibers, and fabrics act as the fibrous portion of many high-strength composite materials. These fibers are lightweight, very strong, chemically inert, and can form semiconductor and conductor materials.

Diene polymers undergo cyclization in the presence of cationic initiators such as sulfuric acid. 1,2- and 3,4-diene polymers undergo this cyclization forming extensive fused ring groupings.

The polymerization of butadiene using certain catalytic systems such as butyl lithium and tetramethylenethylene diamine gives poly(1,2-polybutadiene). The polybutadiene, in turn, can undergo internal cyclization via cationic reactions forming a sort of linear saturated polycyclohexane. Further heating, resulting in dehydrogenation, with chloranil gives a fused ring product similar to that of carbon fibers when heated to about 1500°C (Figure 12.8). This material is sold under the trade name Pluton by 3M. This sequence is described below. While the final product is insoluble and infusible, prespinning is done on the soluble saturated intermediate.

12.17 CARBON NANOTUBES

There are several materials that form “nanotubes” including boron–nitrogen compounds. Here we will focus on nanotubes derived from carbon. Carbon nanotubes (CNTs) have

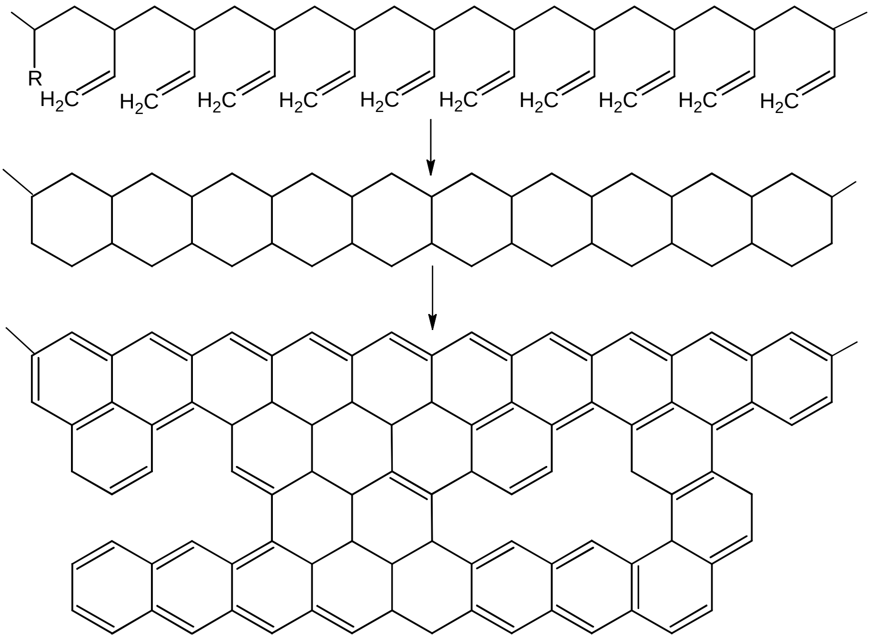


FIGURE 12.8 Idealized structures for the synthesis of carbonlike materials from poly(1,2-butadiene).

probably been made in small amounts since the first fires reduced trees and organic material to ashes. It was not until recently, as part of the so-called nano revolution, that we first recognized the existence of these nanotubes. In 1991, Sumio Iijima, NEC Fundamental Research Laboratory in Japan, first observed CNTs as by-products of the arc-discharge synthesis of fullerenes.

CNTs are carbon allotropes that have attracted much attention. Some have suggested that CNTs will be one of the most important 21st century materials because of the exceptional properties and ready abundance of the feedstock, carbon. CNTs are generally classified into two groups. Multiwalled CNTs (MWCNTs) are comprised of 2–30 concentric graphitic layers with diameters ranging from 10 to 50 nm with lengths that can exceed 10 μm. Single-walled CNTs (SWCNTs) have diameters ranging from 1.0 to 1.4 nm with lengths that can reach several micrometers.

An ideal CNT can be envisioned as a single sheet of fused hexagonal rings, i.e., graphite, that has been rolled up forming a seamless cylinder with each end "capped" with half of a fullerene molecule. SWCNT can be thought of as the fundamental cylindrical structure, with MWCNTs simply being concentric tubes. They can also be conceived of as being the fundamental building block of ordered arrays of SWCNTs called ropes.

12.17.1 STRUCTURES

CNTs are composed of sp^2 bonds similar to those in graphite. They naturally form ropelike structures where the ropes are held together by van der Waals secondary forces.

Geometrically, CNTs can be described in terms of a two-dimensional graphene (graphite) sheet. A chiral vector is defined on the hexagonal lattice as

$$C_\mathrm{h} = nx + my \tag{12.24}$$

where x and y are unit vectors, and n and m are intergers, also tube indices. The chiral angle is measured relative to the direction defined by nx.

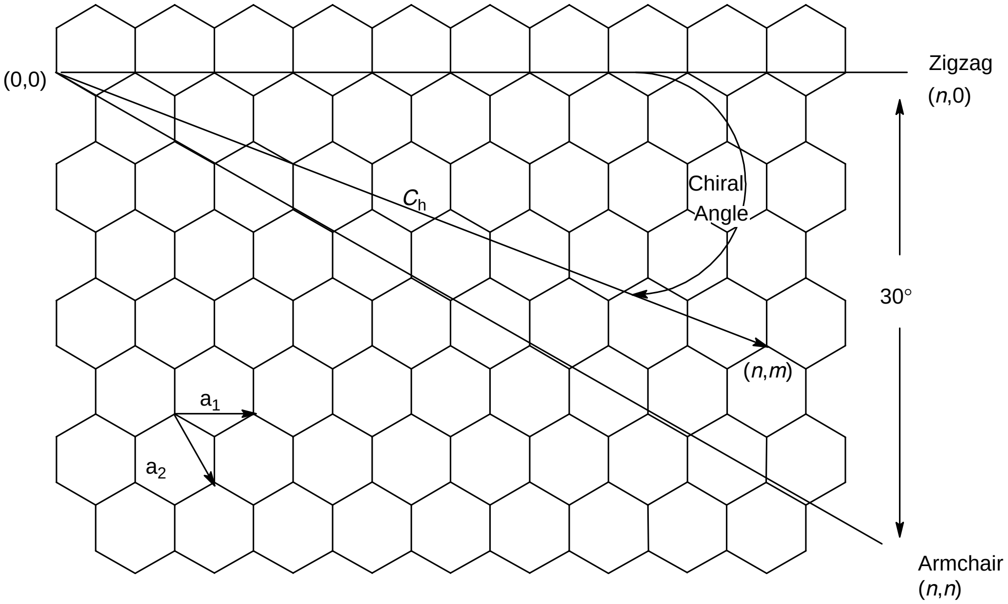


FIGURE 12.9 Graphite sheet representation showing the θ or chiral angle. For a chiral angle of 0°, the structure is a zigzag; for 30° it is an armchair; and in between it is helical. The figure is drawn with a 30° angle between the zigzag and armchair.

When the graphene sheet is rolled up forming a nanotube, the two ends of the chiral vector meet one another. The chiral vector thus forms the circumference of the CNTs circular cross-section. Different values of *n* and *m* give different nanotube structures with different diameters (Figure 12.9).

There are three general types of CNT structure (Figure 12.10). The zigzag nanotubes correspond to (*n*,0) or (0,*m*) and have a chiral angle of 0°. The carbon–carbon position is parallel to the tube axis. Armchair nanotubes have (*n*,*n*) with a chiral angle of 30°. The carbon–carbon positions are perpendicular to the tube axis. Chiral nanotubes have general (*n*,*m*) values and a chiral angle of between 0° and 30°, and as the name implies, they are chiral.

In real life, nothing is perfect. As is the case with CNTs the defects are mainly inclusion of wrong-membered rings. Pentagonal defects, i.e., the replacement of a hexagonal with a five-membered ring, result in a positive curvature causing the tube to curve inwards like a horseshoe. The closure of an open cyclindrical surface necessarily involves topological defects—often formation of pentagons. Heptagonal defects result in a negative curvature with the lattice looking expanded around the defect.

The tendency to include pentagonal units can be seen by comparing the presence of pentagonal units in fullerene structures. The C_{60} structure contains 12 pentagons and 20 hexagons. The larger the fullerenes the smaller the ratio of pentagons/hexagons. This is consistent with the use of pentagons to “cause” sharper bends and greater curvature in comparison to hexagons. Interestingly, fullerene C_{60} is one of the most strained molecules known but it exhibits good kinetic stability. It begins to decompose at about 750°C. There are a number of higher numbered (carbon number) fullerenes including C_{70}, C_{76}, C_{78} (two geometric isomers), $C_{80}, \ldots .$ Fullerenes can act as a source of the CNTs with the different-sized fullerenes producing different nanotubes. The three general structures of nanotubes can be produced using different fullerenes with C_{60} giving armchair nanotubes, C_{70} giving zigzag structures, and C_{80} giving helical forms of nanotubes. Figure 12.10 illustrates representations of these three fullerenes.

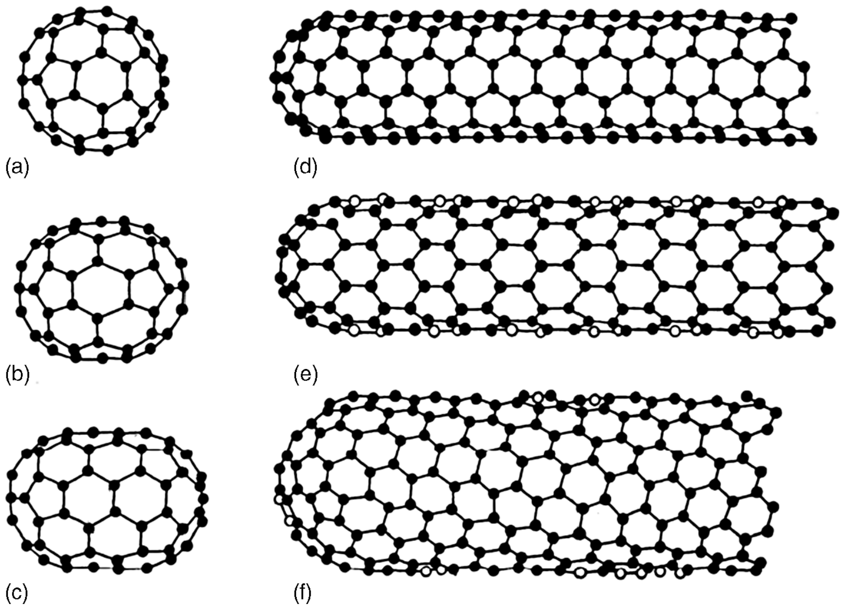


FIGURE 12.10 Representations of the three major structural forms of carbon nanotubes: armchair (d), zigzag (e), and helical (f) and of C_{60} (a), C_{70} (b), and C_{80} (c) fullerene structures.

This difference in structure also influences the electrical conductivity with the armchair form being conductive or metal-like in its conductivity, and most of the other forms act as semiconductors.

Two other forms of CNTs are recognized. The fullerite is a highly incompressible form with a diamondlike hardness. The torus is a donut-shaped nanotube. These circular nanotubes have extremely high magnetic moments and outstanding thermal stability. The particular properties are dependent on the radius of the tube.

One of the major reasons for the intense interest in CNT is their extreme and varied properties. Table 12.7 contains a comparison between SWCNTs and competitive materials and techniques. Another reason is that CNTs are produced from readily available inexpensive materials and are being considered for use as both bulk materials, such as in composites and clothing, and as components in computers, electrical devices, etc.

The number of potential and real uses where an essential ingredient is CNTs is growing almost daily. The length and kind of tubes formed can be controlled. Because the starting material is so plentiful and inexpensive, this is an area where most of the limits are ones we impose on ourselves. Following is a discussion of some of the application areas for CNTs.

Electrical—Nanotubes can be metallic or semiconducting, depending on their diameters and helical arrangement. Armchair ($n = m$) tubes are metallic. For all other tubes (chiral and zigzag) when tube indices $(n + m)/3$ are a whole number integer, the tubes are metallic, otherwise they are semiconducting. CNTs can in principle play the same role as silicon does in electronic circuits, but on a molecular scale where silicon and other standard semiconductors cease to work. SWCNT bundles have been used to construct elementary computing circuits known as logic gates. Applications include composites and coatings for enclosures and gaskets and as stealth material. They perform better than tungsten filaments in incandescent lamps.

Conductive Adhesives and Connectors—Because of their molecular-level characteristics they have been used to connect electronic circuits and to bind together electrical units acting as a molecular solder.

TABLE 12.7
Comparison between Selected Properties of Single-Walled CNTs (SWCNTs) and Competitive Materials or Techniques

Property	SWCNTs	Comparison
Size	0.6–1.8 nm in diameter	Electron beam lithography can create lines 50 nm wide and a few nm thick
Density	1.33–1.40 g/cm^3	Aluminum has a density of 2.7 g/cm^3 and titanium has a density of 4.5 g/cm^3
Tensile strength	~45 billion pascals	High-strength steel alloys break at about 2 billion pascals
Resilience	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries
Current carrying capacity	Estimated at 1 billion A/cm^3	Copper wires burn out at about 1 million A/cm^3
Heat transmission	Predicted to be as high as 6000 W/m·K	Diamond transmits 3320 W/m·K
Field emission	Can activate phosphors at 1–3 V if electrodes are spaced 1 μm apart	Molybdenum tips require fields of 50–100 V/μm and have limited lifetimes
Temperature stability	Stable up to 2800°C in vacuum, 750°C in air	Metal wires in microchips melt at 600°C–1000°C

Mechanical—CNTs have superior resilience and tensile strength. They can be bent and pressed over a large angle before they begin to ripple or buckle, finally developing kinks. Until the elastic limit is exceeded, the deformations are elastic disappearing when the stress is removed. It is envisioned that buildings and bridges built from them may sway during an earthquake rather than fracturing and crumbling.

Field Emission—When stood on end, electrified CNTs act as a lightning rod concentrating the electrical field at their tips. While a lightning rod conducts an arc of electricity to a ground, a nanotube emits electrons from its tip at a rapid rate. Because the ends are so sharp, the nanotube emits electrons at lower voltages than do electrodes made from other materials, and their strength allow nanotubes to operate for longer periods without damage. Field emission is important in several industrial areas including lighting and displays. Commercial use of CNTs as field emitters has begun. Vacuum-tube lamps in six colors have been developed that are twice as bright as conventional light bulbs, longer-lived, and at least 10 times more energy-efficient as conventional light bulbs.

Hydrogen and Ion Storage—While we can picture CNTs as being composed of hexagonal carbon atoms with lots of empty space between the carbons, atoms "thrown" against them generally just bounce off. Even helium atoms at an energy up to 5 eV do not readily penetrate the nanotube. Thus the graphene sheet and CNTs are really membranes or fabrics that are one atom thick made of the strongest material that is also impenetrable (to a limit). Thus, CNTs can be used for hydrogen storage in their hollow centers with release being controlled allowing them to act as inexpensive and effective fuel cells.

Chemical and Genetic Probes—Nanotube-tipped atomic force microscopes can trace a strand of DNA and identify chemical markers that reveal DNA fine structure. A miniaturized sensor has been constructed based on coupling the electronic properties of nanotubes with the specific recognition properties of immobilized biomolecules by attaching organic molecules handles to these tubular nanostructures. In one study, the pi-electron network on the CNT is used to anchor a molecule that irreversibly adsorbs to the surface of the SWNT. The anchored molecules have a "tail" to which proteins, or a variety of other molecules, can be covalently attached. The result is that these molecules are immobilized on the sidewall of the nanotube with high specificity and efficiency. The molecule's tail is tipped with a succinimidyl ester group, which is readily displaced when an amine group attacks the ester function, forming an amide bond. Thus, the CNTs are used as both highly sensitive probes and highly selective immobilizing sites that allow specific reactions to occur.

Analytical Tools—SWCNTs are being used as turbidity probes (TUP) of scanning electron microscopes. Because of their strength, stability, and controllable and reproducible size, the TUPs allow better image fidelity and longer lifetimes.

Solar Cells—Some nanotubes exhibit a photovoltaic effect and can replace material in solar cells acting as a transparent conductive film allowing light to pass to the active layers and generate photocurrent. It has also been shown that nanotubes can be used in conjunction with other materials to act as an ignition device that is triggered with a simple camera flash.

Filters—CNTs have been used to filter carbon dioxide from power plant emissions and so may be a future air pollution filter material. They have also been used to filter water, removing the salt content by allowing water to pass through but capturing the chloride ions.

Catalyst Supports—CNTs have a very high surface area. Each carbon atom is exposed to the interior and exterior surface. Because of the chemist's ability to connect almost any moiety to their surface, a number of CNTs have been shown to act as outstanding catalyst supports when catalysts have been attached to them. Because of their high strength, they perform well to the rigors of being a catalysts support. Their ability to conduct electricity and heat suggests additional ways CNTs can be used to assist catalytic behavior.

Superconductors—CNTs offer unique electronic properties due to quantum confinement. According to quantum confinement, electrons can only move along the nanotube axis. Metallic CNTs are found to be high-temperature superconductors.

Fibers and Fabrics—Textiles spun from CNTs have been made into clothing such as slacks. Along with offering outstanding liquid shedding clothing made from them, the clothing possesses outstanding wear resistance. Penetration-resistant body and vehicle armor can be made from composites containing CNT fibers. They are also being studied for use in transmission line cables. Addition of nanotubes to concrete increases its tensile strength and stops crack propagation. Addition to PE increases its elastic modulus. (For more fiber applications please see "composites" below.)

Energy Storage—CNTs have a very high surface area (about 10^3 m^2/g), good electrical conductivity and can be made very linear (straight). They have been used to make lithium batteries with the highest reversible capacity of any carbon material and employed to make supercapacitor electrodes. CNTs are used in a variety of fuel cell applications where durability is important.

Biomedical Applications—CNTs allow cells to grow on and over them without adherence to the nanotubes and without toxic reaction. Potential applications range from their use within coatings and composites to be used within the body, for prosthetics, and in the construction of vascular stents and neuron growth and regulation.

Heat Conductivity—Their outstanding anisotropic thermal conductivity allows them to be used when heat must be moved from one location to another.

Composites—CNTs, because of their fiber nature on a molecular level makes them outstanding fibers for composites where strength, electrical and thermal conductivity, stiffness, and toughness are needed. Because CNTs contribute to high values of all of these properties, composites can be constructed where outstanding behavior in any one of these areas is needed. Sports wear such as lighter and stronger golf club shafts, bike parts, baseball bats, and tennis rackets have been produced from nanotubes containing composites.

Electronic motor brushes have been made from nanotube composites that are better lubricated, cooler running, stronger, less brittle, and more accurately moldable in comparison to the traditional carbon black brushes.

Coatings—Because of their good strength, thermal and electrical conductivity, and slipperiness, CNTs offer potential interesting coating applications. Thus, a building can be coated with a CNT-containing material that has great durability, will remain free from dust, dirt, and organic growth, and can be used to capture energy via heat and electrical conductivity.

Films—Films have been formed from CNTs that are high strength, conductive, and transparent. They are being investigated for use in LCDs, photovoltaic devices, flexible displays (foldable TV screens) and touch screens, and are intended to replace indium tin oxide (ITO) in many applications.

Nanomotors—MWCNTs exhibit an interesting telescoping behavior where they can slide within the outer tube with essentially no friction allowing the creation of an almost frictionless linear or rotating bearings. This behavior allowed the construction the world's smallest rotational motor and nanorheostat.

Along with their high tensile strengths they also offer a high elastic modulus on the order of 1 TPa. It has a relatively low density of 1.3–1.4 g/mL. While they offer extremely high strengths when tension is applied, they are not as strong under compression because of their hollow structure. Another problem is defects. Although we can synthesize almost defect-free tubes, many of them contain defects. Because these nanotubes are essentially one-dimensional structures, the defect acts as the weak link and can lower the tensile strength by 85%. The presence of defects also lowers the thermal and electronic conductivity properties. Most of the defects are of the Stone Wales variety where a pentagon and heptagon pair is formed by rearrangement of the bonds.

As we are studying CNTs other interesting properties are being found. For instance, recently it was found that CNTs are like hot-wheel tubes allowing water and gas to flow 100–10,000 times faster than as predicted by classical models. It is believed that just as Teflon sheds water because of its inert surface, so also CNTs are slick because of its atomically smooth surface and lack of polarity differences within the tube allowing almost a zero friction situation. Under high pressure, CNTs can be forced together exchanging some of the sp^2 bonding for sp^3 bonding giving the possibility for forming strong wiring. Electrically and thermally conductive carbon nanopaper can be made that is 250 times stronger than steel and much lighter than that can be used as a heat sink for chipboards, blacklight for LCD screens, and to protect electronic devices.

CNTs have been used as templates producing other nanotubes such as gold and zinc oxide nanotubes. These nanotubes are hydrophilic while CNTs are hydrophobic allowing alternative uses where the behavior of the tube can be varied according to its environment.

12.18 BITUMENS

The petroleum industry, including the commercial bitumen industry, was born in the United States on August 27, 1859 when Colonel Drake drilled a hole about 70 ft deep near Titusville, Pennsylvania, to "bring in" the first producing well. By 1908, Henry Ford began to mass-produce his Model "T" Ford creating an additional need for this petroleum in the form of gasoline. The distillation residue became more plentiful and a need for large-scale usage of bitumens increased.

Even so, the bitumen is a very old material. They were used in the waterproofing of the cradle that baby Moses was floated in. It was used by the ancient Egyptians in their mummification process. Bitumens were used in sand stabilization and for lighting the naval base by the Second Muslim Caliph, Omar ben Khattab, at Basra on Shattul-Arab on the West Coast of what is now Saudi Arabia around A.D. 640.

Bitumens occur naturally or are formed as the residue in the distillation of coal tar, petroleum, etc. Industrially, the two most important bitumens are asphalt and coal tar. Asphalt is a brown to black tarlike variety of bitumen that again occurs naturally or is the residue of distillation. Coal tar is the black, thick liquid obtained as the residue from the distillation of bituminous coal.

Bitumens are examples of materials that have only an approximate structure. Bitumens are carbon-intense small polymers with molecular weights from about 200–1000 Da for coal tar with a calculated average number of carbons in a chain of about 15–70. Asphalt has a molecular weight averaging about 400–5000 Da with a calculated average number of carbons in a chain of about 30–400. Thus, they are generally oligomeric to short polymers. Asphalt has a C/H ratio of about 0.7 while coal tar has a C/H ratio of about 1.5 approaching that of a typical hydrocarbon where the C/H ratio is about 2.

As with most nonpolar hydrocarbon-intense polymers, bitumens exhibit good resistance to attack by inorganic salts and weak acids. They are dark, generally brown to black, and their color is difficult to mask with pigments. They are thermoplastic materials with a narrow service temperature range unless modified with fibrous fillers and/or synthetic resins. They are abundant materials that are relatively inexpensive, thus their use in many bulk applications.

At temperatures above the T_g, bitumens generally show Newtonian behavior. Below the T_g bitumens have rheological properties similar to elastomers.

Bitumens are consumed at an annual rate in excess of 75 billion pounds in the United States. Bitumens are generally used in bulk such as pavements (about 75%), and in coatings for roofs (15%), driveways, adhesive applications, construction, metal protection, etc. where it acts as a weather barrier. Bituminous coatings are generally applied either hot or cold. Hot-applied coatings are generally either filled or nonfilled. Cold-applied coatings are generally either nonwater or water-containing. In the hot-applied coatings, the solid is obtained through a combination of cooling and liquid evaporation, whereas in the cold-applied coatings the solid material is arrived at through liquid evaporation. One oft-used coating employs aluminum pigments compounded along with solvents. These coatings are heat-reflective and decrease the energy needs of building that use them. The aluminum–metallic appearance is generally more desirable than black, and the reflective nature of aluminum reflects light that may damage the bitumen coating, allowing it a longer useful life. Today, many of the bitumen coatings contain epoxy resins, various rubbers, and urethane polymers.

12.19 CARBON BLACK

Carbon black is another of the carbon-intensive materials. It is formed from the burning of gaseous or liquid hydrocarbons under conditions where the amount of air is limited. Such burning favors “soot” formation, i.e., carbon black formation. It was produced by the Chinese over 1000 years ago. Today, it is produced in excess of 1.5 million tons annually in the United States. Furnace black is the most widely used carbon black. The particle size of this raw material is relatively large, about 0.08 mm. It is soft with a Mohs scale hardness of less than one.

In addition to carbon, carbon black also contains varying amounts of oxygen, hydrogen, nitrogen, and sulfur. A typical carbon black contains about 98% carbon, 0.3%–0.8% hydrogen, 0.3%–1.2% oxygen, 0.0%–0.3% nitrogen, and 0.3%–1% sulfur. The impurities in the water employed to quench the burning carbon are mainly responsible for the noncarbon and hydrogen content, and the sulfur comes mainly from the feedstock.

Although some describe the structure of carbon black as small chainlike structures, recent information shows it as being graphitelike in structure where the parallel planes are separated by about 0.35–0.38 nm, always greater than the interlayer distance for graphite of 0.335 nm (Figure 12.11). The microstructure of carbon black has been studied extensively employing varying spectroscopies including ATF, high-resolution transmission electron microscopy

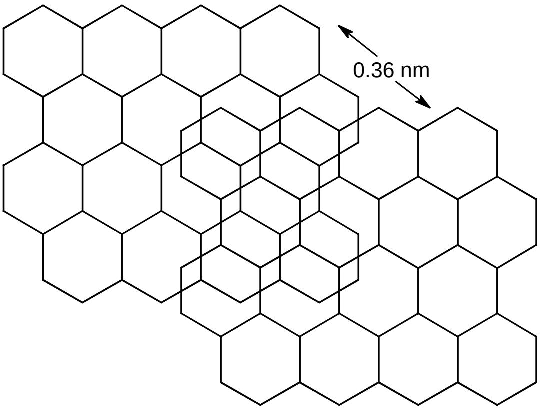


FIGURE 12.11 Sheets of carbon black.

(TEM), and x-ray diffraction. Various models have been developed to describe the average structure in greater detail. These models are related to the structure of graphite.

As with other polymeric materials, the surface structure is different from the bulk and is related to the conditions under which the material was manufactured. Since the material is formed in air, the surface is rich in oxygen. These oxygen atoms play an important role in the resulting carbon black properties. The surface can be modified using a variety of treatments. Heat treatments above 800°C act to increase the amount of crystallinity in the overall structure. Under inert conditions surface groups are modified and the amount of oxygen decreased with heating from 200°C–1200°C. Plasma treatments are employed to modify the carbon black surface creating and destroying various functional groups in the presence of other reactants. Chemical oxidation is also employed to modify carbon black employing oxidizing agents such as air, nitric acid, and ozone. Surface grafting is also employed to provide desired surface functional groups.

The nature of the surface is especially important for carbon black since most applications employ it as an additive forming blends and alloys. These blends can be bound by simple physical contact or by chemical binding through formation of chemical bonding between the various phases.

A major use of carbon black is in rubbers. Incorporation of carbon black into a rubber matrix can result in an increase in strength-related properties, such as abrasion resistance, viscosity, and modulus. Thus, carbon black is a reinforcing agent rather than simply an inexpensive additive. The reinforcing effect is dependent on the particle size, amount, aggregate structure, surface area, surface activity, etc. The reinforcing effect mainly occurs because of the interaction between the interfacial surfaces of the rubber matrix and the carbon black. Carbon blacks can be divided roughly as to being reinforcing (<35 nm) or semireinforcing (>35 nm) depending on the particle size. The antiabrasion of carbon black increases with increase in particle size.

Carbon black is the most important additive to rubber comprising between 30% and 70% of the bulk rubber product. Tire goods consume about 65% of the carbon black, mechanical goods another 25%, with only about 10% employed for nonrubber applications.

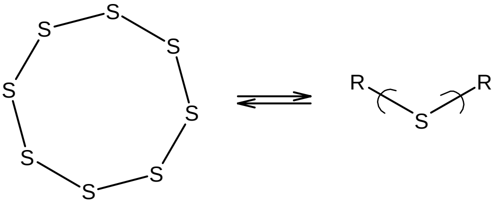
A typical tire rubber formulation for tire tread will contain various rubbers, mainly styrene–butadiene (50%) and *cis*-polybutadiene (12%), various processing aids (2%), softeners (3%), vulcanizing agent (mainly sulfur; 1%), accelerators, and reinforcing filler (namely carbon black; 30%) so that by bulk, carbon black is the second most used material.

Of the 10% of carbon black used for nonrubber applications, about 35% is used for plastics, 30% for printing inks, 10% coating, and 5% for paper. In plastics, carbon black enhances a variety of properties including UV shielding, electrical conductance, pigment, opacity, and mechanical properties. Plastics that use carbon black filler may contain only several percent to having over half of the weight being carbon black.

In xerography, carbon black is the most important pigment in printing or duplicating toner applications. Here, blackness, good dispersion, and needed electrical properties are provided by carbon black. Similarly, these properties are useful for applications in coatings, inks, and printing, though rheological properties in liquid media are also important.

12.20 POLYSULFUR

Sulfur is present in the petrochemicals derived from once-living matter as it is present in certain amino acids. Because of its removal from industrial waste, sulfur has been stockpiled and is available at a low price in large amounts. While the stable form of sulfur at room temperature is cyclooctasulfur (S_8), linear polysulfur is formed on heating. Unfortunately, the thermodynamically stable form of sulfur is the cyclooctasulfur monomer and the polymer undergoes depolymerization after sometime.



(12.25)

Methods have been studied to inhibit this reversal process. Some have involved the addition of olefins such as limonene, myrcene, and cyclopentadiene to the ends to inhibit the depolymerization. Such stabilized polysulfur has been incorporated into concrete and asphalt mixes to strengthen them. Concrete blocks, posts, and parking tire restrainers containing polysulfur are now being produced.

12.21 CERAMICS

The term "ceramics" comes from the Greek *keramikos*, which means "potter's clay" or "burnt stuff." While traditional ceramics were often based on natural clays, today's ceramics are largely synthetic materials. Depending on which ceramic and which definition is to be applied, ceramics have been described as inorganic ionic materials and as inorganic covalent (polymeric) materials. In fact, many ceramics contain both covalent and ionic bonds and can thus be considered "to be or not to be" (shades of Shakespeare) polymeric materials. Many of the new ceramics, such as the boron nitriles and the silicon carbides, are polymeric without containing any ionic bonds.

Ceramics are typically brittle, strong; resistant to chemicals such as acids, bases, salts, and reducing agents; and they are high-melting. They are largely composed of carbon, oxygen, and nitrogen, and made from silicates such as clay, feldspar, bauxite, silica. But now ceramics contain other materials such as borides, carbides, silicides, nitrides.

Ceramics are generally made by two processes—sintering and fusing. In sintering, the starting material is reduced to a powder or granular form by a series of crushing, powdering, ball-milling, etc. The ground preceramic material is then sized, separated according to particle size, using different-sized screens.

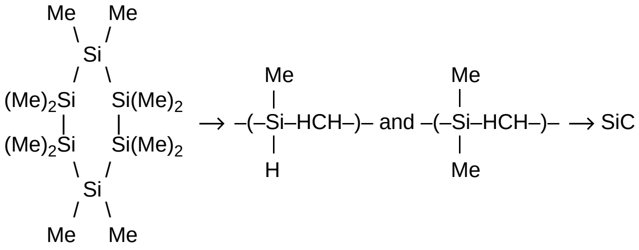
Ceramic material is generally shaped by pressing it into a form or through extruding, molding, jiggering, or slip-casting. Slip-casting uses a suspension of the preceramic material in water. The mixture must be dilute enough to allow it to be poured. Deflocculates are often added to assist in maintaining the suspension. The “slip” is poured into a plaster of Paris mold that absorbs water, leaving the finished shape. The preceramic material hardens next to the mold and surplus slip material poured off leaving a hollow item. At this point, the molded material is referred to as a “green body,” which has little strength. Coffeepots and vases are formed using this technique.

In jiggering, machines press the preceramic material into a rotating mold of desired shape. Dinnerware products are often made using jiggering.

Abrasives and insulators are formed from simply pressing the preceramic material into a mold of desired shape. In extrusion, the preceramic material is forced through an opening in a “shaping” tool. Bricks and drainpipes are formed using extrusion.

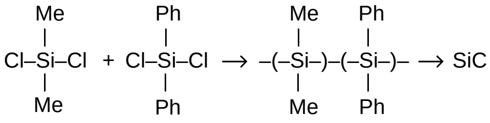
After the product has dried, it is heated or fired in a furnace or kiln. Modern ceramics generally require certain heating schedules that include the rate and duration of heating and conditions such as the presence or absence of air. This is similar to procedures used to produce carbon fibers where the heating schedule is critical to the end product’s properties.

In one approach, six-membered silicon-containing rings are pyrolized giving mixed carbosilane preceramic polymers through heating to 400°C, and subsequently forming silicon carbides or poly(carbosilanes) at 800°C.



$$\begin{array}{c} \mathrm{Me}\quad \mathrm{Me} \\ \backslash\ \ / \\ \mathrm{Si} \\ /\ \ \backslash \\ \mathrm{(Me)_2Si}\quad \mathrm{Si(Me)_2} \\ |\qquad\qquad | \\ \mathrm{(Me)_2Si}\quad \mathrm{Si(Me)_2} \\ \backslash\ \ / \\ \mathrm{Si} \\ /\ \ \backslash \\ \mathrm{Me}\quad \mathrm{Me} \end{array} \longrightarrow -(-\underset{\mathrm{H}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{HCH}-)-\ \text{and}\ -(-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{HCH}-)- \longrightarrow \mathrm{SiC} \tag{12.26}$$

SiC fibers can be formed using dimethyl dichlorosilicon and diphenyl dichlorosilicon heated together.



$$\mathrm{Cl}-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-\mathrm{Cl} + \mathrm{Cl}-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-\mathrm{Cl} \longrightarrow -(-\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}-)-(-\underset{\mathrm{Ph}}{\overset{\mathrm{Ph}}{\mathrm{Si}}}-)- \longrightarrow \mathrm{SiC} \tag{12.27}$$

Such “ceramic” fibers offer uniquely strong and resistant inexpensive materials including new ceramic composites that have great fracture toughness.

There are a number of other “nonoxygen” or nonoxide ceramics including phosphonitric chlorides (PN backbone), boron nitriles (BN), aluminum nitriles (AlN), titanocarbosilanes (Si–Ti–C backbone), and silazanes (Si–C–N backbones).

Many ceramic products are coated with a glassy coating called a glaze. The glaze increases the resistance of the material to gas and solvent permeability makes the surface smoother in art objects used for decoration.

One group of advanced material ceramics are the zirconia ceramics. Most of these are based on zirconia (zirconium (IV) oxide) that contains small amounts of magnesia (magnesium oxide). They have bending strengths 2–3 times that of corundum and alumina; high fracture toughness (about five times that of corundum ceramics); high resistance to wear and corrosion; and they are high density (5.8 g/cm^3). They are used in the construction of shear blades in textile industry, plungers in food and drink industry, valves in petroleum industry, and as milling balls in materials industry.

Zirconia exists in three solid phases (Equation 12.28)

$$\text{Monoclinic} \leftarrow 1200^\circ\text{C} \rightarrow \text{Tetragonal} \leftarrow 2400^\circ\text{C} \rightarrow \text{Cubic} \leftarrow 2700^\circ\text{C} \rightarrow \text{Liquid} \qquad (12.28)$$

The transformations between the monoclinic and tetragonal phases involve large and abrupt volume changes introducing fractures in the material. This is minimized through the use of di- and trivalent oxides of the cubic symmetry such as calcium oxide and magnesium oxide. This results in a lowering of the transition temperatures (M→T and T→C) and also lowers the expansion coefficient of the zirconia and the subsequent volume changes associated with the phase changes reducing ceramic fracturing. The addition of calcium oxide or magnesium oxide is said to "stabilize" the ceramic.

Strength, brittleness, and solvent permeability properties are limited because of lack of control of the ceramic composition on a macro- and microlevel. Even small particle sizes are large compared with the molecular level. There have been a number of attempts to produce uniform ceramic powders including the sol–gel synthesis in which processing involves a stable liquid medium, coprecipitation in which two or more ions are precipitated simultaneously. More recently, Carraher and Xu have used the thermal degradation of metal containing polymers to deposit metal atoms and oxides on a molecular level.

12.22 HIGH-TEMPERATURE SUPERCONDUCTORS

12.22.1 Discovery of the 123-Compound

In early 1986, George Bedorz and K. Alex Muller reported a startling discovery—a ceramic material, La–Ba–Cu–O, lost its resistance to electrical current at about 30 K. This was the first report of a so-called high T_c superconductor. Intensive efforts were then concentrated on substituting the component ions with similar elements on both the La and Ba sites. The first success was reported by Kishio et al. with an $(La_{1-x}\,Sr_x)_2CuO_4$ system that exhibited a higher T_c to about 37 K. Then the substitution on the La sites led Wu and coworkers to find another superconductor, the Y–Ba–Cu–O system with a T_c of 93 K in February 1987. This finally broke the technological barrier that would allow superconductivity at temperatures above liquid nitrogen. The superconducting phase was identified as $Y_1Ba_2Cu_3O_7$ (commonly referred to as the 123-compound). The 123-compound was the first of the 90 K plus superconductors to be discovered and it has been the most thoroughly studied.

12.22.2 Structure of the 123-Compound

The structure of the 123-compound is related to that of an important class of minerals called perovskites. These minerals contain three oxygen atoms for every two metal atoms. It has six metal atoms in its unit cell and would be expected to have nine oxygen atoms if it were an ideal perovskite. In fact, it has, in most samples, between 6.5 and 7 oxygen atoms. In other words, by comparison to an ideal perovskite, about one-quarter of the oxygen atoms are missing. The unit cell can be thought of as a pile of three cubes. Each cube has a metal atom at its center, barium in the bottom cube, yttrium in the middle one, and barium in the top one. At the corners of each cube a copper would be surrounded by six oxygen atoms in an octahedral arrangement linked at each oxygen in an ideal perovskite. Each barium and yttrium would then be surrounded by 12 oxygen atoms. But x-ray and neutron diffraction studies have shown that the unit cell does not conform to this simple picture because certain oxygen positions are vacant. In fact, all oxygen positions in the horizontal plane containing yttrium are vacant. The other vacancies are located in the top and bottom of the Cu–O planes.

The two copper oxide layers can be considered as polymeric since the covalent character is in the same range as for the carbon fluoride bond in Teflon. Thus, the 123-superconductors consist of two types of polymeric copper oxide layers held together by ionic bonding metals such as barium and yttrium. This theme of polymeric layers held together by ionic bonding to metals is common in the silicates and other minerals.

12.23 ZEOLITES

At least three major themes are helping drive polymer synthesis and use of polymers today. These involve synthesis and assembling on an individual scale (nano-level); synthesis in confined spaces (selected inorganic zeolites and biological syntheses); and single-site catalysis (both selected biological and synthetic polymer syntheses). Superimposed on this are the application aspects including the human genome/biomedical, electronic/communications, etc.

Zeolites are three-dimensional microporous crystalline solids. Zeolites include a whole group of aluminosilicates with an approximate formula of $SiAlO_4$. With respect to type of bonding, zeolites can be divided into three groups. The natrolite group (mesolite, thomsonite, edingtonite, natrolite) consists of structures build up from rings of four $SiAlO_4$ tetrahedral linked together into chains with fewer linkages between the chains so that cleavage along the chain direction is preferred. These materials generally have a fibrous character. In the heulandite group (stilbite, epistilbite, and heulandite), the $SiAlO_4$ tetrahedra form sheets of six-membered rings with few linkages between the sheets. These materials are micalike in behavior. The third group, the so-called framework zeolites, has the density of bonding similar in all three directions. This group includes most of the zeolites mentioned below.

Framework zeolites can be described as aluminosilicates composed of tetrahedra linked by the sharing of oxygen atoms into rings and cages that can accommodate water molecules, metallic ions, as well as selected organic molecules. Although there are a variety of structures, the framework zeolites can be briefly described as having an open arrangement of corner-sharing tetrahedra where the SiO_4 are partially replaced by AlO_4 units when there are enough cations present to be neutral. There are well over 100 different synthetic and natural framework zeolites know today with more being found. Magic-angle NMR indicates that there are five distinct zeolite groups where $n = 0$–4 for $Ai(AiO)_n(SiO)_{4-n}$. The open structures give materials with lower densities (on the order of 2.0–2.2 g/mL), as expected, than similar materials with closed structures such as feldspar (density about 2.6–2.7 g/mL).

The three major applications of zeolites are absorption, catalysis, and ion exchange.

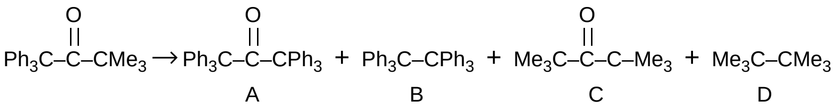
Molecular sieves was the name first given to framework zeolites dehydrated by heating in vacuum to about 350°C because of their ability to capture and remove water and certain other species. This sieve action is due to a regular pore structure such that materials are removed on a size exclusion basis. There exist zeolites with different ring or pore sizes so they can selectively remove selected materials. They are defined by the ring size of the opening. Thus, the term "8 ring" refers to a closed loop constructed from eight tetrahedral coordinated silicon or aluminum atoms. Today, other materials, such as microporous silicas and aluminum phosphate, are also employed as molecular sieves.

Syntheses that occur within confined spaces typically give products with a specificity that is not available by other modes. The specificity may be general such as in the case of the synthesis of lignins in plants where synthesis between plant layers produces a largely two-dimensional material with only an average structure. It may be highly, though not totally, selective as in the case of zeolites and hollow nanofibers. Or it may be essentially totally selective as in the case of many of the biologically important proteins and nucleic acids where both spacial and electronic interactions act to give a highly "preordained" structure.

Zeolites can accommodate a wide variety of cations that are loosely held and can be replaced by more tightly bound often "heavy metal" cations. Thus, they have been extensively employed as water-softening materials removing calcium, iron, magnesium, etc., in "hard water." Smaller ringed zeolites have been used to remove water, carbon dioxide, and sulfur dioxide from low-grade natural gas streams. In medicine, they are used to extract oxygen from air for patients who need to breathe in a high-oxygen content atmosphere. Zeolites are also used in the laundry detergent market and in soil treatment providing a source of slowly released nutrients that have previously been added to the zeolite.

Zeolites and related ordered clay—associated materials have been suggested to be involved in the initial primeval synthesis of basic elements of life—are also being involved in the synthesis of a number of polymeric and nonpolymeric materials. Zeolites come in a variety of forms and different shapes and sizes with researchers associating the particular size and shape with a particular desired synthesis. This is somewhat akin to the considerations that are made in effectively employing crown phase transfer agents and related materials.

Zeolites have been employed in the preferential synthesis of optically active sites and in determining the particular products formed from certain reactions. In looking at the products formed from the decomposition and reformations involving an unsymmetrical ketone, the major products are a combination of products listed below:



$$\mathrm{Ph_3C{-}\overset{\overset{O}{\|}}{C}{-}CMe_3} \rightarrow \underset{A}{\mathrm{Ph_3C{-}\overset{\overset{O}{\|}}{C}{-}CPh_3}} + \underset{B}{\mathrm{Ph_3C{-}CPh_3}} + \underset{C}{\mathrm{Me_3C{-}\overset{\overset{O}{\|}}{C}{-}C{-}Me_3}} + \underset{D}{\mathrm{Me_3C{-}CMe_3}} \qquad (12.29)$$

Employing a single zeolite that selectively accommodates the Me_3C radical results in a preferential formation of D and little C because of preferential diffusion of the Me_3C radical as it is formed with the other radicals being "washed" past. The use of two zeolites in conjunction, one preferentially accepting the Me_3C radical and the second accepting the Ph_3C radical, results in the preferential formation of B and D.

An additional consideration involves matching the "hardness" or flexibility of the confined space. Zeolites offer hard or inflexible confined spaces, whereas liquid crystals and some other polymer media offer softer confined spaces. While the zeolites offer a "safe haven" for selected species enabling the hosted species a relatively long existence, they do not allow for ready movement and mixing. By comparison, a more flexible container such as those especially designed PEs allow a more flexible environment, which allows for variations in the product sizes and shapes and some assembling to occur within the more flexible confines. Thus, the reaction of 1-naphthyl esters was carried out in an appropriate zeolite and appropriate PE. In solution, eight products are formed. In the zeolite only one product, the result of a specific geminate–pair recombination, is formed. In PE, several products are formed primarily as the isomeric products of geminate–pair recombinations.

12.24 SUMMARY

1. Inorganic polymers are widely employed in the construction and building businesses, as abrasives and cutting materials, as fibers in composites, as coatings and lubricants, and as catalysts. They also serve as the basis of rocks and soils.
2. Portland cement is the least expensive, most widely used synthetic polymer. It has a complex (short-range order and long-range disorder; average structure), three-dimensional structure.
3. There are many specialty cements including reinforced concrete, lightweight concrete, prestressed concrete, gypsium, and heavy glass.
4. Silicates are among the most widely found materials on the face of the earth. They form the basis for much of the soil, sand, and rocks with most of this being of the crystalline variety

of silicates. As amorphous materials they are found as the fiber material in fiberglass, as window glass and a whole host of specialty glasses including safety glass, borosilicate glasses, lead (or heavy) glasses, colored glasses, and glazes. Glass can be shaped by drawing, pressing, casting, and blowing. Most of these glasses have the approximate structure of silicon dioxide. Many of the rocks are present in crystalline silicate forms as quartz and feldspar. Today the sol–gel technique is important in making many materials including aerogels, among the least dense solids known today. In nature, silicates are found as polymeric sheets such as asbestos, three-dimensional materials such as the zeolites, and linear materials.

5. There are many widely used carbon polymers. These include the hardest known material diamond, graphite a sheet material with little strength holding together the sheets, carbon fibers used in high-strength composites, CNTs one of the most important new materials for the 21st century, bitumens used in asphalt, and carbon black widely used as a filler material. Diamonds structurally have a carbon at the center of a tetrahedron composed of four other carbon atoms. They can be industrially synthesized and used for cutting and shaping. Graphite occurs as sheets of hexagonally fused benzene rings. The bonds holding the bused benzene rings together are covalent bonds while the bonding between the sheets results from the weaker overlapping of pi-electron orbitals. Thus, many of the properties of graphite are anisotropic. The weak forces holding the sheets together are responsible for its slipperiness. Graphite is commercially made from charcoal or coke.
6. Many ceramics are partially polymeric in structure. These include the new superconductive materials that exist as polymeric sheets connected by metal ions similar to many of the silicate sheets.

GLOSSARY

alumina Complex aluminum-containing silicate.

annealing Subjecting a material to near its melting point.

asbestos Group of silica-intensive materials containing aluminum and magnesium that gives soft, threadlike fibers.

asbestosis Disease that blocks the lung sacks with thick fibrous tissue.

borosilicate glass Relatively heat-shock-resistant glass with a small coefficient of thermal expansion, such as Kimax and Pyrex.

calcium–aluminate cement Contains more alumina than Portland cement.

chrysotile Most abundant type of asbestos.

concrete Combination of cement, water, and filler material such a rock and sand.

diamonds Polymeric carbon where the carbon atoms are at centers of tetrahedra composed of four other carbon atoms; hardest known natural material.

feldspars Derivatives of silica where one-half to one-quarter of the silicon atoms are replaced by aluminum atoms.

fibrous glass (fiberglass) Fibers of drawn glass.

float glass Glass made by cooling sheets of molten glass in a tank of molten time: most common window glass is of this type.

glass Inorganic product of fusion which has been cooled to a rigid condition without crystallization; most glasses are amorphous silicon dioxide.

glass sand Impure quartz crystals.

glaze Thin, transparent coatings fused on ceramic materials.

granite Hard crystalline rock containing mainly quartz and feldspar.

graphite Polymeric carbon consisting of sheets of hexagonally fused rings where the sheets are held together by weak overlapping pi-electron orbitals; anisotropic in behavior.

gypsum Serves as the basis of plaster of Paris, Martin's cement, etc.; shrinks very little on hardening and rapid drying.

high-temperature superconductors Polymeric copper oxide layers containing metal atoms that hold them together which are superconductors above the boiling point of liquid nitrogen.
inorganic polymers Polymers containing no organic moieties.
kaolinite Important type of asbestos.
lead glass (heavy glass) Glass where some or all of the calcium oxide is replaced by lead oxide.
lime Calcium carbonate from oyster shells, chalk, and marl.
magnesia cement Composed mainly of magnesium oxide; rapid hardening.
optical fibers Glass fibers coated with highly reflective polymeric coatings; allows light entering one end to pass through the fiber to the other end with little loss of energy.
piezoelectric effect Materials that develop net electronic charges when pressure is applied; sliced quartz is piezoelectric.
Portland cement Major three-dimensional inorganic construction polymer containing calcium silicates, lime, and alumina.
precast concrete Portland concrete cast and hardened prior to being taken to the site of use.
prestressed concrete Portland concrete cast about steel cables stretched by jacks.
quartz Crystalline forms of silicon dioxide: basic material of many sands, soils, and rocks.
reinforced concrete Portland concrete cast about steel rods or bars.
safety glass Laminated glass; sandwich containing alternate layers of soda-lime glass and poly(vinyl butyral).
sand Loose grains of minerals or rocks larger than silt but smaller than gravel.
sandstone Granular quartz.
silica Based on SiO_2; finely ground sand.
silicon glass Made by fusing pure quartz crystals or glass sand; high-melting.
soda Na_2O.
soda ash Na_2CO_3.
sodia-lime glass Most common glass; based on silica, soda, and lime.
soil Contains mineral and organic particles; majority by weight is sand.
tempered safety glass Single piece of specially treated glass.
tempering Process of rapidly cooling glass resulting in an amorphous glass that is weaker but less brittle.
vitreous enamels Thin, normally somewhat opaque-colored inorganic coatings fused on materials.
vycor 96% silicon glass; made from silicon and boron oxides; best variety is called fused quartz.

EXERCISES

1. What properties of glass correspond to those of organic polymers?
2. Why is Portland cement an attractive large-bulk use building material?
3. Name five important synthetic and five important natural inorganic polymers.
4. Describe three-dimensional polymers. Name five important three-dimensional polymers and two general properties typical of them.
5. Why are specialty cements and concretes necessary?
6. What is intended by the comment that "glass is a supercooled liquid?"
7. What are the major techniques employed to shape glass?
8. Why are specialty glasses important in today's society?
9. Name two important inorganic fibers employed with resins to form useful materials.
10. Which would you predict to be more brittle—quartz, fibrous glass, or window glass?
11. Briefly describe the piezoelectric effect.
12. We do not live in a risk-free society. Discuss this statement in terms of asbestos.
13. What does anisotropic behavior mean? Why does graphite exhibit anisotropic behavior?
14. Briefly compare the structures of diamond and graphite.
15. Speculate as to why "nature" has emphasized polymers of carbon and silicon.
16. What are some advantages to having glass lenses?
17. What evidence do we have that glass is actually a very slow-moving liquid?
18. Why are glass and Portland cement so widely used in our society?
19. Why are inorganic materials employed rather than organic dyes to color or stain glass?
20. Are ceramics really polymeric? Why?

21. Why is the structure of Portland cement so difficult to study?
22. How is the silicon employed in optical fibers and computer chip manufacture related?
23. If asbestos of a size that was much larger than the size of the lung sacks was found, would it have a sizable marketplace in today's society?
24. Name some applications of carbon nanotubes.
25. Why is simple sand that is found at the beach not used in glass making?

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13 Testing and Spectrometric Characterization of Polymers

Public acceptance of polymers is usually associated with an assurance of quality based on knowledge of successful long-term and reliable testing. In contrast, much of the dissatisfaction with synthetic polymers is related to failures that might have been prevented by proper testing, design, and quality control. The ASTM, through its various committees, has developed many standard tests which may be referred to by all producers and consumers. There are also cooperating groups in many other technical societies: the American National Standards Institute (ANSI), the International Standards Organization (ISO), and standards societies such as the British Standards Institution (BSI) in England, and Deutsche Normenausschuss (DNA) in Germany, and comparable groups in every nation with developed polymer technology throughout the world.

Testing is done by the industry to satisfy product specifications and for public protection using standardized tests for stress–strain relationships, flex life, tensile strength, etc. The U.S. tests are overseen by the ASTM through a committee arrangement. For instance, Committee D-1 oversees tests related to coatings, whereas Committee D-20 oversees tests on plastics. New tests are continuously being developed, submitted to the appropriate ASTM committee, and after adequate verification through "round-robin" testing, finally accepted as standard tests. These tests are published by the ASTM. Each ASTM test is specified by a unique combination of letters and numbers, along with exacting specifications regarding data gathering, instrument design, and test conditions, making it possible for laboratories throughout the world to reproduce the test and hopefully the test results if requested to do so. The Izod test, a common impact test, has the ASTM number D256-56 (1961). The latter number, 1961, is the year the test was first accepted. The ASTM publication gives instructions for the Izod test specifying test material shape and size, exact specifications for the test equipment, detailed description of the test procedure, and how results should be reported. Most tests developed by one testing society have analogous tests or more often utilize the same tests so that they may have both ASTM, ISO, and other standardized society identification symbols.

A number of physical tests emphasizing stress–strain behavior will be covered in Chapter 14. Here, we will concentrate on other areas of testing, emphasizing thermal and electrical properties and on the characterization of polymers by spectral means. Spectroscopic characterization generally concentrates on the structural identification of materials. Most of these techniques, and those given in Chapter 14, can also be directly applied to nonpolymeric materials such as small organic molecules, inorganic compounds, and metals.

The testing of materials can be based on whether the tested material is chemically changed or is left unchanged. Nondestructive tests are those that result in no chemical change in the material which may include many electrical property determinations, most spectroanalyses, simple phase change tests (T_g and T_m), density, color, and most mechanical property determinations. Destructive tests result in a change in the chemical structure of at least a portion of the tested material. Examples include flammability and chemical resistance tests when the material is not resistant to the tested material.

13.1 SPECTRONIC CHARACTERIZATION OF POLYMERS

13.1.1 INFRARED SPECTROSCOPY

The infrared (IR) range spans the region bound by the red end of the visible region to the microwave region at lower frequencies. Molecular interactions that involve vibrational modes correspond to this energy region. IR spectroscopy is one of the most common spectronic techniques used today to identify polymer structure. Briefly, when the frequency of incident radiation of a specific vibration is equal to the frequency of a specific molecular vibration, the molecule absorbs the radiation. Today, most IR machines are rapid scan where the spectra are Fourier-transformed. For the most part, IR band assignments for polymers are analogous to those made for small molecules.

Following are brief discussions of some of the more important techniques used specifically for polymer analysis.

Attenuated total reflectance infrared (ATR-IR) is used to study films, coatings, threads, powders, interfaces, and solutions. (It also serves as the basis for much of the communication systems based on fiber optics.) ATR occurs when radiation enters from a more-dense material (i.e., a material with a higher refractive index) into a material that is less dense (i.e., with a lower refractive index). The fraction of the incident radiation reflected increases when the angle of incidence increases. The incident radiation is reflected at the interface when the angle of incidence is greater than the critical angle. The radiation penetrates a short depth into the interface before complete reflection occurs. This penetration is called the evanescent wave. Its intensity is reduced by the sample which absorbs.

Specular reflectance infrared involves a mirrorlike reflection producing reflection measurements of a reflective material or a reflection–absorption spectrum of a film on a reflective surface. This technique is used to look at thin (from nanometers to micrometers thick) films.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is used to obtain spectra of powders and rough polymeric surfaces such as textiles and paper. IR radiation is focused onto the surface of the sample in a cup resulting in both specular reflectance (which directly reflects off the surface having equal angles of incidence and reflectance) and diffuse reflectance (which penetrates into the sample subsequently scattering in all angles). Special mirrors allow the specular reflectance to be minimized.

Photoacoustic spectroscopy (PAS) infrared is used for highly absorbing materials. Generally, modulated IR radiation is focused onto a sample in a cup inside a chamber containing an IR-transparent gas such as nitrogen or helium. The IR radiation absorbed by the sample is converted into heat inside the sample. The heat travels to the sample surface and then into the surrounding gas causing expansion of the boundary layer of gas next to the sample surface. The modulated IR radiation thus produces intermittent thermal expansion of the boundary layer creating pressure waves that are detected as photoacoustic signals.

PAS spectra are similar to those obtained using ordinary Fourier transform infrared (FTIR) spectroscopy except truncation of strong absorption bands which occurs due to photoacoustic signal saturation. PAS allows the structure to be studied at different thicknesses because the slower the frequency of modulation, the deeper the penetration of IR radiation.

Emission infrared spectroscopy is used for thin films and opaque polymers. The sample is heated so that energy is emitted. The sample acts as the radiation source and the emitted radiation is recorded giving spectra similar to those of classical FTIR. In some cases, IR frequencies vary because of differences in the structures at different depths and interactions between surface and interior emissions.

Infrared microscopy allows the characterization of minute amounts of a material or trace contaminants or additives. Samples as small as 10 μm can be studied using IR microscopy. The microscope, often using fiber optics, allows IR radiation to be pinpointed.

Today, there are many so-called hyphenated methods with IR. These methods include gas chromatography-infrared (GC-IR) where the IR spectra are taken from materials as they are evolved through the column. Related to this are high-performance liquid chromatography-infrared (HPLC-IR), thermogravimetry-infrared (TG-IR), and multispectral infrared (MS-IR).

13.1.2 RAMAN SPECTROSCOPY

Raman spectroscopy is similar to IR spectroscopy in that it investigates polymer structure focusing on the vibrational modes. IR is a result of energy being absorbed by a molecule from the ground state to an excited state, whereas Raman spectroscopy is a scattering phenomenon where the energy of photons is much larger than the vibrational transition energies. Most of these photons are scattered without change (so-called Rayleigh scattering). Even so, some are scattered from molecular sites with less energy than they had before the interaction resulting in Raman–Stokes lines. Another small fraction of photons have energies that are now greater than they originally had leading to the formation of anti-Stokes lines. Only the Raman–Stokes photons are important in Raman spectroscopy. Although many chemical sites on a polymer are both IR and Raman active, i.e., they both give rise to bands, some are less active or even nonactive because of the difference between groups that can absorb and those that scatter. These differences are generally described in terms of symmetry of vibration. Briefly, an IR absorption occurs only if there is a change in the dipole moment during the vibration, whereas a change in polarizability is required for Raman scattering to occur. Even so, the spectra are generally similar and a comparison of the two allows for additional structural characterization beyond that obtained from either of the techniques alone.

Carraher and Williams showed that for many polymers, differences in symmetry and band production were similar for small molecules as they were for the same groups found in polymers. Thus, observations from the literature and in model-compound studies are generally applicable to similar moieties present in polymeric systems for both Raman and IR spectral analyses.

As in the case with IR spectrometers, there exists a wide variety of specialty techniques especially applicable to polymer analysis.

In **surface-enhanced Raman spectroscopy** (SERS) samples are adsorbed onto microscopically roughened metal surfaces. Spectra are the intensities and frequencies of scattered radiation originating from a sample that has been irradiated with a monochromatic source such as a laser. SERS spectra are of molecules that are less than 50 Å from the surface.

13.1.3 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for polymer structure characterization. Certain isotopes have two or more energy states available when exposed to a magnetic field. The transitions between these energy states are the basis for NMR. These magnetically active nuclei have a property called spin. As a consequence of this spin, these nuclei have an angular momentum and magnetic moment. The ratio of these two properties is called the magnetogyric ratio. Each isotope has a distinct magnetogyric ratio that varies a little with the particular chemical environment in which they are placed.

While NMR has been a strong characterization tool for polymers for many years, it has increased in its usefulness because of continually improved instrumentation and techniques. When a nucleus is subjected to a magnetic field, two phenomena are observed: Zeeman splitting and nuclear precession. Zeeman splitting creates $2I + 1$ magnetic energy states where I is the spin quantum number. When the atomic mass and atomic number are even numbers, $I = 0$, so that these nuclei are unable to have multiple energy levels when exposed to a magnetic field. Thus, ^{12}C which has both an even atomic number and atomic mass is NMR inactive, whereas ^{13}C, which has an uneven atomic mass, is NMR active. Nuclear precession is the motion of a spinning body whose axis of rotation changes orientation. The precessional frequency is equal to the magnetic field strength times the magnetogyric ratio.

In a magnetic field, NMR-active nuclei can be aligned with the magnetic field (low-energy state) or aligned against the field (high-energy state). At room temperature, there are slightly more nuclei in the lower-energy state than in the higher-energy state. As magnetic energy is supplied that corresponds to the energy gap, quantum level, between the low- and high-energy states, some nuclei in the low-energy state move to the high-energy state, resulting in an absorption of energy which is recorded as an NMR spectra. The difference between the two energy states is related to the strength of the external magnet. Better spectra are obtained when instruments with larger magnetic fields are employed.

Because of the small but consistent concentrations of ^{13}C present in all organic compounds, it is necessary to use more sophisticated NMR spectroscopy for determining the effect of neighboring electrons on these nuclei. However, ^{13}C-NMR spectroscopy is a valuable tool for investigating polymer structure.

Following is a short description of some of the newer advances.

Nuclear Overhauser effect—The nuclear Overhauser effect (NOE) occurs only between nuclei that share a dipole coupling, i.e., their nuclei are so close that their magnetic dipoles interact. Techniques that use NOE enhance ^{13}C spectra and allow spacial relationships of protons to be determined.

Two-Dimensional NMR—Basically, the two-dimensional NMR techniques of nuclear Overhauser effect spectroscopy (NOESY) and correlation spectroscopy (COSY) depend on the observation that spins on different protons interact with one another. Protons that are attached to adjacent atoms can be directly spin-coupled and thus can be studied using the COSY method. This technique allows assignment of certain NMR frequencies by tracking from one atom to another. The NOESY approach is based on the observation that two protons closer than about 0.5 nm perturb one another's spins even if they are not closely coupled in the primary structure. This allows spacial geometry to be determined for certain molecules.

The use of actively shielded magnetic field gradients has made the use of pulsed field gradients possible. The use of pulsed field gradients reduces experiment time, minimizes artifacts, and allows for further solvent suppression.

In *pulsed NMR*, the magnetic field is turned on for the time necessary to rotate the magnetization vector into a plane called the 90° rotation or 90° pulse. The field is turned off and the magnetization vector rotates at a nuclear precession frequency relative to the coil. This induces an NMR signal that decays with time as the system returns to equilibrium. This signal is called the *free induction decay* (FID).

After a sample is excited, the spin loses excess energy through interactions with the surroundings eventually returning to its equilibrium state. This process is exponential and is called *spin-lattice relaxation*. The decay is characterized by an exponential time constant. Two-dimensional experiments allow the more precise determination of coupling relationships. Such experiments are carried out by collecting a series of FID spectra. The time between the pulses is called the *evolution time*. The evolution time is systematically increased as each successive FID is obtained. Each new FID shows a continued change in the couplings in the polymer. The FID spectra are treated using Fourier transformation. A new series of FID spectra are now created by connecting points for each spectra and these new FIDs are again treated by Fourier transformation producing a two-dimensional spectra that are often presented as contour plots. Nuclei that share J-coupling produce a correlation peak.

Such approaches allow better interpretation of dipole couplings, molecular diffusion, J-coupling, and chemical exchange.

Solids—Many polymers are either soluble or insoluble. NMR of solids generally give broad lines because of the effects of dipolar coupling between nuclei and the effect of *chemical shift anisotropy* (CSA). Both of these effects are greatly reduced for polymers in solution and allow for decent spectra of soluble polymers in solution.

CSA effects are large for solids and are the result of the directional dependence of electronic shielding. CSA effects are overcome through rapidly spinning the sample at an angle to the magnetic field known as the *magic angle*. Solid probes use spinning rotors to hold and spin the sample. The sample is rotated at the magic angle and spun fast enough to remove CSA effects. High-power decouplers or multiple pulse line narrowing allow the decoupling between protons and carbon by using a series of pulses to average the dipolar interactions through spin reorienting. Cross-polarization uses dipolar coupling to increase the sensitivity of less-sensitive nuclei. The combination of cross-polarization and magic angle spinning (CPMAS) allows good spectra to be obtained for solid polymers.

13.1.4 NUCLEAR MAGNETIC RESONANCE APPLICATIONS

The various types of spectroscopes complement one another, sometimes giving "new" information and other times giving similar information. The amount of crystallinity and preference for syndiotactic, isotactic, and atactic structure has been determined employing a number of techniques including x-ray. This information can be correlated with information that can be readily obtained from IR and NMR, so that product control can be easily monitored. For instance, NMR spectra of poly(methyl methacrylate) (PMMA), made by different synthetic routes give different proton shifts that allow the determination of the amounts of isotactic, syndiotactic, and atactic material. Briefly, production of PMMA via so-called high-temperature free radical polymerization gives a largely atactic material. The proton chemical shifts for the α-methyl appear at about 8.8, 8.9, and 9.1 (chemical shifts are based on the tetramethylsilane peak having a value of 10 ppm). Largely isotactic PMMA produced using anionic polymerization shows an enhanced peak at about 8.8 that is assigned to the configuration where the α-methyl group in the PMMA repeat unit is flanked on both sides by units of the same configuration. It is the major peak in the 8.8–9.1 triad. PMMA produced employing low-temperature free radical polymerization gives largely syndiotactic product. The peak at 8.9 is assigned to the α-methyl present in a heterotactic configuration so that the units on either side of it are unlike the central mer since it now becomes the major peak. The 9.1 peak is the largest for the higher-temperature product produced via free radical polymerization and is due to the triad central unit being flanked by a like and unlike mer.

Today's NMR capability allows the determination of additional structural features in solution and solid state including the identification of end groups, branches, and defects. Also, sufficient experience of the positioning of bands has been gathered to develop computer programs that create spectra and assignments based on submitted structures. While such spectra can be created, they are no substitute for actually running the spectra, but can be used to help in peak assignment.

Combinations of solid state NMR and IR allow the molecular description of the affect of stress or strain, exposure to various conditions including chemical treatments, radiation, and heat on materials.

13.1.5 ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY

Electron paramagnetic resonance (EPR) spectroscopy or electron spin resonance (ESR) spectroscopy is a valuable tool for measuring the relative abundance of unpaired electrons present in macromolecules. For example, macroradicals are formed by the homogeneous cleavage of nylon-6,6 chains when these filaments are broken, with the concentration of macroradicals increasing as the stress is increased.

13.1.6 X-RAY SPECTROSCOPY

X-ray diffraction is a widely used tool for structural identification for almost all solids under the right conditions. X-ray diffractometers are generally either single crystal or powder.

Single-crystal studies allow the absolute configurational determination of polymeric materials that have high degrees of crystallinity. Such determinations are costly with respect to time because of the complexity of polymeric materials.

Powder x-ray spectroscopy can employ smaller crystalline samples from 1 to several hundred nanometers. These crystallites have broadened peak profiles as a result of incomplete destructive interference at angles near the Bragg angle defined as

$$n\lambda = 2d \sin\theta \tag{13.1}$$

where n is the order of a reflection, λ is the wavelength, d is the distance between parallel lattice planes, and θ is the angle between the incident beam and a lattice plane known as the Bragg angle. This broadening allows determination of crystallite size and size distribution. (Note that this is not particle size.)

X-ray analysis of proteins and nucleic acids is especially important as the absolute structure is needed for many advances in the field of medicine and biochemistry.

13.2 SURFACE CHARACTERIZATION

Everything has a surface or an interface. These surfaces have their own kinetic and thermodynamic features that affect their formation and behavior. Sperling notes that for most polymers, the end groups reside perpendicular to the bulk of the polymers probably because the end is less hydrophobic to the bulk and the polymer surfaces generally are “faced” with an air atmosphere that is more hydrophilic. When a polymer solution is deposited onto a surface to “dry,” the concentration has an influence on the orientation of the polymer chains at the surface in the dried solid. Thus, when the amount of polymer is small, the polymer chain lays parallel to the surface in a “pancake” form (Figure 13.1). As the concentration increases, the surface is not able to accommodate the entire polymer chain and it begins to form an inner tangled chain with only the end and some of the chain segments facing the surface forming a “mushroom” shape. Finally, as the concentration of polymer increases, only the ends of the polymer chains occupy the surface with the polymer ends forming “brushes.”

There is no exact, universally accepted definition of a surface. Here, the surface will be defined as the outermost atomic layers, including absorbed foreign atoms. The chemical and

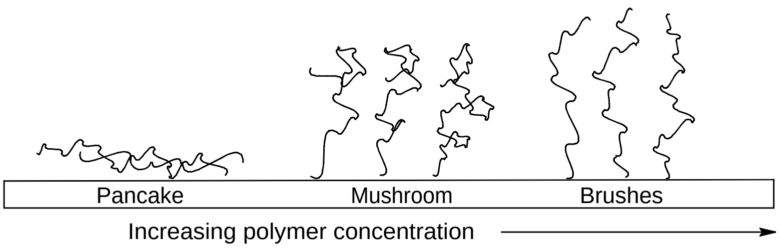

FIGURE 13.1 General surface structures as a function of polymer concentration.

physical composition, orientation, and properties of surfaces typically differ from those of the bulk material.

Current surface characterization techniques fall into two broad categories: those that focus on the outermost few layers (to within the 10–20 layer boundary) and those whose focus includes components present to several thousand angstroms into the solid (hundred to several hundred layers).

ATR typically employs special cells fitted onto traditional IR, FTIR, or UV instruments. While some outer surface aspects are gleaned from such techniques, information to several thousand angstroms is also present in the spectra from ATR.

Techniques that analyze the first few atomic layers generally involve low-energy electrons or ions since the incident radiation should penetrate only the top few layers. Normally, a combination of techniques is employed to clearly define the composition of the outer layers. Special precautions are employed to minimize sample surface contamination.

Sections 13.2.1 through 13.2.5 provide a brief description of some of these modern surface characterization techniques.

13.2.1 AUGER ELECTRON SPECTROSCOPY AND X-RAY PHOTOELECTRON SPECTROSCOPY

Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are the two principle surface analysis techniques. They are used to identify the elemental composition, i.e., the amount and nature of species present at the surface to a depth of about 1 nm.

In Auger transitions, incident electrons interact with the inner shell electrons (E_i) of the sample. The vacancy created by an ejected inner shell electron is filled by an outer shell electron (E_1), and a second outer shell electron (E_2) is ejected leaving the atom in a doubly ionized state. The electrons ejected from the outer shells are called Auger electrons, named after the Frenchman Pierre Auger, who discovered the effect. Thus, AES measures the energies of the Auger electrons (E_a) emitted from the first 10 Å of a sample surface. The energy equation is expressed as

$$E_a = E_1 - E_i + E_2 \tag{13.2}$$

The kinetic energies of these ejected electrons originating within the first 30 Å of the sample surface are measured by XPS. In XPS, a sample is bombarded by a beam of x-rays with energy $h\nu$ and core electrons are ejected with a kinetic energy E_k that overcomes the binding energy E_b, and the work function (ϕ). These core electrons are called the x-ray photoelectrons. The energy equation is expressed as follows:

$$E_k = h\nu - E_b - \phi \tag{13.3}$$

The energies of these photoelectrons are reflected in the kind and environment of the atoms present at the surface.

13.2.2 NEAR-FIELD SCANNING OPTICAL MICROSCOPY

Optical microscopes have one serious drawback, their resolution, resulting from the fundamental physics of lenses. Lord Rayleigh, over 100 years ago, defined the currently accepted maximum optical lens resolution to be one-half of the wavelength of the imaging radiation. In truth, conventional optical microscopy did not achieve this level of definition mainly because of out-of-focus light. This prevented the observation of atoms and single molecules.

Near-field scanning optical microscopy (NSOM) allows an extension of optical microscopy to near that of electron microscopy. The central feature is the optical element that is similar, and sometimes the same, to that employed in atomic force microscopy (AFM). Essentially, light is directed through the probe tip onto the sample from just immediately above the sample surface. The light emanating from the probe tip is smaller than its wavelength and spreads out over the surface. This results in the maximum influence occurring at the surface with little contribution from regions nearby (such as within 30 nm) resulting in little out-of-focus light. Depending upon the surface and sample thickness, the light is measured as absorption or fluorescence and collected and recorded electronically. NSOM can be fitted onto a regular optical microscope or coupled with scanning probe microscopy (SPM).

13.2.3 ELECTRON MICROSCOPY

The upper limit of magnification for optical microscopes is about 2000 times. Thus, additional forms of microscopy have been developed that allow near to actual atomic observation of polymer surfaces. Electron microscopy utilizes an electron beam to act as the sensing radiation in place of light. High-energy electrons take on wave character as they approach the speed of light. The wavelength is inversely proportional to the electron speed or velocity. When accelerated over large voltages, electrons can be made to travel at speeds to permit wavelengths on the order of 0.003 nm. The electron beam is focused and the image is formed using magnetic lenses. The two most common forms of electron microscopy are transmission electron microscopy (TEM) and scanning electron microscopy (SEM).

In SEM, the surface of the polymeric surface is scanned using an electron beam with the reflected or backscattered beam of electrons collected and displayed on a cathode ray tube screen. The image represents the surface contour of the scanned material. Because the surface must be conductive, most polymer surfaces must be overlaid with a conductive coating. Magnifications up to about 50,000 are carried out using SEM.

TEM utilizes an image formed by an electron beam that passes through the sample. This allows internal microstructures to be determined. Structural details of materials can be observed on an atomic level by looking at contrasts in the image caused by various concentrations of different elements. Very thin films are employed. Under good conditions, magnifications up to 1 million are possible employing TEM.

13.2.4 SCANNING PROBE MICROSCOPY

SPM encompasses a group of surface-detection techniques that include AFM and scanning tunneling microscopy (STM) that allow the topographic profiling of surfaces. SPM techniques investigate only the outermost few atomic layers of the surface with nanometer resolutions and at times atomic-level resolution.

STM is generally used with electrically conductive materials applied to polymeric materials giving overlays consisting of conducting material layered over the surface of the sample. STM experiments typically require extremely low pressures less than 1×10^{-10} mbar. By comparison, AFM can be run under room conditions and does not require the use of electrically conductive material. In this procedure, the metallic tip is held close (about 0.5–1 nm) to the surface. A voltage, applied between the tip and sample surface, drives a tunneling current. The conductive surface reconstructs the atomic positions via minimizing the surface free energy. This gives topographic superstructures with specific electronic states which are recorded as surface contours or images.

AFM can be run under room conditions. It can be performed in either of the two forms—a contact mode and a noncontact mode. It does not require the use of electrically conductive material since (in the contact mode) the tip actually "touches" the surface rather than residing immediately above it, as is the case with STM. In both the contact and the noncontact mode, light is used as the sensing source rather than an applied voltage. In contact AFM, a cantilever with as sharp a point as possible is laid onto the sample surface with a small loading force in the range of 10^{-7}–10^{-10} N. Tips of differing size and shape are tailor-made. Data is obtained optically by bouncing an incident laser beam onto the cantilever toward a quadrant detector on or in an interferometer. The AFM can work in two modes—either a contact mode or a noncontact mode. In the noncontact mode, the attractive force is important and the experiment must be carried out under low pressures similar to those employed in STM.

In the contact mode, the tip acts as a low-load, high-resolution profiler. Along with structure determination, the AFM is also used to "move" atoms about allowing the construction of images at the atomic level. The AFM is also an important tool in the nanotechnology revolution.

Nanotubes are being used as points in some SPM units. The ends of these nanotubes can be closed or functionalized offering even "finer" tips and tips that interact with specific sites allowing manipulation on an atom-by-atom basis. These nanotubes are typically smaller than silicon tips and are generally more robust.

AFM is useful in identifying the nature and amount of surface objects. AFM, or any of its variations, also allows studies of polymer phase changes, especially thermal phase changes, and results of stress or strain experiments. In fact, any physical or chemical change that brings about a variation in the surface structure can, in theory, be examined and identified using AFM.

Today there exists a wide variety of AFMs that are modifications or extensions of traditional AFM. Following is a brief summary of some of these techniques.

Contact Mode AFM is the so-called traditional mode of AFM. Topography contours of solids can be obtained in air and fluids.

Tapping Mode AFM measures contours by "tapping" the surface with an oscillating probe tip thereby minimizing shear forces that may damage soft surfaces. This allows increased surface resolution. This is currently the most widely employed AFM mode.

There are several modes that employ an expected difference in the adhesion and physical property (such as flexibility) as the chemical nature is varied. *Phase imaging* experiments can be carried out that rely on differences in surface adhesion and viscoelasticity. *Lateral force microscopy* (LFM) measures frictional forces between the probe tip and sample surface. *Force modulation* measures differences between the stiffness and/or elasticity of surface features. *Nanoindenting or scratching* measures mechanical properties by "nanoindenting" to study hardness, scratching, or wear including film adhesion and coating durability. LEM identifies and maps relative differences in surface frictional characteristics. Polymer applications include identifying transitions between different components in polymer blends, composites, and other mixtures, identifying contaminants on surfaces, and looking as surface coatings. *Noncontact AFM* measures the contour through sensing van der Waals attractive forces between the surface and the probe tip held above the sample. It provides less resolution than tapping mode AFM and contact mode AFM.

There are several modes that employ differences in a material's surface electronic and/or magnetic character as the chemical nature of the surface varies. *Magnetic force microscopy* (MFM) measures the force gradient distribution above the sample. *Electric force microscopy* (EFM) measures the electric field gradient distribution above a sample surface. EFM maps the gradient of the electric field between the tip and the sample surface. The field due to trapped charges, on or beneath the surface, is often sufficient to generate contrast in an EFM image. The voltage can be induced by applying a voltage between the tip and the surface. The voltage can be applied from the microscopes electronics under AFM control or from an external power supply. EFM is performed in one of three modes: phase detection, frequency modulation (FM), or amplitude detection. Three-dimensional plots are formed by plotting the cantilever's phase or amplitude as a function of surface location. *Surface potential (SP) microscopy* measures differences in the local surface potential across the sample surface. SP imaging is a nulling technique. As the tip travels above the surface, the tip and the cantilever experience a force whenever the surface potential differs from that of the tip. The force is nullified by varying the voltage of the tip so that the tip remains at the same potential as the immediate surface. The voltage applied to the tip to maintain this constant potential as the tip surveys the surface with the results plotted as a function of the surface coordinates creating a surface potential image. For best results, SP and EFM do the best job with conductive materials. *Force volume* measurements involve producing two-dimensional arrays of force–distance values allowing a mapping of the force variation and surface topology with individual force curves to be constructed.

Force–distance microscopy measures repulsive, attractive, and adhesion forces between the time and surface during approach, contact, and separation. This technique combines electrical with adhesion or physical property as a means to study sample surfaces.

Scanning thermal microscopy (SThM) measures two-dimensional temperature distributions across a sample surface. This is a special thermal technique.

In **electochemical microscopy**, ECSTM and ECAFM, the material is immersed in electrolyte solution and the surface and properties of conductive materials are studied.

Information derived from several of these techniques go together to give a clearer idea of the nature of the surface.

AFM results can be utilized in conjunction with other techniques. While some techniques, such as small-angle x-ray scattering (SAXS) and small-angle neutron scattering (SANS), allow structural information to be inferred, AFM gives real space results. While some of the polymeric structural designs may not be unambiguously determined, many can be determined employing ATM. The major limitation concerns whether the structures observed at or near the surface are similar to those in the interior. We are well aware that surface composition differs from the interior composition. For instance, surfaces may be less organized being enriched in chain ends, loops, and switchboard chain segments. Further, for "sliced" samples does the "slicing" disturb the fine structure along the "cut" surface. For instance, the structure of linear polymers such as PE has been suggested to consist of ordered or sharp folds, switchboard-like, loops with loose folds, buttressed loops, and combinations of these features. Magonov and Godovsky and others recently investigated the surface structures of a number of polymers employing ATM. For single crystals of PE, ordered grains 10–12 nm in size are found. For melt-crystallized LLDPE spherulites of several microns are the major morphological features. Edge-on standing lamellae and lamellar sheets are found. Dark areas are assigned as amorphous regions. The lamellar edges are on the order of 25–40 nm, while the strands are several microns in length. By comparison, melt-crystallized LDPE, which is only about 30% crystalline, shows only spherulitic patterns with ill-defined ring patterns. The grain sizes are about 15–25 nm with fibrillar structures visible. A sample of melt-crystalized ULDPE with low crystallinity (about 15%) gives largely an ill-defined surface consistent of the surface being largely amorphous. As higher force is applied to press through the surface layer, grains of 0–10 nm and finally 9–11 nm become visible with some grains up to about 100–150 nm visible.

Other polymers have been studied. For instance, iPP shows well-defined spherulites with grains (15–20 nm) embedded in an amorphous material. The grains are assembled in circles and in some cases, along the radial direction, an ordered texture exists. PVDF shows numerous spherulites with fibrils 12–15 nm in width. The granular nanostructure of spherulites has also been found for polyesters and polyurethanes. ATM and other studies (including wide-angle x-ray scattering [WAXS] and SAXS) suggest that the nanoscale grains are elementary building blocks of the crystalline architecture in most polymers. These grains or blocks can have more or less similar structure within them. The overall crystalline structure may be developed as a one-dimensional assembling of grains into fibrils and a two-dimensional assembling of grains into lamella. A correlation between grain size and the size of molecular coils has not yet been answered using ATM.

Spin-cast films of PEO show a flat crystalline morphology with lamellar sheets of different shapes. When melted and then cooled, PEO crystallizes with a similar morphology, except that the lamellar sheets are smaller. When it is again melted and cooled, crystallization proceeds more slowly and the PEO morphology is dominated by spiral crystallites formed via a screw dislocation mechanism. In all cases, the thickness of the lamellar sheets is about 12 nm indicating multiple folding of the PEO chains. The lamellar sheets disappear at about 60°C though the melting point is listed to be 70°C. On cooling, the lamellar structures reappear at about 50°C.

The morphology of spin-cast film, thickness of 180 nm, from polycaprolactone shows many spherulitic structures with fibrillar nanostructures formed of lamellae lying edge on (about 10 nm thick) and areas with lamellar sheets lying flat on. Different crystalline structures are found when the sample is melted and crystallized as a function of temperature. These two studies reinforce the complex inner relationship between physical treatment and nanostructure.

While some structures show seemingly independent spherulitic structures on the surface, we know from other studies that these structures are connected to one another and to the more amorphous regions overall giving a material with a characteristic flexibility and strength. In general, chains are shared with adjacent areas allowing a sharing of stress or strain factors.

AFM is important for biological as well as synthetic macromolecules. Several examples are given to illustrate applications. Collagen is an important natural protein that is present in many tissues including bones, skin, tendons, and the cornea. It is also employed in medical devices such as artificial skin, tendons, cardiac valves, ligaments, hemostatic sponges, and blood vessels. There are at least 13 different types of collagen. ATF can image collagen molecules and fibers and their organization, allowing identification of the different kinds of collagen and at least surface interactions.

AFM allows the study of cell membranes. The precise organization of such cell membranes is important since they play a role in cell communication, replication, and regulation. It is possible to study real-time interactions of such biologically important surfaces. Further, bilayers, modeled or containing naturally produced bilayers are used as biosensors. Again, interactions of these biomembranes can be studied employing AFM. For instance, the degradation of bilayers by phospholipases, attachment of DNA, etc. can be studied on a molecular level. In another application, antibody–antigen interactions have been studied employing AFM. One application of this is the creation of biosensors to detect specific interactions between antigens and antibodies.

13.2.5 SECONDARY ION MASS SPECTROSCOPY

Secondary ion mass spectroscopy (SIMS) is a sensitive surface analysis tool. Here, the mass analysis of negative and positive ions sputtered from the polymer surface through ion bombardment is analyzed. The sputtering ion beam is called the primary ion beam. This beam causes erosion of the polymer surface removing atomic and molecular ions. Then, these newly created ions, composing what is called the secondary ion beam, are analyzed as a function of mass and intensity. Depth of detection for SIMS is of the order of 20–50 Å. Because it is the ions in the secondary ion beam that are detected, the mass spectra obtained from SIMS are different from those obtained using simple electron impact methods. The extent of particular ion fragments observed is dependent on a number of factors including the ionization efficiency of the particular atoms and molecules composing the polymer surface.

SIMS can detect species that are present on surfaces of the order of parts-per-million to parts-per-billion.

TABLE 13.1
Techniques Employed to Study the Amorphous Regions of Polymers

Short-Range Interactions	Long-Range Interactions
Magnetic birefringence	Electron diffraction
Raman scattering	Wide-angle x-ray scattering
Depolarized light scattering	Electron microscopy
Rayleigh scattering	Density
Bruillouin scattering	Small-angle neutron scattering
NMR relaxation	
Small-angle x-ray scattering	

13.3 AMORPHOUS REGION DETERMINATIONS

Experimental tools that have been employed in an attempt to characterize amorphous regions are given in Table 13.1. Techniques such as birefringence and Raman scattering give information related to the short-range (less than 20 Å) nature of the amorphous domains while techniques such as neutron scattering, electron diffraction, and electron microscopy gives information concerning the longer range nature of these regions.

Birefringence measures order in the axial, backbone direction. The birefringence of a sample can be defined as the difference between the refractive indices for light polarized in two directions 90° apart. Thus, a polymer sample containing polymer chains oriented in a preferential direction by stretching or some other method will exhibit a different refractive index along the direction of preferred chain alignment compared to that obtained at right angles. This change in birefringence gives information concerning the amount of order, thus, information about disorder.

SANS results indicate that vinyl polymers exist in random coils in the amorphous state. Results from electron and x-ray diffraction studies show diffuse halos consistent with the nearest-neighbor spacings being somewhat irregular. It is possible that short-range order and long-range disorder exist within these amorphous regions.

13.4 MASS SPECTROMETRY

There are a number of mass spectrometry techniques available and directly applicable to polymers. Since high polymers have high molecular weights, determination of unbroken chains is not usual. Even so, determination of structures of ion fragments of segments of the polymers is straightforward and a valuable tool in determining the unit structure.

The exception to this is the application of matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). In 1981, Barber and Liu and coworkers independently introduced the concept of employing MALDI where the absorption of the matrix is chosen to coincide with the wavelength of the employed laser to assist in the volatilization of materials. In 1988, Tanaka, Hillenkamp, and coworkers employed the laser as the energy source, giving birth to MALDI-MS.

MALDI-MS was developed for the analysis of nonvolatile samples and was heralded as an exciting new MS technique for the identification of materials with special use in the identification of polymers. It has fulfilled this promise to only a limited extent. While it has become a well-used and essential tool for biochemists in exploring mainly nucleic acids and proteins, it has been only sparsely employed by synthetic polymer chemists. This is because of lack of congruency between the requirements of MALDI-MS and most synthetic polymers.

Classical MALDI-MS requires that the material should be soluble in a suitable solvent. A "suitable solvent" means a solvent that is sufficiently volatile to allow it to be evaporated prior to the procedure. Further, such a solvent should dissolve both the polymer and the matrix material. Finally, an ideal solvent will allow a decent level of polymer solubility, preferably a solubility of several percentage and greater. For most synthetic polymers, these qualifications are only approximately attained. Thus, traditional MALDI-MS has not achieved its possible position as a general use modern characterization tool for synthetic polymers. By comparison, MALDI-MS is extremely useful for many biopolymers where the polymers are soluble in water. It is also useful in the identification of synthetic polymers, such as PEO where the solubility requirements are fulfilled. Thus, for PEO we have determined the molecular weight distribution of a series of compounds with the separations in ion fragment mass 44 Da corresponding to CH_2–CH_2–O units.

Recently, Carraher and coworkers, especially Sabir and Cara Carraher, reported on the use of MALDI-MS except focusing on the formation of fragments from the laser bombardment. This approach is named fragmentation matrix-assisted laser desorption/ionization mass spectrometry (FMALDI-MS) because it is the fragmentation fragments that are emphasized in the study. The technique should be applicable to any solid when the proper operating conditions are employed. While it is unable to give molecular weight data it is able to generate identifiable units to the 100,000–200,000 Da range, the upper limit thus far tested. For lower-molecular weight samples, entire chains are identifiable.

13.5 THERMAL ANALYSIS

Because polymeric materials are expected to perform under a variety of temperature conditions, thermal properties are important. Thermal property investigations can also allow better design of materials that meet the thermal requirements and may also give added structural data.

Major instrumentation involved with the generation of thermal property behavior of materials includes thermogravimetric analysis (TG, TGA), DSC, differential thermal analysis (DTA), torsional braid analysis (TBA), thermomechanical analysis (TMA), thermogravimetric-mass spectrometry (TG-MS) analysis, and pyrolysis gas chromatography (PGC). Most of these analysis techniques measure the polymer response as a function of time, atmosphere, and temperature.

One of the simplest techniques is PGC in which the gases, resulting from the pyrolysis of a polymer, are analyzed by gas chromatography. This technique may be used for qualitative and quantitative analysis. The latter requires calibration with known amounts of a standard polymer pyrolyzed under the same conditions as the unknown.

There are several different modes of thermal analysis described as DSC. DSC is a technique of nonequilibrium calorimetry in which the heat flow into, or away from, the polymer is measured as a function of temperature, atmosphere, and/or time. This differs from DTA where the temperature difference between a reference and a sample is measured. Even so, the distinction is not always clear. DSC equipment measures the heat flow by maintaining a thermal balance between the reference and sample by changing a current passing through the heaters under the two chambers. For instance, the heating of a sample and a reference proceeds at a predetermined rate until heat is emitted or consumed by the sample. The circuitry is programmed to give a constant temperature between the reference and sample compartments. If an endothermic occurrence takes place, such as the melting of the sample, the temperature of the sample will be less than that of the reference. Less current is given to the sample and the amount of the decrease reflects the amount of energy needed to melt the sample. The amount of energy required to melt the sample is generally given as the area under the resulting curve. The advantages of DSC and DTA over a good adiabatic calorimeter include speed, low cost, and the ability to use small samples.

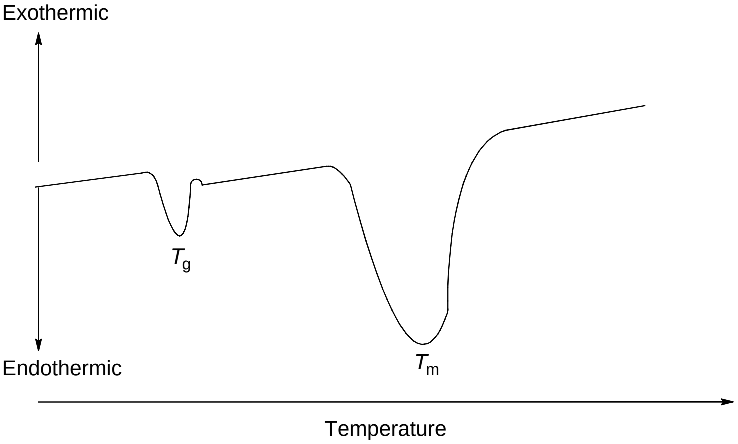

FIGURE 13.2 Representative DCS thermogram.

The resultant plot of ΔT as a function of temperature is known as a thermogram. Figure 13.2 contains a thermogram emphasizing T_g and T_m endothermic regions for a polymer sample that is approximate 50% crystalline. Several things should be noted. First, the magnitude of the T_m is greater than T_g because it requires more energy to gain entire chain mobility than to achieve segmental mobility. There is a small exothermic region after the T_g that reflects a tendency to form crystalline micelles when there is sufficient mobility to allow their formation.

Possible determinations from DSC or DTA measurements include: (1) heat of transition, (2) heat of reaction, (3) sample purity, (4) phase diagram, (5) specific heat, (6) sample identification, (7) percentage incorporation of a substance, (8) reaction rate, (9) rate of crystallization or melting, (10) solvent retention, and (11) activation energy. Thus, thermocalorimetric analysis can be a useful tool in describing the chemical and physical relationship of a polymer with respect to temperature.

In TGA, a sensitive balance is used to follow the weight change of a polymer as a function of time, atmosphere, or temperature. Figure 13.3 shows a typical TGA thermogram for a

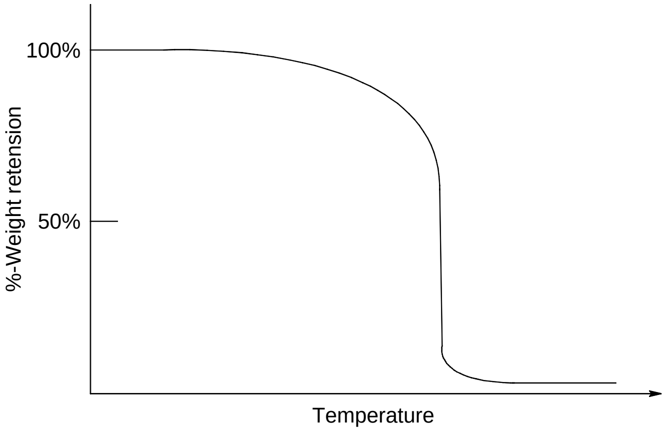

FIGURE 13.3 TGA thermogram for a typical vinyl polymer.

vinyl polymer such as PE. For such polymers, where there is a similar thermal energy stability of the backbone, the TGA decrease generally occurs with one downward sweep beginning at about 200°C and being completed before 300°C. There is normally some residue that is high in carbon content remaining to over 1000°C.

Along with a determination of the thermal stability of the polymer, TGA can be used to determine the following: (1) sample purity, (2) identification, (3) solvent retention, (4) reaction rate, (5) activation energy, and (6) heat of reaction.

TMA measures the mechanical response of a polymer looking at (1) expansion properties including the coefficient of linear expansion, (2) tension properties such as measurement of shrinkage and expansion under tensile stress, i.e., elastic modulus, (3) volumetric expansion, i.e., specific volume, (4) single-fiber properties, and (5) compression properties such as measuring the softening or penetration under load.

In TBA, changes in structure are measured. The name TBA is derived from the fact that measurements were initially made of fibers that were "braided" together to give the test samples connected between or onto vice-like attachments or hooks.

Reading and coworkers have pioneered in the adaptation of nanoassociated AFM for thermal analyses. The tip of the AFM is replaced with a miniature resistive heater that is used to heat or measure temperature differences on a nanoscale. This allows differentiation between phases and (at times) individual polymer chains and segments (e.g., block and graft segments of copolymers). T_g, T_m, and melting temperatures are based on differences in thermal conductivity and diffusivity. This technique of using the microthermal sensor, microthermal differential scanning calorimetry (MTDSC) is called calorimetric analysis with scanning microscopy (CASM). The probe can also be used to measure certain mechanical properties performing a micro-thermal mechanical analysis with scanning microscopy (MASH).

Newer techniques are being developed and modifications of existing techniques continue.

13.6 THERMAL PROPERTY TESTS

In general, thermal properties such as T_g, T_m, and softening temperatures are really ranges. Because of the large size of polymers, the structures are varied within them so that different amounts of heat are needed to cause disruption of the different sites when heating occurs. On cooling, time is needed to allow the chains to arrange themselves. Heating rates contribute to the particular range obtained. In general, the faster the heating rate, the wider the range. Some of these different conformational sites are shown in Figure 13.4.

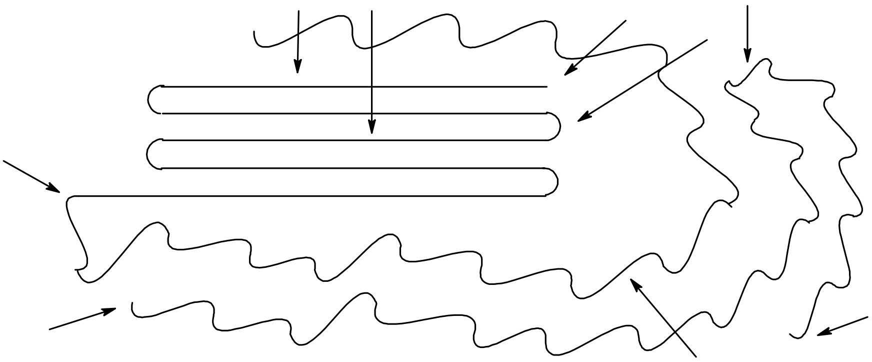

FIGURE 13.4 Simple chain arrangement for a linear polymer containing both ordered and unordered structures.

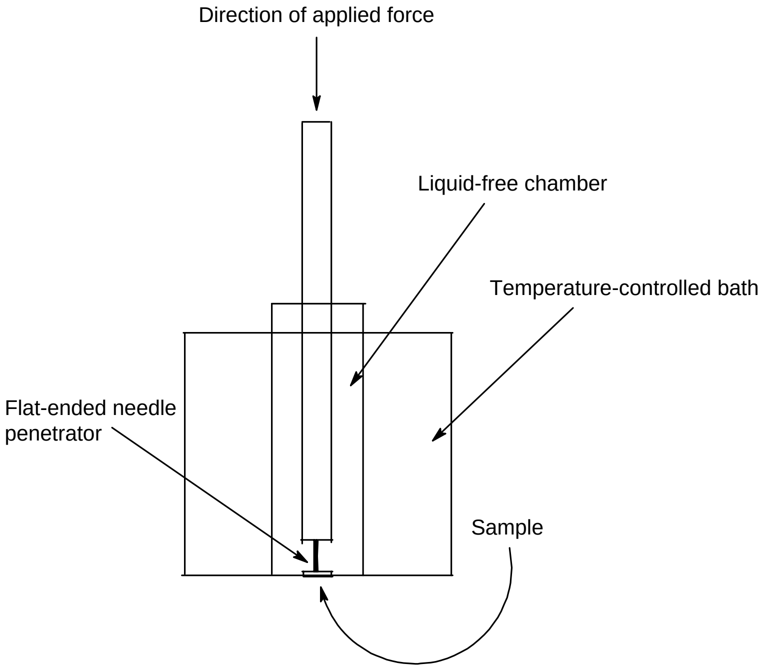

FIGURE 13.5 Vicat apparatus for determining softening points.

13.6.1 SOFTENING RANGE

Softening ranges are dependent on the technique and procedure used to determine them. Thus, listings of softening ranges should be accompanied with how they are determined. Following are some of the techniques used to determine softening ranges. While DSC gives a more precise measurement of not only the T_g, it often approximates the softening range. The capillary method of determining the melting point of small molecules can also be used to gain some idea as to the softening point. Another related technique is to simply use a Fisher–John melting point apparatus and apply some pressure to a sample contained between two glass slides.

The viscat needle method (Figure 13.5) consists of determining the temperature at which a standard needle penetrates a sample. In the ring-and-ball method, the softening range is determined by noting the temperature at which the sample, held within a ring, can be forced through the ring by application of a standard force.

13.6.2 HEAT DEFLECTION TEMPERATURE

The heat deflection temperature (ASTM D-648) is determined by noting the temperature where a simple beam under a specific load deflects a specific amount (generally 0.01 in.; 0.25 mm; Figure 13.6) within an environment. As in other ASTM, the experimental conditions are specified including sample size.

13.6.3 GLASS TRANSITION TEMPERATURES

Qualitatively, the T_g corresponds to the onset of short-range (typically 1–5 chain atoms) coordinated motion. Actually, many more (often 10–100) chain atoms may attain sufficient thermal energy to move in a coordinated manner at T_g. The T_g (ASTM D-3418) is the

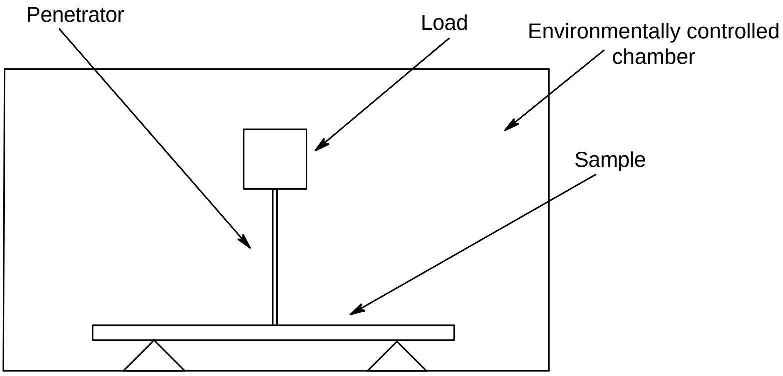

FIGURE 13.6 Deflection temperature test assembly.

temperature at which there is an absorption or release of energy as the temperature is raised or lowered, respectively. The T_g can be measured by any means that allows changes in the conformation of the chains to be detected. Thus, most of the thermal techniques allow T_g to be determined. Also, most of the spectral techniques allow T_g to be determined as well as techniques that measure volume changes. Dynamic mechanical spectroscopy (DMS) is also used to measure chain changes by subjecting the sample to repeated small-amplitude stains in a cyclic fashion as a function of temperature. The polymer molecules store some of the imparted energy and dissipate a portion in the form of heat. Since the amount of energy stored and converted to heat is related to molecular motion, changes in the ratios of energy stored to energy converted to heat are used to measure T_g. Sperling compared literature reports of T_g values for some common polymers and found differences of tens of degrees not uncommon.

13.6.4 THERMAL CONDUCTIVITY

As energy in the form of heat, magnetic, or electric, is applied to one side of a material, the energy is transmitted to other areas of the sample. Heat energy is largely transmitted through the increased amplitude of molecular vibrations. The heat flow Q from any point in a solid is related to the temperature gradient, dt/dl through the thermal conductivity λ as follows:

$$Q = -\lambda(dt/dl) \tag{13.4}$$

Table 13.2 contains a listing of the thermal conductivities of selected materials.

Most polymers have thermal conductivity values in the general range between 10^{-1} and 1 W/m-K. For polymers, transmission of thermal energy, heat, is favored by the presence of ordered crystalline lattices and covalently bonded atoms. Thus graphite, quartz, and diamond are relatively good thermal conductors. Crystalline polymers such as HDPE and iPP exhibit somewhat higher thermal conductivities than amorphous polymers such as LDPE and atactic polystyrene (aPS). In general, thermal conductivity increases with increasing density and crystallinity for the same polymer. For amorphous polymers, where energy is transmitted through the polymer backbone, thermal conductivity increases as the chain length increases. Addition of small molecules, such as plasticizers, generally decreases thermal conductivity.

As long as a polymer does not undergo a phase change, thermal conductivity is not greatly affected by temperature changes. Aligning of polymers generally increases their thermal conductivities along the axis of elongation. For instance, the conductivity of HDPE increases tenfold along the axis of elongation at 10% strain.

TABLE 13.2
Thermal Conductivities of Selected Materials

Material	Approximate Thermal Conductivity (W/m-K)	Material	Approximate Thermal Conductivity (W/m-K)
Copper	7200	aPS	0.16
Graphite	150	PS (foam)	0.04
Iron	90	PVC	0.16
Diamond	30	PVC (foam)	0.03
Quartz	10	Nylon-6,6	0.25
Glass	1	PET	0.14
PMMA	0.19	NR	0.18
HDPE	0.44	PU	0.31
LDPE	0.35	PU (foam)	0.03
iPP	0.24	PTFE	0.27
PVC (35% plasticizer)	0.15		

Foamed cellular materials have much lower thermal conductivities because the gas employed to create the foam is a poor conductor. Thus, foams are employed as commercial insulators in buildings, thermal jugs, and drinking mugs.

13.6.5 THERMAL EXPANSION

Coefficients of thermal expansion generally refer to differences in length, area, or volume as a function of a temperature unit. Relative to metals such as steel, polymers have large coefficients of thermal expansions. Polymers also have quite varied coefficients of thermal expansion. Both of these factors are troublesome when different materials are bound together, including composites, and exposed to wide temperature ranges. Such wide temperature ranges regularly occur in the aerospace industry (aircraft), within computer chips (and many other electrical devices), engines, motors, etc. Thus, it is critical to match the coefficients of thermal expansions of materials that are to be bound through mechanical (e.g., screws and bolts) and chemical (polymer blends, alloys, adhered through use of an adhesive) means, or stress will develop between the various components resulting in fracture or separation.

For polymeric materials, factors that restrict gross movement, such as cross-linking, typically result in lowered coefficients of expansion. Thus, the typical range for coefficients of expansion for cross-linked thermosets is lower than the typical range found for thermoplastics. Further, materials such as glass, graphite, and concrete also exhibit low coefficients of expansion for the same reason.

13.7 FLAMMABILITY

Since many polymeric materials are used as clothing, household items, components of automobiles and aircraft, etc. flammability is an important consideration. Some polymers such as polytetrafluoroethylene and PVC are “naturally” flame-resistant, but most common polymers such as PE and PP are not. Small-scale horizontal flame tests have been used to estimate the flammability of solid (ASTM D-635), cellular (ASTM D-1692-74), and foamed (ASTM D-1992) polymers, but these tests are useful for comparative purposes only. Large-scale tunnel tests (ASTM E-84) are more accurate, but they are also more expensive to run than ordinary laboratory tests cited before.

One of the most useful laboratory flammability tests is the oxygen index (OI) test (ASTM D-2043 and ASTM D-2863). In this test, the polymer is burned by a candle in controlled mixtures of oxygen and nitrogen. The minimum oxygen concentration that produces downward flame propagation is considered the OI or ignitability of the polymer.

It is interesting that we have the ability to make structures more flame-resistant, but in the past did not take advantage of these means. For instance, the steel inner structures of many high-rise buildings can be made to withstand most fires through coating the steel with flame-resistant polymers. The practice of using such coatings was resisted because of added cost and the need to have trained workers to apply such coatings. Even so, because insurance companies lowered the premium for buildings possessing such coatings, today such coating is a general practice.

13.8 ELECTRICAL PROPERTIES: THEORY

Polymers have served as important materials in the electronics industry. Generally, they have served as coating and containers because of their lack of conductivity; i.e., they are nonconductors. More recently, polymers have become major materials as conductors.

Some important dielectric behavior properties are dielectric loss, loss factor, dielectric constant, direct current (DC) conductivity, alternating current (AC) conductivity, and electric breakdown strength. The term "dielectric behavior" usually refers to the variation of these properties as a function of frequency, composition, voltage, pressure, and temperature.

The dielectric behavior is often studied by employing charging or polarization currents. Since polarization currents depend on the applied voltage and the dimensions of the condenser, it is customary to eliminate this dependence by dividing the charge, Q, by the voltage, V, to get a parameter called the capacitance (capacity), C:

$$C = Q/V \tag{13.5}$$

and then using the dielectric constant ε, which is defined as

$$\varepsilon = C/C_0 \tag{13.6}$$

where C is the capacity of the condenser when the dielectric material is placed between its plates in a vacuum and C_0 is the empty condenser capacity.

Dielectric polarization is the polarized condition in a dielectric resulting from an applied AC or DC field. The polarizability is the electric dipole moment per unit volume induced by an applied field or unit effective intensity. The molar polarizability is a measure of the polarizability per molar volume; thus it is related to the polarizability of the individual molecules or polymer repeat unit.

Conductivity is a measure of the number of ions per unit volume and their average velocity in the direction of the applied field. Polarizability is a measure of the number of bound charged particles per cubic unit and their average displacement in the direction of the applied field.

There are two types of charging currents and condenser charges, which may be described as rapidly forming or instantaneous polarizations and slowly forming or absorptive polarizations. The total polarizability of the dielectric is the sum of contributions due to several types of charge displacement in the materials caused by the applied field. The relaxation time is the time required for polarization to form or disappear. The magnitude of the polarizability, k, of a dielectric is related to the dielectric constant, ε, as follows:

$$k = 3(\varepsilon - 1)/4\pi(\varepsilon + 2) \tag{13.7}$$

The terms "polarizability constant" and "dielectric constant" are often used interchangeably in a qualitative discussion of the magnitude of the dielectric constant. The k values obtained

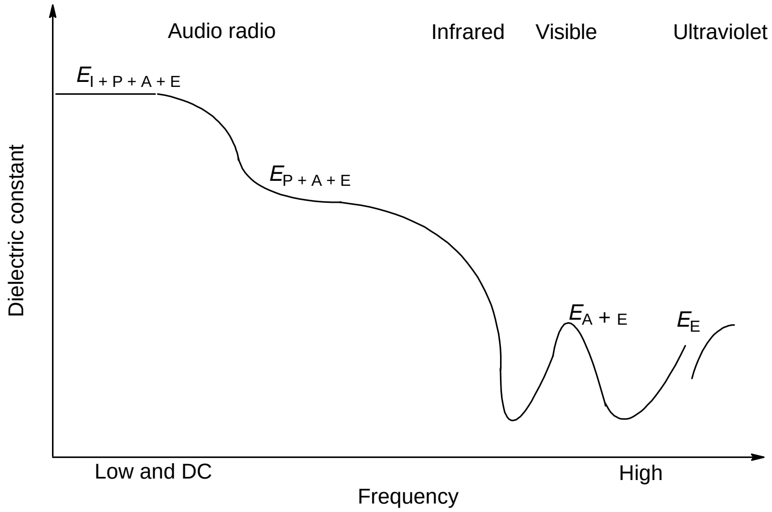

FIGURE 13.7 Relationship of dielectric constant with frequency-emphasizing interfacial (I), dipole (P), atomic (A), and electronic (E) polarization contributions.

utilizing DC and low-frequency measurements are a summation of electronic (E), atomic (A), dipole (D), and interfacial (I) polarizations as shown in Figure 13.7. Only the contribution by electronic polarizations is evident at high frequencies. The contributions to dielectric constant at low frequencies are additive as shown in Figure 13.7.

Instantaneous polarization occurs when rapid (less than 10^{-10} s) transitions occur, i.e., at frequencies greater than 10^{10} Hz or at wavelengths less than 1 cm. Electronic polarization falls within this category and is due to the displacement of charges within the atoms. *Electronic polarization* is directly proportional to the number of bound electrons in a unit volume and inversely proportional to the forces binding these electrons to the nuclei of the atoms.

Electronic polarization occurs so rapidly that there is no observable effect of time or frequency on the dielectric constant until frequencies are reached that correspond to the visible and UV spectra. For convenience, the frequency range of the IR through the UV region is called the optical frequency range, and the radio and the audio range is called the electric frequency range. Electronic polarization is an additive property dependent on the atomic bonds. Thus, the electronic polarizations and related properties are similar for both small molecules and polymers. Accordingly, values obtained for small molecules can be applied to analogous polymeric materials. This does not apply when the polymeric nature of the material plays an additional role in the conductance of electric charges, as in the case for whole-chain resonance or whole-chain delocalization of electrons.

Atomic polarization contributes to the relative motion of atoms in the molecule affected by perturbation by the applied field of the vibrations of atoms and ions having a characteristic resonance frequency in the IR region. The atomic polarization is large in inorganic materials which contain low-energy conductive bonds and approaches zero for nonconductive polymers. The atomic polarization is rapid, and this, as well as the electronic polarization, constitutes the instantaneous polarization components.

The remaining types of polarization are absorptive types with characteristic relaxation times corresponding to relaxation frequencies. Debye, in 1912, suggested that the high dielectric constants of water, ethanol, and other highly polar molecules were due to the presence of permanent dipoles within each individual molecule and that there is a tendency

TABLE 13.3
Selected Electrical Primary and Derived Units

Electrical Value	Symbol	SI Units Primary	SI Units Derived
Capacitance	C	s^2-C^2/kg-m^2	F
Conductivity	S	s-C^2/kg-m^3	1/Ω-m
Dielectric constant	e, e_r	Simple ratio with no units	
Dielectric displacement	D	C/m^2	F-V/m^2
Electric charge	Q	C	C
Electrical current	I	C/s	A
Electric polarization	P	C/m^2	F-V/m^2
Electric potential	V	kg-m^2/s^2-C	V
Permittivity	E	s^2-C^2/kg-m^3	F/m
Resistance	R	kg-m^2/s-C^2	Ω
Resistivity	R	kg-m^3/s-C^2	Ω-m

for the molecules to align themselves with their dipole axes in the direction of the applied field. The major contributions to *dipole polarizations* are additive and are similar whether the moiety is within a small or large (macromolecule) molecule. Even so, the secondary contributions to the overall dipole polarization of a sample are dependent on both the chemical and physical environment of the specific dipole unit, its size, and its mobility. Thus, dipole contributions can be used to measure the T_g and T_m.

The polarizations noted above are the major types found in homogeneous materials. Other types of polarization, called *interfacial polarizations*, are the result of heterogeneity. Ceramics, polymers with additives, and paper are considered to be electrically heterogeneous.

Table 13.3 contains often used electrical units.

13.9 ELECTRIC MEASUREMENTS

Material response is typically studied using either direct (constant) applied voltage (DC) or alternating applied voltage (AC). The AC response as a function of frequency is characteristic of a material. In the future, such electric spectra may be used as a product identification tool, much like IR spectroscopy. Factors such as current strength, duration of measurement, specimen shape, temperature, and applied pressure affect the electric responses of materials. The response may be delayed because of a number of factors including the interaction between polymer chains, the presence within the chain of specific molecular groupings, and effects related to interactions in the specific atoms themselves. A number of properties, such as relaxation time, power loss, dissipation factor, and power factor are measures of this lag. The movement of dipoles (related to the dipole polarization (P) within a polymer can be divided into two types: an orientation polarization (P′) and a dislocation or induced polarization.

The relaxation time required for the charge movement of electronic polarization E to reach equilibrium is extremely short (about 10^{-15} s) and this type of polarization is related to the square of the index of refraction. The relaxation time for atomic polarization A is about 10^{-3} s. The relaxation time for induced orientation polarization P′ is dependent on molecular structure and it is temperature-dependent.

The electric properties of polymers are also related to their mechanical behavior. The dielectric constant and dielectric loss factor are analogous to the elastic compliance and mechanical loss factor. Electric resistivity is analogous to viscosity. Polar polymers, such as ionomers, possess permanent dipole moments. These polar materials are capable of storing more electric energy than nonpolar materials. Nonpolar polymers are dependent almost entirely on induced dipoles for electric energy storage. Thus, orientation polarization is produced in addition to the induced polarization when the polar polymers are placed in an electric field. The induced dipole moment of a polymer in an electric field is proportional to the field strength, and the proportionality constant is related to the polarizability of the atoms in the polymer. The dielectric properties of polymers are affected adversely by the presence of moisture, and this effect is greater in hydrophilic than in hydrophobic polymers.

The Clausis–Mossotti equation (Equation 13.8) shows that the polarization of a polymer (P) in an electric field is related to the dielectric constant, i.e., the molecular weight, M, and the density, ρ.

$$P = (\mathrm{e} - 1/\mathrm{e} + 2)M/\rho \tag{13.8}$$

At low frequencies, the dipole moments of polymers are able to remain in phase with changes in a strong electric field resulting in low power losses. However, as the frequency increases the dipole reorientation may not occur sufficiently rapid to maintain the dipole in phase with the electric field and power losses occur.

13.9.1 DIELECTRIC CONSTANT

As previously noted, the dielectric constant, e (ASTM D-150-74), is the ratio of the capacity of a condenser made with or containing the test material compared with the capacity of the same condenser with air as the dielectric. Polymers employed as insulators in electrical applications should have low dielectric constants, while those used as semiconductors or conductors should have high dielectric constants.

The dielectric constant is independent of electrical frequency at low to moderate frequencies, but varies at higher frequencies. For most materials, the dielectric constant is approximately equal to the square of the index of refraction and to one-third of the solubility parameter.

13.9.2 ELECTRICAL RESISTANCE

There are a number of electrical properties related to electrical resistance (ASTM D-257). These include insulation resistance, volume resistivity, surface resistivity, volume resistance, and surface resistance.

The bulk (or volume)-specific resistance is one of the most useful general electrical properties. Specific resistance is a physical quantity that may vary more than 10^{23} in readily available materials. This unusually wide range of conductivity allows wide variety of electrical applications. Conductive materials, such as copper, have specific resistance values of about 10^{-6} Ω-cm, whereas good insulators such as polytetrafluoroethylene and LDPE have values of about 10^{17} Ω-cm. Specific resistance is calculated from the following equation where R is the resistance in ohms, a is the pellet area in square centimeters, t is the pellet thickness in centimeter, and P is the specific resistance in ohm-centimeter:

$$P = R(a/t) \tag{13.9}$$

13.9.3 DISSIPATION FACTOR AND POWER LOSS

The dissipation factor (ASTM D-150) has been defined in several ways including the following:

1. Ratio of the real (in phase) power to the reactive (90° out of phase) power
2. Measure of the conversion of the reactive power to real power or heat

3. Tangent of the loss angle and the cotangent of the phase angle
4. Ratio of the conductance of a capacitor (in which the material is the dielectric material) to its susceptibility

Both the dielectric constant and dissipation factor are measured by comparison of results obtained with those obtained from a sample with known dissipation factor or dielectric constant values or substitution in an electrical bridge.

The power factor is the energy required for the rotation of the dipoles of a polymer in an applied electrostatic field of increasing frequency. Typical values vary from 1.5×10^4 for polystyrene to 5×10^{-2} for plasticized cellulose acetate. Values increase at T_g and T_m because of the increased chain mobility gained so that T_g and T_m have been measured using differences in the power factor as temperature is increased.

The loss factor is the product of the power factor and the dielectric constant, and is a measure of the total electric loss in a material.

13.9.4 ELECTRICAL CONDUCTIVITY AND DIELECTRIC STRENGTH

A steady current does not flow in a perfect insulator in a static electric field, but energy is "stored" in the sample as a result of dielectric polarization. Thus, the insulator acts as a device to store energy. In reality, some leakage of current occurs even for the best insulators.

The insulating property of materials breaks down in strong electrical fields. This breakdown strength, called the electric or dielectric strength (DS) is the voltage where material electrical failure occurs. The DS is often related to material thickness, L, as shown in the following equation:

$$\text{DS is proportional to } L^{-0.4} \tag{13.10}$$

Breakdown may occur below the measured DS because of an accumulation of energy through inexact dissipation of the current. This leads to an increase in temperature and thermal breakdown. Breakdown means sudden passage of excessive current through the material that often is visible.

The DS is high for many insulating polymers and may be high as 10^3 MV/m. The upper limit of the DS is dependent on the ionization energy of the polymer. Electric or intrinsic decomposition (breakdown) occurs when electrons are removed from their associated nuclei resulting in secondary ionization occurring and accelerated decomposition. The DS is reduced by mechanical loading of the sample and by increasing the temperature, both making the material more susceptible to degradation.

DS (ASTM D-149) is an indication of the electrical strength of an insulating material and it is dependent on the particular test conditions.

Following are some relationships that are generally pertinent to describing the electrical properties of polymers.

For conductive polymers, and other materials, conductivity is defined by Ohm's law which says

$$U = RI \tag{13.11}$$

where I is the current in amperes through a resistor, U is the drop in potential in volts, and the relationship between I and U is called the resistance generally measured in ohms. Resistance, R, is measured by applying a known voltage across the material and measuring the current that passes though it. The reciprocal of resistance ($1/R$) is called conductance. Ohm's law is an empirical law related in irreversible thermodynamics to the flow of the current, I, as a result of a potential gradient that leads to energy being dissipated. (Not all materials obey Ohms law.) Gas discharges, semiconductors, and vacuum tubes are what are called one-dimensional conductors and generally deviate from Ohm's law.

For materials that obey Ohm's law, the resistance is proportional to the length, l, of a sample and inversely proportional to the material cross section, A.

$$R = \rho l/A \tag{13.12}$$

where ρ is the resistivity measured in ohm-meters.

The resistivity is the resistance per unit distance such as ohms per centimeter.

As noted earlier, the inverse of ρ is called conductivity and is generally given in siemens per centimeter (S/cm) (S = 1/ohm). The SI unit of conductivity is S/m, but it is often reported as S/cm so attention should be paid as to which unit is being used. A graph of conductivity for many materials is given in Section 19.1.

Conductivity depends on a number of factors including the number of density of charge carriers (number of electrons, n) and how rapidly they can move in the sample called mobility μ.

$$\text{Conductivity} = n\mu e_c \tag{13.13}$$

where e_c is the electron charge.

Conductivity also varies with temperature generally decreasing for "metallic" materials such as silver and copper, but increasing as temperature is increased for semiconductive materials such as insulator, semiconductive, and conductive polymers (Section 19.1).

The capacitance, C, relates the ability of a material to hold or store electrical charge and is defined as

$$C = Q/V \tag{13.14}$$

where Q is the charge in coulombs, C.

Alternating currents generally are displaced in time such that it is out of phase with the voltage by an angle δ. The tangent of this angle is the dissipation factor and is related to the power loss as follows:

$$W_{\text{loss}} = 2\pi f C_{\text{p}} \text{ (tangent } \delta) V^2 \tag{13.15}$$

where W_{loss} is the work loss in watts, f is the frequency of the voltage, and C_{p} is the parallel capacitance of the sample. The relative dielectric constant, permittivity, is described as

$$\varepsilon = C_{\text{p}}/C_{\text{v}} \tag{13.16}$$

where C_{v} is the capacitance of vacuum. The dielectric loss constant, ε', also called the loss factor is described as follows:

$$W_{\text{loss}} \cong \varepsilon \text{ tangent } \delta = \varepsilon' \tag{13.17}$$

13.10 OPTICAL PROPERTIES TESTS

Since polymers are often used as clear plastics or coatings and have many applications where transparency is an important property, knowledge of the optical properties of specific polymers is essential. The radiation scale, of course, includes microwave, IR, UV, and visible

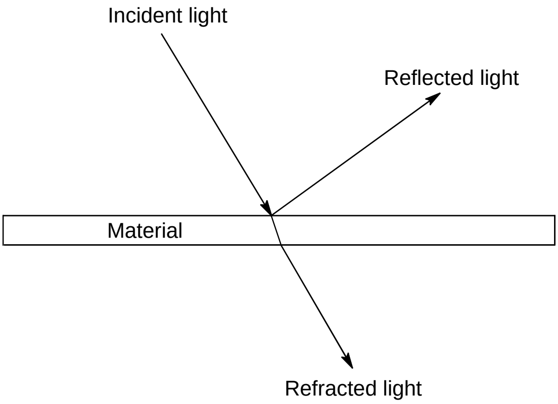

FIGURE 13.8 Refraction and reflection of incident light at the surface of a solid.

regions. It is important to recognize the difference between refraction (associated with properties such as refractive index) and reflection (associated with properties such as haze). This difference is illustrated in Figure 13.8.

13.10.1 INDEX OF REFRACTION

Optical properties are related to both the degree of crystallinity and the actual polymer structure. Most polymers do not possess color site units, so are colorless and transparent. But, some phenolic resins and polyacetylenes are colored, translucent, or opaque. Polymers that are transparent to visible light may be colored by the addition of colorants, and some become opaque as a result of the presence of additives such as fillers, stabilizers, moisture, and gases.

Many of the optical properties of a polymer are related to the refractive index, n, which is a measure of the ability of the polymer to refract or bend light as it passes through the polymer. The refractive index n is equal to the ratio of the sine of the angles of incidence, i, and refraction, r, of light passing through the polymer.

$$n = \sin i / \sin r \tag{13.18}$$

The magnitude of n is related to the density of the substance and varies from 1.000 and 1.3333 for vacuum and water, to about 1.5 for many polymers and 2.5 for white pigment, titanium (IV) oxide (titanium dioxide). The value of n is often high for crystals and is dependent on the wavelength of the incident light and on the temperature. It is usually reported for the wavelength of the transparent sodium D line at 298 K. Typical refractive indices for polymers range from 1.35 for polytetrafluoroethylene to 1.67 for polyarylsulfone.

13.10.2 OPTICAL CLARITY

Optical clarity or the fraction of illumination transmitted through a material is related by the Beer–Lambert relationship:

$$\log\ I/I_0 = -\mathrm{AL} \quad \text{and} \quad I/I^0 = \mathrm{e}^{-\mathrm{AL}} \tag{13.19}$$

where the fraction of illumination transmitted through a polymer (I/I_0) is dependent on the path length of the light (L) and the absorptivity of the polymer at that wavelength of light (A).

Clarity is typical for light passing through a homogeneous material, such as a crystalline-ordered polymer or completely amorphous polymer. Interference occurs when the light beam passes through a heterogeneous material in which the polarizability of the individual units varies causing interference that disrupts optical clarity.

13.10.3 Absorption and Reflectance

Colorless materials range from being almost totally transparent to opaque. The opacity is related to the light-scattering process occurring within the material. Incident radiation passes through nonabsorbing, isotropic, optically homogeneous samples with essentially little loss in radiation intensity. Actually, all materials scatter some light. The angular distribution of the scattered light is complex because of the scattering due to micromolecular differences.

Transparency is defined as the state permitting perception of objects through a sample. *Transmission* is the light transmitted. In more specific terms, transparency is the amount of undeviated light, i.e., the original intensity minus all light absorbed, scattered, or lost through other means. The ratio of reflected light intensity to the incident light intensity is called the *absorption coefficient*.

13.11 WEATHERABILITY

Polymers are used in almost every conceivable environment. They are tested for their ability to interact with radiation, weather, and microorganisms. Weathering includes the ability to resist attacks by freezing and heating cycles, resistance to frictional damage caused by rain and air, and influence of low and high temperatures as the polymeric materials are used. Many of the results are measured using chemical testing as described in Section 13.12 or “real time/condition” testing.

Moisture is an important factor for some polymers, especially those with non-carbon backbones, where hydrolysis, and subsequent degradation, can bring about drastic changes in chain length and consequently, polymer properties. Such attack can occur on the surface and is indicated, as can many chemical attacks, by a discoloration generally followed by crazing and cracking. Other attack can occur within the matrix with the polymer absorbing moisture.

Resistance to biological attack is important for many polymer applications including almost all of the biomedical applications, food storage and protection, and coatings where microorganism destruction is important. Most synthetic polymers are “naturally” resistant to destruction by microorganisms. This is particularly true for nonpolar polymers, but less so for condensation polymers such as nylons and polyesters where microorganisms may recognize similarities to bonds they ordinarily hydrolyze. Various preservatives and antimicroorganism additives are added, when appropriate, to protect the material against microbial attack. Tests include destructive degradation and simple growth of the microorganism on the material.

13.12 CHEMICAL RESISTANCE

The classic test for chemical resistance (ASTM D-543) measures the percentage weight change of test samples after immersion in different liquid systems. Tests for chemical resistance have been extended to include changes in mechanical properties after immersion. Since chemical attack involves changes in chemical structure, it can be readily observed by many instrumental methods that measure chemical structure, in particular, surface structure.

Tables 13.4 and 13.5 contain a summary of typical stability values for a number of polymers and elastomers against typical chemical agents. As expected, condensation polymers generally exhibit good stability to nonpolar liquids while they are generally only (relatively) moderately or unstable toward polar agents and acids and bases. This is because of the polarity of the connective “condensation” linkages within the polymer backbone. By comparison, vinyl type of polymers exhibit moderate to good stability toward both polar and

TABLE 13.4
Stability of Various Polymers to Various Conditions

Polymer	Nonoxidizing Acid 20% Sulfuric	Oxidizing Acid 10% Nitric	Aqueous Salt Sol. NaCl	Aqueous Base NaOH	Polar Liquids Ethanol	Nonpolar Liquids Benzene	Water
Nylon-6,6	U	U	S	S	M	S	S
Polytetrafluoroethylene	S	S	S	S	S	S	S
Polycarbonate	M	U	S	M	S	U	S
Polyester	M	M	S	M	M	U	S
Polyetheretherketone	S	S	S	S	S	S	S
LDPE	S	M	S	—	S	M	S
HDPE	S	S	S	—	S	S	S
Poly(phenylene oxide)	S	M	S	S	S	U	S
Polypropylene	S	M	S	S	S	M	S
Polystyrene	S	M	S	S	S	U	S
Polyurethane	M	U	S	M	U	M	S
Epoxy	S	U	S	S	S	S	S
Silicone	M	U	S	S	S	M	S

S = satisfactory; M = moderate to poor; U = unsatisfactory.

nonpolar liquids and acids and bases. This is because the carbon–carbon backbone is not particularly susceptible to attack by polar agents and nonpolar liquids, at best, will simply solubilize the polymer. All of the materials show good stability to water alone because all of the polymers have sufficient hydrophobic character to repeal the water.

13.13 MEASUREMENT OF PARTICLE SIZE

Particle size is important in many polymer applications including coatings, creation of suspensions, and in quality control procedures such as the determination of contaminants.

Table 13.6 contains some of the analytical techniques that allow particle size determination. Before a technique is chosen, the relative particle size and type of size information

TABLE 13.5
Stability of Selected Elastomeric Materials to Various Conditions

Polymers	Weather–Sunlight Aging	Oxidation	Ozone Cracking	NaOH (Dil/Con)	Acid (Dil/Con)	Degreasers: Chlorinated Hydrocarbons	Degreasers: Aliphatic Hydrocarbons
Butadiene	P	G	B	F/F	F/F	P	P
Neoprene	G	G	G	G/G	G/G	P	F
Nitrile	P	G	F	G/G	G/G	G	G
Polyisoprene (natural)	P	G	B	G/F	G/F	B	B
Polyisoprene (synthetic)	B	G	B	F/F	F/F	B	B
Styrene–butadiene	P	G	B	F/F	F/F	B	B
Silicone	G	G	G	G/G	G/F	B	F–P

G = good; F = fair; P = poor; B = bad.

TABLE 13.6
Particle Size and Distribution Determination Techniques

Capillary hydrodynamic chromatography
Fraunhofer diffraction
Light-scattering photometry
Phase Doppler anemometry
Ultrasonic spectroscopy
Field flow fractionation
Light obscuration
Microscopy
Sedimentation

needed should be determined. Simple microscopy measurements generally allow the determination of particle size and shape. Since some techniques require spherical samples for the best relationship between measured values and particle size, deviation of sample shapes from spherical introduces error. Thus, if the particle shape deviates scientifically from being spherical, another technique should be considered.

The type of measurements that are needed to accomplish the task should also be considered. Refractive index values are generally needed for measurements based on light scattering. Densities are often needed for techniques based on acoustics and sedimentation. Further, most approaches require the samples to be dissolved or suspended in a liquid. Thus, information related to how the liquid affects particle shape and association is also important.

Light obscuration (LO) is one of the major techniques used to determine particle size. LO is based on the observation that particles whose refractive index is different from the suspending liquid scattered light. This scattering is the same as that employed in molecular weight determination employing light-scattering photometry. In fact, light-scattering photometry can be employed to determine particle shape and size. Even so, LO instruments have been developed whose main function is particle size determination. Stirring is often required to maintain a somewhat homogeneous suspension. Wetting of the particles by the suspending liquid, often achieved by addition of a wetting agent, is also often required. Dispersion of the particles is assisted by sonication for situations where single particle size is important. Sonication is not recommended if particle aggregation sizes are important.

Sedimentation techniques are also utilized for particle size distribution for particles on the order of 0.1–50 μm. Capillary hydrodynamic chromatography (HDC) gives particle size distributions for particles of about 0.005–0.7 μm.

13.14 MEASUREMENT OF ADHESION

Adhesion is the binding of two surfaces where they are held together by primary and/or secondary bonding forces. A discussion of the types of adhesives is given in Section 18.10. A discussion of surface analysis is given in Sections 13.2 and 13.3. Here, we will look at the mechanical measurement of adhesion. As with all of polymer testing, the conditions of testing are important and experiments and experimental conditions should be chosen to reflect the particular conditions and operating conditions under which the material may be subjected to. During the fracture of adhered surfaces, the bonded surfaces and adhesives are both deformed (Figure 13.9).

Failure can be affected through a variety of mechanisms. The major mechanisms are peeling, shearing, and detachment.

In peel separation, the adhesive simply "peels" away from the surface. Lap shear occurs when the adhered material is subjected to a force that is applied parallel to the bonding plane. Here, the bond becomes deformed and stretched after initial rupture of some portion of the bond. It is a "sliding" type of failure. In tensile detachment, bond disruption occurs as force is applied at right angles to the bonding surface. Tensile detachment is a "ripping" type of bond disruption.

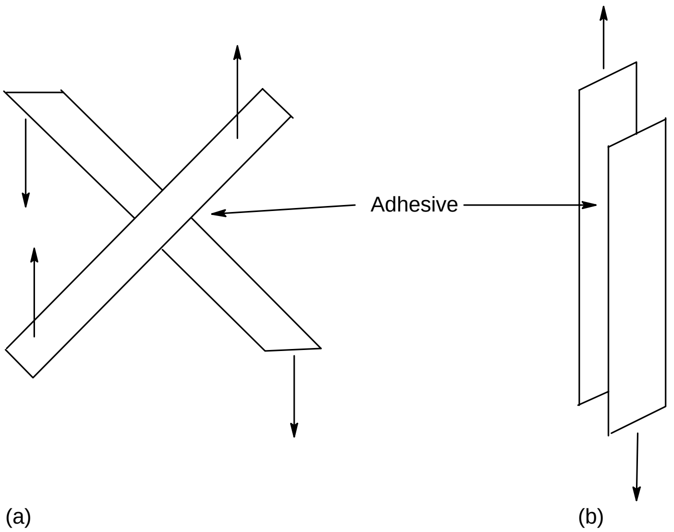

FIGURE 13.9 Descriptions of simple tensile detachment (a) and simple lap shear (b) assemblies for testing adhesion.

Scratch testing—Often some type of "scratch" testing can be used to measure adhesion of thin films. Fingernail and pencil tip results are often used as a first measure of adhesion. Thus, a person presses their fingernail against the adhered surface watching to see if the adhesive is removed from the surface. Even in more complex scratch tests, such tests create both elastic and plastic deformations around the probe tip. The critical load for adhesion failure depends on the interfacial adhesion and on the mechanical properties of the adhesive. Today, there exist techniques that give better measures of adhesion. In the micro-impact test, the test probe continuously impacts the adhesive along the wear track. This allows the effects of impacts adjacent to prior impacts to be studied allowing the influence of large area damage near the impact to be studied.

Peel testing—Peel angle is important with 180° and 90° peel angles being the most common. In general, a small amount of the adhesive is "peeled" away and the force necessary to continue the peel measured.

Tensile detachment testing—A simple description of tensile tests involves attaching two thick microscope slides to one another so that the slides are at right angles to each other. After the bond is allowed to set up a desired amount, the ends of the top microscope are attached to the measuring device and the ends of the second, bottom, slide are attached to a load-bearing segment of the apparatus. Eventually, deformation and finally bond breakage occur as the load is increased.

Lap shear testing—Shear can be applied in a number of ways: cyclic, intermittent, static (or constant), or increasing. A simple overlap shear test is described in ASTM-D-1002. This can be illustrated again using two strong microscope slides. Here, the microscope slides are adhered in parallel to one another except offset. After the appropriate set-up time, the top and bottom of the slide combination are attached to the shear tensile-measuring device and the experiment is carried out.

13.15 PERMEABILITY AND DIFFUSION

Permeability is a measure of the rate of passage of gas or liquid through a material. Diffusion is the movement of material from one chemical potential to another. Thus, these two terms are similar. The diffusion of gases and vapors in polymers and the permeability of polymers to gases and vapors are of importance in packaging and coatings, and also demonstrate the kinetic agitation of the diffused gas or vapor through the polymer matrix. The diffusion process, such as the passing of gas molecules through a polymer coating or membrane or the movement of plasticizer molecules within a polymer matrix, is generally described in terms of random jumps and hole filling by the smaller molecules.

The diffusion of larger organic vapor molecules is related to absorption. The rate of diffusion is dependent on the size and shape of the diffusate molecules, their interaction with the polymer molecules, and the size, shape, and stiffness of the polymer chains. The rate of diffusion is directly related to the polymer chain flexibility and inversely related to the size of the diffusate molecules.

Diffusion and permeability are inversely related to the density, degree of crystallinity, orientation, filler concentration, and cross-link density of a polymeric film. Generally, the presence of smaller molecules, such as plasticizers, increases the rate of diffusion in polymers since they are more mobile and can create holes or vacancies within the polymer. The rate of diffusion or permeability is fairly independent of polymer chain length just as long as the polymer has a moderately high chain length.

Permeation of gases, liquids, and vapors through a polymeric film can be looked at as a three-step process as follows: (1) the rate of dissolution of the small molecules in the polymer, (2) the rate of diffusion of the small molecules in the polymer film in accordance with the concentration gradient, and (3) the energies of the smaller molecules on the opposite side of the polymer.

Permeation is dependent on the segmental motion of the polymer chains and the free volume within the polymer matrix. The free volume decreases and chain stiffness increases as the temperature of the polymer membrane or film is lowered toward the T_g. The free volume is predicted to be similar for all polymers at the T_g.

The diffusion of a liquid or gas through a membrane is similar to the diffusion in liquid systems. The mechanism for each case involves a transfer of a small molecule to a hole in the liquid or membrane. For diffusion, the jumping frequency from hole to hole is dependent on the activation energy, E_D, for this jump, which is dependent on the size and shape of the diffusing molecule and the size of the holes in the membrane, i.e., the free volume. For permeation, the activation energy is on the order of 20–40 kJ/mol. The values of E_D are somewhat higher.

The rate of diffusion, D, and the rate of permeability, P, increase exponentially as shown by the Arrhenius equation for diffusion

$$D = D_0 \, e^{-E_D/RT} \tag{13.20}$$

where D_0 is the rate of diffusion at some base temperature, R is the ideal gas constant, and T is the Kelvin temperature.

Diffusion can be described by Fick's law,

$$F = -D[dc/dx] \tag{13.21}$$

where F is the weight of diffusate crossing a unit area per unit time and is proportional to the concentration gradient, dc/dx. The proportionality constant D is directly related to the pressure differential across the membrane and inversely related to the membrane thickness.

When the diffusion coefficient D is dependent on concentration, the diffusion process is said to be Fickian. In such cases, D is inversely related to solubility, S, and to permeability, P, as follows:

$$D = 76 \, P/S \tag{13.22}$$

It has been suggested that linear alkanes diffuse through the holes of membranes by alignment with the segments of the organic polymer chains. Such alignments are more difficult for branched alkanes so that they diffuse more slowly.

The diffusion coefficient D is inversely related to the cross-link density of vulcanized rubbers. When D is extrapolated to zero concentration of the diffusing small molecules, it is related to the distance between the cross-links. Thus, as the cross-link density increases D becomes smaller, as expected. Further, the diffusion coefficient is less for crystalline polymers in comparison with the same polymer except in the amorphous state. In fact, this can be roughly stated as follows.

$$D_c = D_a\,(1 - x) \tag{13.23}$$

where D_c is the diffusion constant for the crystalline material, D_a is the diffusion constant for the amorphous material, and x is the extent of crystallinity.

The permeability coefficient P is related to the diffusion coefficient D, and the solubility coefficient S as shown by Henry's law:

$$P = DS \tag{13.24}$$

Thus, the permeability values are high when the solubility parameters of the diffusion molecules are similar to that of the polymer film.

While some polymers exhibit non-Fickian diffusion below the T_g, many of these become Fickian as the temperature is raised to above the T_g.

13.16 SUMMARY

1. The ASTM and comparable organizations throughout the world have established meaningful standards for the testing of polymers.
2. Spectroscopic techniques that are useful for small molecules are equally as important with macromolecules. These techniques give both structural data and data related to the morphology of the polymers.
3. Surface properties are important to the physical and chemical behavior of polymers. Similar to smaller molecules, polymer surface structures can be determined using a variety of techniques including AES, near-field optical microscopy, electron microscopy, SPM, SIMS, and certain IR and MS procedures.
4. Thermal analysis measurements allow the measure of polymer behavior as a function of temperature, time, and atmosphere. DSC or DTA measures change in energy as temperature is changed and allows the determination of many valuable parameters including T_g and T_m. TGA measures weight changes as a function of temperature.
5. The electrical properties of materials are important for many of the higher technology applications. Measurements can be made using AC and/or DC. The electrical properties are dependent on voltage and frequency. Important electrical properties include dielectric loss, loss factor, dielectric constant, conductivity, relaxation time, induced dipole moment, electrical resistance, power loss, dissipation factor, and electrical breakdown. Electrical properties are related to polymer structure. Most organic polymers are nonconductors, but some are conductors.
6. Important physical properties of polymers include weatherability, chemical resistance, and optical properties. Polymers generally show good to moderate chemical resistance when compared to metals and nonpolymers.

GLOSSARY

ASTM American Society for Testing and Materials.

BSI British Standards Institution.

chemical shifts Peaks in NMR spectroscopy.

dielectric constant Ratio of the capacitance of a polymer to that in a vacuum.

dielectric strength Maximum applied voltage that a polymer can withstand.

differential scanning calorimetry (DSC) Measurement of the difference in changes in the enthalpy of a heated polymer and a reference standard based on power input.

differential thermal analysis (DTA, DT) Measurement of the difference in the temperature of a polymer and a reference standard when heated.

environmental stress cracking Cracking of polymers.

glass transition temperature Temperature where the onset of local or segmental mobility begins.

heat deflection temperature Temperature at which a simple loaded beam undergoes a definite deflection.

index of refraction Ratio of the velocity of light in a vacuum to that in a transparent material or mixture.

IR spectroscopy Technique used for the characterization of polymers based on their molecular vibration and vibration–rotation spectra.

ISO International Standards Organization.

loss factor Power factor multiplied by the dielectric constant.

Moh's scale Hardness scale ranging from 1 for talc to 10 for diamond.

nuclear magnetic resonance (NMR) spectroscopy Based on the absorption of magnetic energy by nuclei that have an uneven number of protons or neutrons; this absorption is dependent on the particular chemical structure and environment of the molecule.

oxygen index (OI) Test for the minimum oxygen concentration in a mixture of oxygen and nitrogen that will support a candle-like flame of a burning polymer.

phase contrast microscopy Measurement of differences in indices of index of reflection.

power factor Electrical energy required to rotate the dipoles in a polymer while in an electrostatic field.

Raman spectroscopy Based on the interaction of vibrational modes of molecules with relative high-energy radiation where absorption is based on the chemical moieties that undergo changes in polarization.

scanning probe microscopy (SPM) Group of surface-detection techniques that include atomic force microscopy and scanning tunneling microscopy; measures surface depth differences.

secondary ion mass spectroscopy (SIMS) Mass spectroscopy that looks at the ion fragments generated from the bombardment of surfaces with an ion beam.

thermogravimetric analysis (TG, TGA) Measurement of the change in weight when a polymer is heated.

EXERCISES

1. Why are electrical tests for polymers important?
2. Which is the better insulator: a polymer with (a) a low or (b) high K factor?
3. Why are the specific heats of polymers higher than those of metals?
4. Which IR technique might give you good surface information?
5. Why is the use of the term "flameproof plastics" incorrect?
6. Which plastic should be more resistant when immersed in 25% sulfuric acid at room temperature: (a) HDPE, (b) PMMA, or (c) PVAc?
7. Why is it important to know the nature and structure of the surface of materials?
8. Why is it important to know such things as the values of thermal expansion of materials?
9. How is NMR important in characterizing polymers?
10. What is the UV region of the spectrum?
11. Which would absorb in the UV region: (a) polystyrene, (b) hevea rubber, or (c) PVC?
12. What technique(s) would you use to determine crystallinity in a polymer?
13. What thermal instrumental technique would you use to determine T_g?
14. What is the difference between measuring physical properties and structural determinations?
15. Why is it important to have standard tests?
16. Are the measurements taken today better than those taken 30 years ago?

17. In the TGA for most vinyl polymers, why is there a single somewhat smooth degradation plot of weight loss as a function of temperature?
18. A researcher finds using one testing method that the amount of amorphous character in a sample is 60% and using another testing method finds that the same sample is 70% crystalline. How can this occur?
19. Why are such terms as "flame retardant" or "flame resistant" used rather than "flame proof"?
20. What are some hurdles to adopting better protection in the building and automotive industries?

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14 Rheology and Physical Tests

The main reasons for studying rheology (stress–strain relationships) in this chapter are: (1) to determine the suitability of materials to serve specific applications; and (2) to relate the results to polymer structure and form. Studying structure–property relationships allows a better understanding of the observed results on a molecular level resulting in a more knowledgeable approach to the design of materials.

Polymers are viscoelastic materials meaning they can act as liquids, the "visco" portion, and as solids, the "elastic" portion. Descriptions of the viscoelastic properties of materials generally falls within the area called rheology. Determination of the viscoelastic behavior of materials generally occurs through stress–strain and related measurements. Whether a material behaves as a "viscous" or "elastic" material depends on temperature, the particular polymer and its prior treatment, polymer structure, and the particular measurement or conditions applied to the material. The particular property demonstrated by a material under given conditions allows polymers to act as solid or viscous liquids, as plastics, elastomers, or fibers, etc. This chapter deals with the viscoelastic properties of polymers.

14.1 RHEOLOGY

The branch of science related to the study of deformation and flow of materials was given the name rheology by Bingham, whom some call the father of modern rheology. The prefix *rheo* is derived from the Greek *rheos*, meaning current of flow. The study of rheology includes two vastly different branches of mechanics—fluid and solid. The polymer scientist is usually concerned with viscoelastic materials that act as both solids and liquids.

The elastic component is dominant in solids, hence their mechanical properties may be described by Hooke's law (Equation 14.1), which states that the applied stress (s) is proportional to the resultant strain (γ) but is independent of the rate of this strain ($d\gamma/dt$).

$$s = E\gamma \tag{14.1}$$

Stress is equal to the force per unit area, and strain or elongation is the extension per unit length. For an isotopic solid, i.e., one having the same properties regardless of direction, the strain is defined by Poisson's ratio, $V = \gamma_w/\gamma_l$ which is the change in thickness (lateral contraction) to the change in length.

When there is no volume change, as when an elastomer is stretched, Poisson's ratio is 0.5. This value decreases as the T_g of the polymer increases and approaches 0.3 for rigid solids such as PVC and ebonite. For simplicity, the polymers dealt with here will be considered to be isotropic viscoelastic solids with a Poisson's ratio of 0.5, and only deformations in tension and shear will be considered. Thus, a shear modulus (G) will usually be used in place of Young's modulus of elasticity (E; Equation 14.2) where E is about $2.6G$ at temperatures below T_g.

For comparison, the moduli (G) for steel (HDPE) and hevea rubber (NR) are $86/\text{m}^2$, $0.087/\text{m}^2$, and $0.0006\ \text{dyne}/\text{m}^2$, respectively.

$$ds = G d\gamma \quad \text{and} \quad s = G\gamma \tag{14.2}$$

The viscous component is dominant in liquids; hence their flow properties may be described by Newton's law (Equation 14.3) where η is the viscosity, which states that the applied stress s is proportional to the rate of strain $d\gamma/dt$, but is independent of the strain γ or applied velocity gradient.

$$s = \eta(d\gamma/dt) \tag{14.3}$$

Both Hooke's and Newton's laws are valid for small changes in strain or rate of strain, and both are useful in studying the effect of stress on viscoelastic materials. The initial elongation of a stressed polymer below T_g is reversible due to a stretching of covalent bonds and distortion of the bond angles. Some of the very early stages of elongation by disentanglement of chains may also be reversible. However, the rate of flow, which is related to slower disentanglement and slippage of polymer chains past one another, is irreversible and increases (and η decreases) as the temperature increases in accordance with the following form of the Arrhenius Equation (14.4) in which E is the activation energy for viscous flow.

$$\eta = \text{A}e^{E/RT} \tag{14.4}$$

It is convenient to use a simple weightless Hookean, or ideal, elastic spring with a modulus G and a simple Newtonian (fluid) dashpot or shock absorber having a liquid with a viscosity of η as models to demonstrate the deformation of an elastic solid and an ideal liquid, respectively. The stress–strain curves for these models are shown in Figure 14.1.

In general, the Hookean spring represents bond flexing while the Newtonian dashpot represents chain and local segmental movement. It is customary to attempt to relate stress–strain behavior to combinations of dashpots and springs as indicators of the relative importance of bond flexing and segmental movement.

Again, in general terms, below their T_g polymers can be modeled as having a behavior where the spring portion is more important. Above their T_g where segmental mobility occurs, the dashpot portion is more important.

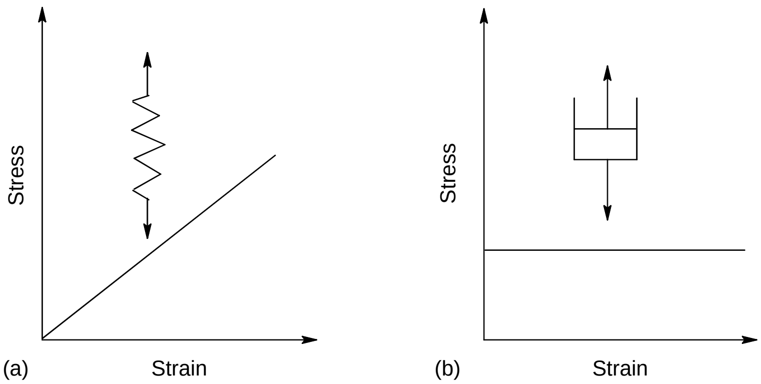


FIGURE 14.1 Stress–strain plots for a Hookean spring (a) where E (Equation 14.1) is the slope, and a Newtonian dashpot (b) where s is a constant (Equation 14.3).

The relative importance of these two modeling parts, the spring and the dashpot, is also dependent on the rate at which an experiment is carried out. Rapid interaction, such as striking with a hammer, with a polymer is more apt to result in a behavior where bond flexibility is more important, while slow interactions are more apt to allow for segmental mobility to occur.

Since polymers are viscoelastic solids, combinations of these models are used to demonstrate the deformation resulting from the application of stress to an isotropic solid polymer. Maxwell joined the two models in series to explain the mechanical properties of pitch and tar (Figure 14.2a). He assumed that the contributions of both the spring and dashpot to strain were additive and that the application of stress would cause an instantaneous elongation of the spring, followed by a slow response of the piston in the dashpot. Thus, the relaxation time (τ), when the stress and elongation have reached equilibrium, is equal to η/G.

In the Maxwell model for viscoelastic deformation, it is assumed that the total strain is equal to the elastic strain plus the viscous strain. This is expressed in the two following differential equations from Equations 14.2 and 14.3.

$$\mathrm{d}\gamma/\mathrm{d}t = s/\eta + \mathrm{d}s/\mathrm{d}t(1/G) \tag{14.5}$$

The rate of strain $\mathrm{d}\gamma/\mathrm{d}t$ is equal to zero under conditions of constant stress (s), i.e.,

$$s/\eta + \mathrm{d}s/\mathrm{d}t(1/G) = 0 \tag{14.6}$$

Then, assuming that $s = s_o$ at zero time, we get

$$s = s_o \mathrm{e}^{-tG/n} \tag{14.7}$$

And, since the relaxation time $\tau = \eta/G$, then

$$s = s_o \mathrm{e}^{-t/T} \tag{14.8}$$

Thus, according to Equation 14.8 for the Maxwell model or element, under conditions of constant strain, the stress will decrease exponentially with time and at the relaxation time $t = \tau$, s will equal 1/e, or 0.37 of its original value, s_o.

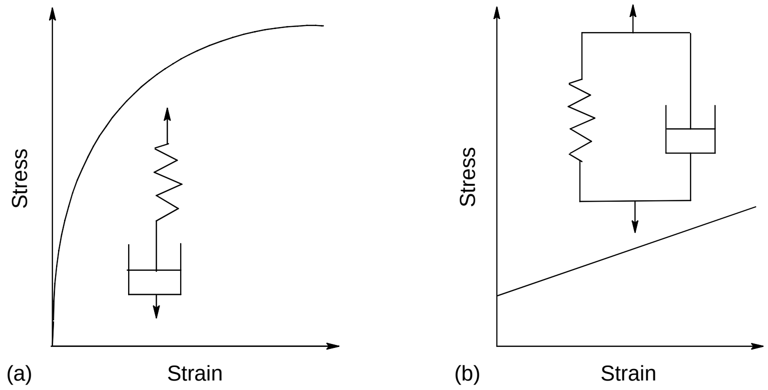


FIGURE 14.2 Stress–strain plot for stress relaxation for the Maxwell model (a) and Voigt–Kelvin model (b).

The parallel dashpot–spring model was developed by Voigt and Kelvin and is known as the Voigt–Kelvin model (Figure 14.2b). In this model or element, the applied stress is shared between the spring and dashpot, and thus the elastic response is retarded by the viscous resistance of the liquid in the dashpot. In this model, the vertical movement of the spring is essentially equal to that of the piston in the dashpot. Thus, if G is much larger than η, the retardation time (η/G) or τ is small, and τ is large if η is much larger than G.

In the Voigt–Kelvin model for viscoelastic deformation, it is assumed that the total stress is equal to the sum of the viscous and elastic stress, $s = s_\mathrm{v} + s_\mathrm{o}$, so that

$$s = \eta(\mathrm{d}\gamma/\mathrm{d}t) + G\gamma \tag{14.9}$$

On integration one obtains

$$\gamma = s/G\left(1 - \mathrm{e}^{-tG/n}\right) = s/G\left(1 - \mathrm{e}^{-t/T}\right) \tag{14.10}$$

The retardation time τ is the time for the strain to decrease to $1-(1/\mathrm{e})$ or $1-(1/2.7)=0.63$ of the original value. The viscoelastic flow of polymers is explained by approximate combinations of the dashpot and spring. The plots of the real data are compared with those predicted by various models. The relative importance of the various components of the model that fits the experimental data, dashpot and spring combinations, indicates the importance that the types of chain movement represented by the dashpot and spring have for that particular polymer under the particular experimental conditions.

14.1.1 RHEOLOGY AND PHYSICAL TESTS

While polymer melts and non-cross-linked elastomers flow readily when stress is applied, structural plastics must resist irreversible deformation and behave as elastic solids when relatively small stresses are applied. These plastics are called ideal or Bingham plastics with their behavior described mathematically by

$$s - s_\mathrm{o} = \eta(\mathrm{d}\gamma/\mathrm{d}t) \tag{14.11}$$

Figure 14.3 contains the stress–strain plots for a number of important flow behaviors. A Bingham plastic exhibits Newtonian flow above the stress yield or stress value (s_o). Liquids that undergo a decrease in viscosity with time are called *thixotropic* or false-bodied. Those that undergo an increase in viscosity with time are called *rheopectic* (shear thickening). The term *creep* is used to describe the slow slippage of polymer chains over a long period of time. The Herschel–Buckley Equation (14.12) is a general equation that reduces to the Bingham equation when $\eta = 1$ and to the Newtonian equation when $\eta = 1$ and $s_\mathrm{o} = 0$, and where ϕ is related to viscosity.

$$(s - s_\mathrm{o})\eta = \phi(\mathrm{d}\gamma/\mathrm{d}t) \tag{14.12}$$

Eyring explained liquid flow using a random hole-filling model in which the holes (vacancies or free volume) account for about 15% of the total volume at room temperature. The size of these holes is similar to that for small molecules. The number of holes increases as the temperature increases, and thus flow or hole filling is temperature-dependent. Small molecules jump into the holes leaving empty holes when their energy exceeds the activation energy. The activation energy for jumping or moving into a hole is smaller, per individual unit, for linear molecules, which fill the holes by successive correlated jumps of chain segments along

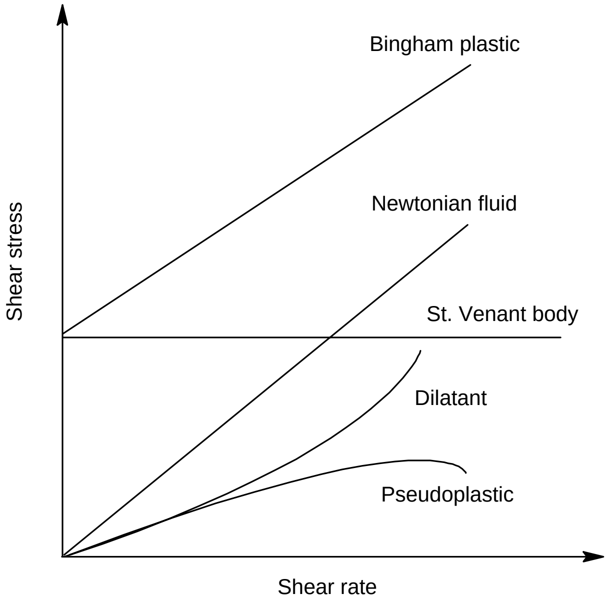


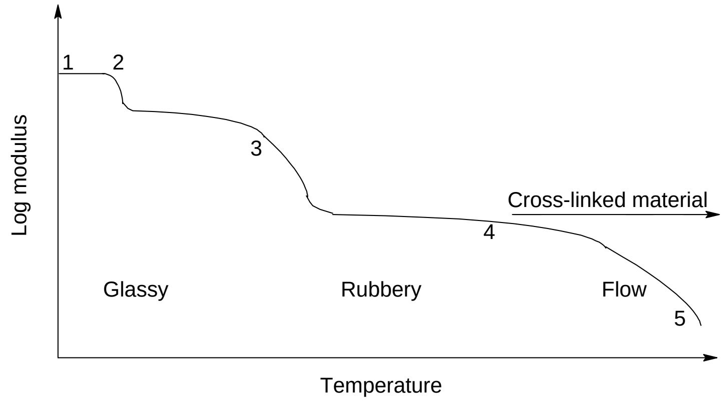
FIGURE 14.3 Various types of polymer flow.

the polymer chain. The jump frequency (ϕ) is governed by a segmental factor with both values related to molecular structure and temperature.

For convenience and simplicity, polymers have generally been considered to be isotropic in which the principle force is shear stress. While such assumptions are acceptable for polymers at low shear rates, they fail to account for stresses perpendicular to the plane of the shear stress, which are encountered at high shear rates. For example, an extrudate such as the formation of a pipe or filament expands when it emerges from the die in what is called the Barus or Weissenberg effect or die swell. This behavior is not explained by simple flow theories.

Viscoelastic behavior can be divided into five subclassifications (Figure 14.4). From 1 to 2, the material behaves as a viscous glass or Hookean elastic or glass, where chain segmental motion is quite restricted and involves mainly only bond bending and bond angle deformation.

The material behaves as a glass such as window glass. At 2 the material is undergoing a glassy transition into the rubbery region, 3–4, which is often referred to as the viscoelastic region where polymer deformation is reversible but time-dependent and associated with both side chain and main chain rotation. In the rubbery region local segmental mobility occurs but total chain flow is restricted by a physical and/or chemical network. At 5 rubbery flow or viscous flow occurs where irreversible bulk deformation and slippage of chains past one another occur. Each of these viscoelastic regions is time-dependent. Thus, given a short interaction time, window glass acts as a Hookean glass or a solid, yet observation of glass over many years would permit the visual observation of flow, with the window glass giving a viscous flow response, thus acting as a fluid. In fact, most polymers give a response as noted in Figure 14.5 for the response of a ball dropped at different rates on to the polymeric material, which is heated to different temperatures. Commercial Silly Putty or Nutty Putty easily illustrates three of these regions. When struck rapidly it shatters as a solid (glass region); when dropped at a moderate rate, it acts as a rubber (rubbery region), and when allowed to reside in its container for some time it flows to occupying the container contour, acting as a liquid. The exact response (Figure 14.5) varies between materials.



Deformation	Hookean glassy	Secondary–primary transitions		Highly elastic	Flow
Molecular motion	Bond stretch and bending	Side groups	Main chain	Main chain-large	Chain slippage

FIGURE 14.4 Characteristic conformational changes as temperature is changed.

There have been many attempts to predict long-range behavior from short-range behavior. This is a dangerous practice if the end-prediction is material failure because, for most polymeric materials, failure is catastrophic and not "well-behaved." But, for other properties application of the Boltzman time–temperature superposition master curves can be used to some advantage, particularly pertaining to predicting behavior as depicted in Figure 14.5.

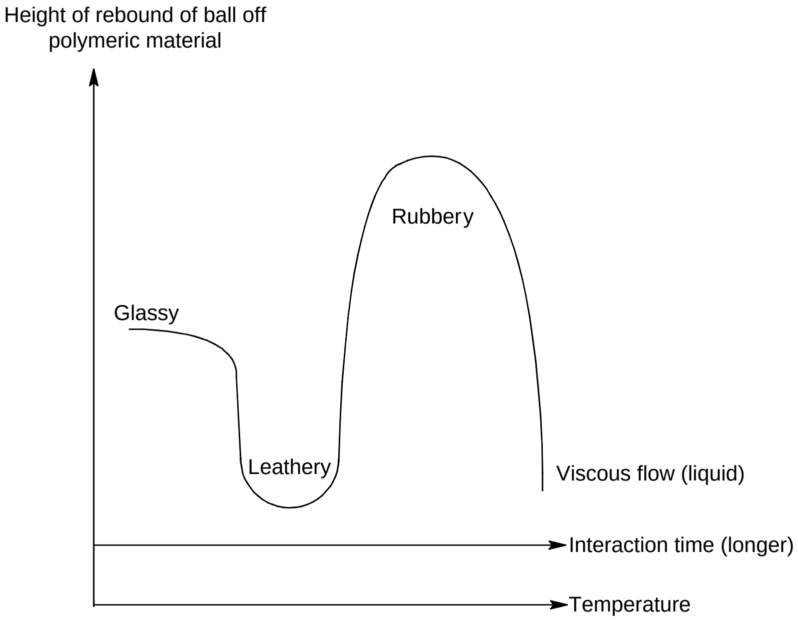


FIGURE 14.5 Regions of material response as a function of interaction (reaction) time and temperature for a typical polymeric material.

This transposition for amorphous polymers is accomplished using a shift factor (a_T) calculated relative to a reference temperature T_r, which may be equal to T_g. The relationship of the shift factor to the reference temperature and some other temperature T, which is between T_g and $T_g + 50$ K, may be approximated by the Arrhenius-like Equation.

$$\log a_T = -(b/2.3TT_g)(T - T_g) \tag{14.13}$$

According to the more widely used Williams, Landel, and Ferry (WLF) equations, all linear, amorphous polymers have similar viscoelastic properties at T_g and at specific temperatures above T_g, such as $T_g + 25$ K, and the constants C_1 and C_2 related to holes or free volume, the following relationship holds:

$$\log a_T = -C_1(T - T_g)/[C_2 + (T - T_g)] \tag{14.14}$$

14.1.2 RESPONSE TIME

We can get a first approximation of the physical nature of a material from its response time. For a Maxwell element, the relaxation time is the time required for the stress in a stress–strain experiment to decay to 1/e or 0.37 of its initial value. A material with a low relaxation time flows easily so it shows relatively rapid stress decay. Thus, whether a viscoelastic material behaves as a solid or fluid is indicated by its response time and the experimental timescale or observation time. This observation was first made by Marcus Reiner who defined the ratio of the material response time to the experimental timescale as the Deborah Number, D_n. Presumably the name was derived by Reiner from the Biblical quote in Judges 5, Song of Deborah, where it says "The mountains flowed before the Lord."

$$D_n = \frac{\text{Response time}}{\text{Experimental timescale}} \tag{14.15}$$

A high D_n designates the solid behavior of a viscoelastic material, while a low D_n corresponds to a viscoelastic material behaving as a fluid. Thus, window glass has a high relaxation time at room temperature. Application of a stress to produce a little strain and looking for it to return to its approximate prestressed state will take a long time as we count our observation time in hours, days, and weeks. Thus, it would have a relatively high D_n under this observation timescale and be acting as a solid. Yet, if we were to have as our observation scale millions of years, the return to the prestressed state would be rapid with the glass acting as a viscous liquid and having a low D_n. Again, this represents only a first approximation measure of the behavior of a material.

14.2 TYPICAL STRESS–STRAIN BEHAVIOR

For perspective, Figure 14.6 contains general ranges for the three major polymer groupings with respect to simple stress–strain behavior.

Most physical tests involve nondestructive evaluations. For our purposes, three types of mechanical stress measures (Figure 14.7) will be considered. The ratio of stress to strain is called *Young's modulus*. This ratio is also called the modulus of elasticity and tensile modulus. It is calculated by dividing the stress by the strain:

$$\text{Young's modulus} = \text{stress (Pa)/strain (mm/mm)} \tag{14.16}$$

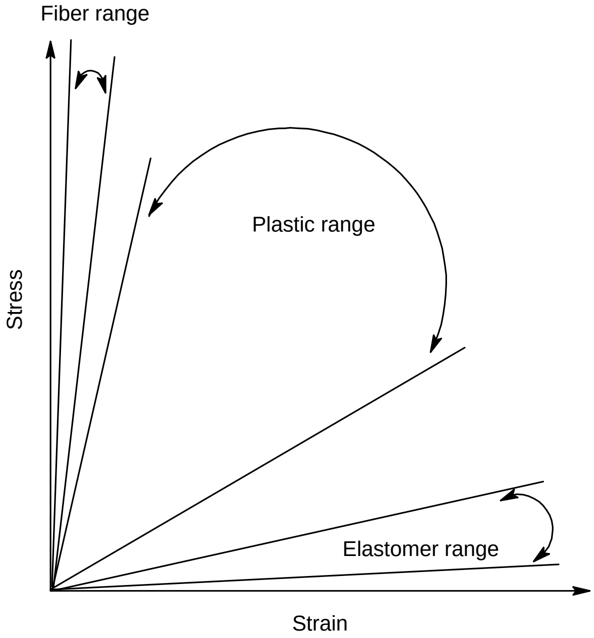


FIGURE 14.6 Typical stress–strain behavior for fibers, plastics, and elastomers.

Large values of Young's modulus indicate that the material is rigid and resistant to elongation and stretching. Many synthetic organic polymers have Young's modulus values in the general range of about 10^4 to 10^{10} Pa. For comparison, fused quartz has a Young's modulus of about 10^6, cast iron, tungsten, and copper have values of about 10^7, and diamond has a value of about 10^8.

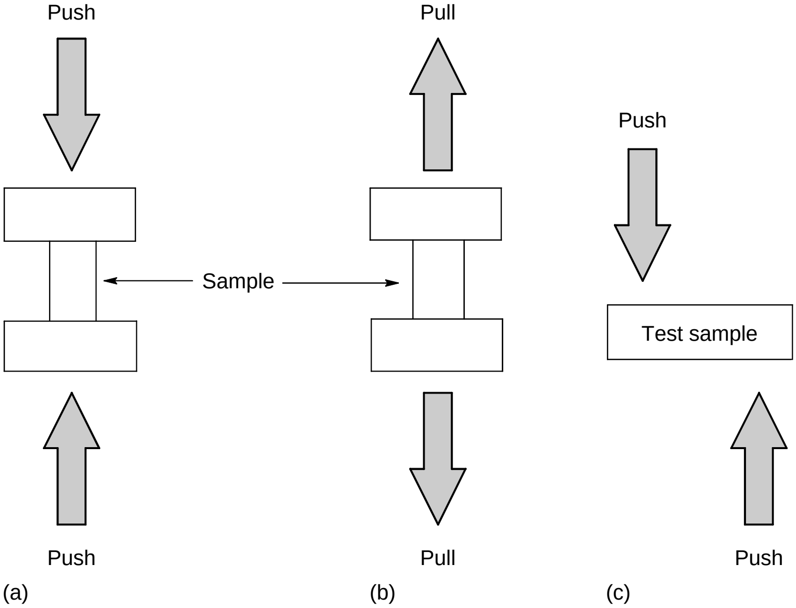


FIGURE 14.7 Major types of stress tests: compressive (a) pulling stress or tensile strength (b) and shear stress (c).

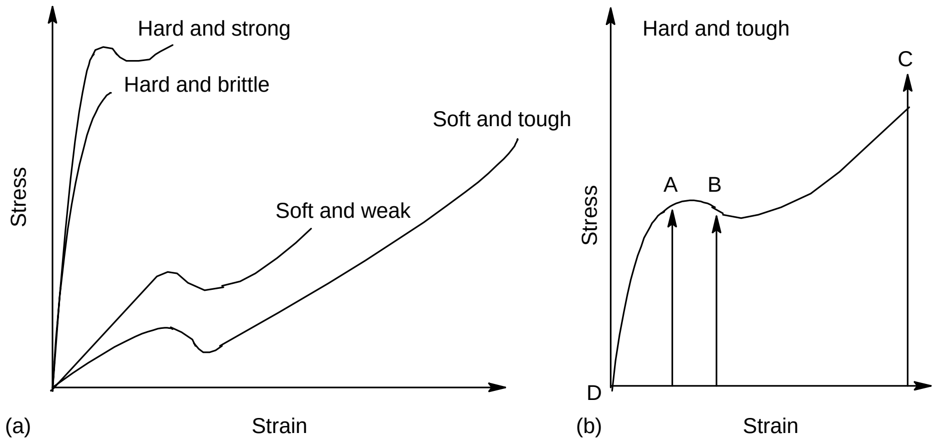


FIGURE 14.8 Typical stress–strain curves for plastics where (right) A is the elongation at yield point, B is the yield stress, C is the elongation at break, and the area under the curve is the ultimate strength.

Carswell and Nason assigned five classifications to polymers (Figure 14.8). It must be remembered that the ultimate strength of each of these is the total area under the curve before breaking. The soft and weak class, such as PIB, is characterized by a low modulus of elasticity, low yield (stress) point, and moderate time-dependent elongation. The Poisson ratio, i.e., ratio of contraction to elongation, for soft and weak polymers is about 0.5, which is similar to that found for many liquids.

In contrast, the Poisson ratio for the hard and brittle class of polymers, such as PS, approaches 0.3. These polymers are characterized by a high modulus of elasticity, a poorly defined yield point, and little elongation before failure. However, soft and tough polymers, such as plasticized PVC, have a low modulus of elasticity, high elongation, a Poisson ratio of about 0.5–0.6, and a well-defined yield point. Soft and tough polymers stretch after the yield point with the area under the entire curve, toughness, or ultimate strength, greater than for the hard and brittle polymers.

Rigid PVC is representative of hard and soft polymers. These polymers have a high modulus of elasticity and high yield strength. The curve for hard and tough polymers, such as ABS copolymers, shows moderate elongation before the yield point followed by nonrecoverable elongation.

In general, the behavior of all classes of polymer behavior is Hookean before the yield point. The reversible recoverable elongation before the yield point, called the elastic range, is primarily the result of bending and stretching of covalent bonds in the polymer backbone. This useful portion of the stress–strain curve may also include some recoverable uncoiling of polymer chains. Irreversible slippage of polymer chains is the predominant mechanism after the yield point.

Since these properties are time-dependent, the soft and weak polymers may resemble the hard and strong polymers if the stress is rapidly applied, and vice versa. These properties are also temperature-dependent and hence resemble those hard and brittle ones when temperature is decreased. The effects of temperature and the mechanisms of elongation are summarized in Figure 14.4.

As noted in Figure 14.7 the major modes for applying stress are axial (compression or tension), flexural (bending or shear), and torsional (twisting; not shown). Superimposed on these can be any number of cyclic arrangements. Several common fluctuating stress–time modes are typically employed. In the regular and sinusoidal time-dependent mode the stress is applied, as both compressional and torsional, in a regular manner with respect to both time and amount. In a second cyclic arrangement the stress, again both compressional and torsional, is applied in an uneven manner with respect to amount and time so that the maxima and minima are asymmetrical relative to the zero stress level.

Associated with such cyclic application of stress is the term *fatigue* to describe the failure that occurs after repeated applications of stress. The fatigue values are almost always less than measurements, such as tensile strength, obtained under static load. Thus, it is important that both static and cyclic measurements be made.

Data are often plotted as stress versus the logarithm of the number of cycles (N) to failure for each sample. Generally tests are taken using about two-thirds of the static parameter value. There is some limiting stress level below which fatigue does not occur (over some reasonably extended time). This value is called the fatigue or endurance limit. The fatigue strength is defined as the stress at which failure will occur for some specified number of cycles. Fatigue life is the number of cycles that are needed to cause failure.

Polymeric materials are dissimilar to metals in a number of respects. For instance, the range of stress–strain behavior is more complex and varied for polymers. Highly elastic polymers can exhibit a modulus as low as 7 MPa or as high as 100 GPa for stiff polymeric fibers. The modulus values for metals are higher (50–400 GPa) but not as varied. Tensile strengths for polymers are on the order of 100 MPa and for some metal alloys 4000 MPa. By comparison, polymers are more deformable with elastic polymers having elongations in excess of 500% while even "moldable" metals having elongations not exceeding 100%. Further, stress–strain behavior for polymers is more temperature-dependent in comparison to metals. For instance, Figure 14.9 contains the stress–strain behavior for a PMMA material. Below the T_g the material behaves as a stiff, brittle solid similar to hard and brittle polymers (Figure 14.9). As the temperature increases, the PMMA gains enough thermal energy to allow for some segmental mobility. The T_g varies greatly for PMMA depending upon the tacticity, with isotactic PMMA having a T_g of about 45°C and for a syndiotactic PMMA having a T_g of

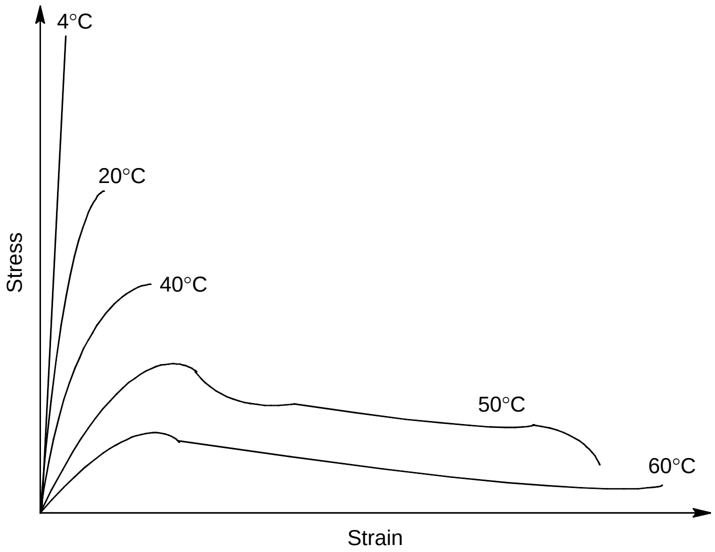


FIGURE 14.9 Influence of temperature on the stress–strain behavior of a sample of poly(methyl methacrylate). (Modeled after Carswell, T.S. and Nason, H.K. *Effects of Environmental Conditions on the Mechanical Properties of Organic Plastics*, 1944. Copyright, ASTM, Philadelphia, PA. With permission.)

about 130°C. The material in Figure 14.9 is largely isotactic with a T_g of about 50°C–60°C. By 50°C the material behaves as a soft and tough material (Figure 14.9).

14.3 STRESS–STRAIN RELATIONSHIPS

Mechanical testing involves a complex of measurements including creep and shear strength, impact strength, etc. Stress–strain testing is typically carried out using holders where one member is movable within a load frame. Studies typically vary with either the stress or strain fixed and the result response measured. In a variable stress experiment a sample of given geometry is connected to the grips. Stress, load, is applied, generally by movement of the grip heads either towards one another (compression) or away from one another (elongation). This causes deformation, strain, of the sample. The deformation is recorded as is the force/area necessary to achieve this deformation. The applied load versus deformation is recorded and translated into stress–strain curves such as those given in Figures 14.3, 14.8, and 14.10.

For many materials, between their T_g and T_m, recovery is not complete. This incomplete recovery is called creep, which is time-dependent and is described as follows:

$$\text{Compliance} = \text{strain}/\text{stress} \tag{14.17}$$

where the compliance and strain are time-dependent.

Creep behavior is similar to viscous flow. The behavior in Equation 14.17 shows that compliance and strain are linearly related and inversely related to stress. This linear behavior is typical for most amorphous polymers for small strains over short periods of time. Further, the overall effect of a number of such imposed stresses is additive. Non-creep-related recovery

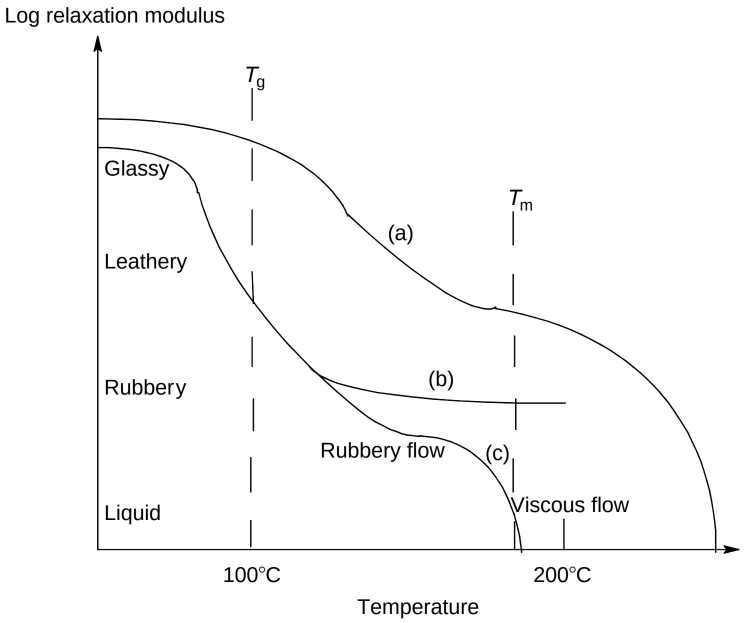


FIGURE 14.10 Logarithm of the relaxation modulus as a function of temperature for three polymer samples. Sample (a) is (largely) crystalline vinyl polymer; sample (b) is an amorphous vinyl polymer that contains light cross-linking; and sample (c) is an amorphous vinyl polymer. The T_g for the amorphous polymer is about 100°C and the T_m for the crystalline polymer is about 180°C.

occurs when the applied stress is relieved. Thus, amorphous polymers and those containing substantial amounts of amorphous regions act as both elastic solids and liquids above their T_g.

Even materials with low creep under the limited times tests are often performed may undergo microlevel creep that eventually results in reorientation of polymer chains. For many materials this results in amorphous regions becoming more crystalline resulting in a material that is less flexible and, although stronger, more brittle.

Phase changes, phase transitions, refer to changes of state. Most low molecular weight materials exist as solids, liquids, and gasses. The transitions that separate these states are melting (or freezing) and boiling (or condensing). By contrast, polymers do not vaporize "intact" to a gas, nor do they boil. The state of a polymer, i.e., its physical response character, depends on the time allotted for interaction and the temperature, as well as the molecular organization (crystalline, amorphous-mix). The term *relaxation* refers to the time required for response to a change in pressure, temperature, or other applied parameter. The term *dispersion* refers to the absorption or emission of energy at a transition. In practice, the terms relaxation and dispersion are often used interchangeably.

Stress–strain plots for many polymers, that are amorphous or contain a mixture of amorphous/crystalline regions, can be given for various conditions resulting in the general behavior shown in Figure 14.4. As noted earlier, the viscoelastic behavior of polymers is both temperature- and time-dependent. One measure of the tendency to deform and rebound is to look at the stress relaxation of materials. Stress relaxation measurements are carried out by rapidly straining a material by tension to a predetermined but low strain level and measuring the stress needed to maintain this strain as a function of time. The stress needed to maintain the strain decreases with time due to a molecular relaxation process with the various bond flexing, and chain and segmental movements influencing this time. Figure 14.10 (similar to Figure 14.4) contains an idealized plot of the logarithm of the relaxation modulus as a function of temperature for a typical vinyl (largely) crystalline polymer, curve a; lightly cross-linked vinyl amorphous polymer, curve b; and an amorphous vinyl polymer, line c. The T_g for the polymer is about 100°C and the T_m is about 180°C.

Four general behavior patterns emerge and correspond to the same regions given in Figure 14.5.

The first region is called the glassy region. Young's modulus for glassy polymers is somewhat constant over a wide range of vinyl polymers having a value of about 3×10^9 Pa. Here the molecular motions are restricted to vibrational and short-range rotational movement, the former sometimes being referred to as bond flexing. Two diverse approaches are often used to describe molecular motion in this range. The cohesive energy density approach measures the energy theoretically required to move a detached segment into the vapor state per unit volume. Using PS as an example, a value of about 3×10^9 Pa is calculated for the modulus. For largely hydrocarbon polymers the cohesive energy density is typically similar to that of PS and similar theoretical modulus values are found. The second approach is based on the carbon–carbon bonding forces as seen using vibrational frequencies. Again, values on the order of 3×10^9 Pa are found. Thus, in the glassy or solid region, below the T_g, only bond flexing and short-range rotational movement occur and the response time is fast for all three samples.

After the precipitous drop that occurs near the T_g, the modulus again is about constant, often on the order of 2×10^6 Pa, until melting is achieved. Over this rubbery range moderate segmental chain mobility is possible when stress is applied, but wholesale mobility does not occur. Thus, an elastic behavior occurs where segmental mobility allows the material to be stretched often to beyond 100% with an approximate return to the prestretched structure after release of the stress. The rubbery region is particularly "interaction-time" sensitive. For instance, if applied stress is maintained, chain slippage will occur for non-cross-linked materials limiting return to the original molecular conformation after release of the stress. For the same polymer the width of this plateau is somewhat molecular weight–dependent such that the longer the polymer chains the broader the plateau.

As the temperature is increased there is available sufficient energy to melt the crystalline polymer, the T_m, and before this for the amorphous polymer sufficient energy so that in both cases ready wholesale movement of polymer chains occurs. The entire polymer now behaves as a viscous liquid such as molasses. For the cross-linked material wholesale mobility is not possible, so it remains in the rubbery region until the temperature is sufficient to degrade the material.

The crystalline portion of the material does not exhibit a T_g but only a T_m, so the leathery and rubbery areas are muted since only bond flexing is largely possible until the T_m is reached. The crystalline polymer is not totally crystalline so it exhibits "amorphous" polymer behavior corresponding to the amount of amorphous regions present. The lightly cross-linked material behaves similar to the amorphous material through the first three regions but cross-linking prevents ready wholesale movement of the polymer chains preventing it from flowing freely. Finally, the amorphous material, curve c, shows all four behaviors. Here, above the T_g, segmental movement occurs and the time required for the chains to return to a relaxed state is considerably greater than that required for simple return of bond flexing. Finally, as the temperature approaches the T_m wholesale movement of the polymer chains becomes possible and the material behaves as a viscous liquid.

14.4 SPECIFIC PHYSICAL TESTS

14.4.1 TENSILE STRENGTH

Tensile strength can be determined by applying force to the material until it breaks as shown in the following equation (including typical units):

$$\text{Tensile strength (Pascals)} = \text{force required to break sample } (N)/\text{cross-sectional area } (\text{m}^2) \tag{14.18}$$

Tensile strength, which is a measure of the ability of a polymer to withstand pulling stresses, is usually measured using a dumbbell-shaped specimen (ASTM D-638-72; Figures 14.11 and 14.12). These test specimens are conditioned under standard conditions of humidity and temperature before testing.

Both heads may be movable as in Figure 14.12 or more often only one head is moving and the other held constant.

The *elastic modulus* (also called tensile modulus or modulus of elasticity) is the ratio of the applied stress to the strain it produces within the region where the relationship between stress and strain is linear. The *ultimate tensile strength* is equal to the force required to cause failure divided by the minimum cross-sectional area of the test sample.

When rubbery elasticity is required for sample performance, a high ultimate elongation is desirable. When rigidity is required, it is desirable that the material exhibits a lower ultimate

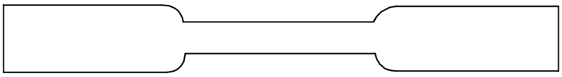


FIGURE 14.11 Typical dumbbell- or dog-bone-shaped sample used for stress–strain measurements.

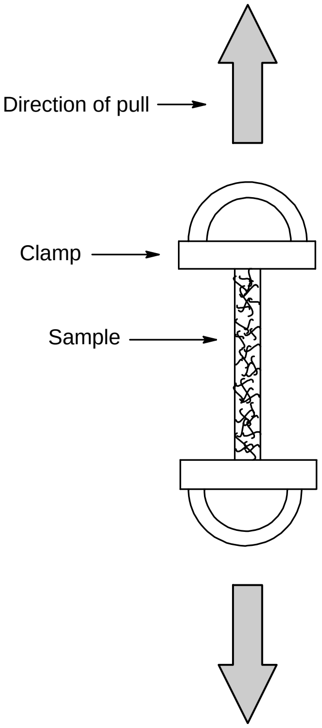


FIGURE 14.12 Typical tensile test assembly where both heads are movable.

elongation. Some elongation is desirable since it allows the material to absorb rapid impact and shock. The total area under the stress–strain curve is indicative of overall toughness.

Pulling stress is the deformation of a test sample caused by application of specific loads. It is the change in length of the test sample divided by the original length. Recoverable strain or elongation is called *elastic strain*. Here, stressed molecules return to their original relative locations after release of the applied force. Elongation may also be a consequence of wholesale movement of chains past one another, i.e., creep or plastic strain. Many samples undergo both reversible and irreversible strain.

Flexural strength, or cross-breaking strength, is a measure of the bending strength or stiffness of a test bar specimen used as a sample beam in accordance with ASTM D-790. The specimen is placed on supports (Figure 14.13). A load is applied to its center at a specified rate

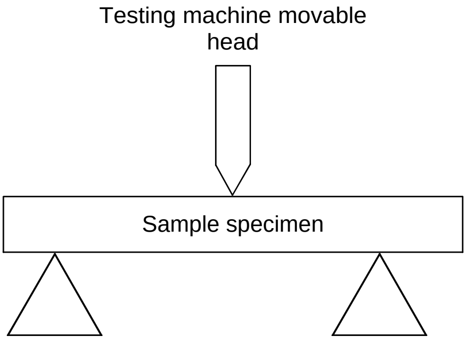


FIGURE 14.13 Typical flexural strength test.

TABLE 14.1
Tensile Strengths of Inorganic and Metallic Materials as a Function of Form

Material	Form	Tensile Strength (MPa)
Graphite	Bulk	1,000
	Fiber	2,800
	Whisker	15,000
Glass	Bulk	1,000
	Fiber	4,000
Steel	Bulk	2,000
	Fiber	400
	Whisker	10,000

with the loading at failure called the flexural strength. However, because many materials do not break even after being greatly deformed, by agreement, the modulus at 5% strain is used as the flexural strength for these samples.

14.4.2 TENSILE STRENGTH OF INORGANIC AND METALLIC FIBERS AND WHISKERS

The tensile strength of materials is dependent on the treatment and form of the material. Thus, the tensile strength of isotropic bulk nylon-6,6 is less than that of anisotropic oriented nylon-6,6 fiber. Inorganics and metals also form fibers and whiskers with varying tensile strengths (Table 14.1). Fibers are generally less crystalline and larger than whiskers.

Many of these inorganic fibers and whiskers are polymeric including many of the oxides (including the so-called ceramic fibers), carbon and graphite materials, and silicon carbide. Carbon and graphite materials are similar but differ in the starting materials and the percentage of carbon. Carbon fibers derived from polyacrylonitrile are about 95% carbon, while graphite fibers are formed at higher temperatures giving a material with 99% carbon.

These specialty fibers and whiskers exhibit some of the highest tensile strengths recorded (Tables 14.1 and 14.2) they are employed in applications where lightweight and high strength

TABLE 14.2
Ultimate Tensile Strength of Representative Organic, Inorganic, and Metallic Fibers

Material	Tensile Strength (MPa)	Tensile Strength/Density
Aluminum silica	4100	1060
Aramid	280	200
Beryllium carbide	1000	400
Beryllium oxide	500	170
Boron–tungsten boride	3450	1500
Carbon	2800	1800
Graphite	2800	1800
UHMWPE	380	3800
Poly(ethylene terephthate)	690	500
Quartz	900	400
Steel	4000	500
Titanium	1900	400
Tungsten	4300	220

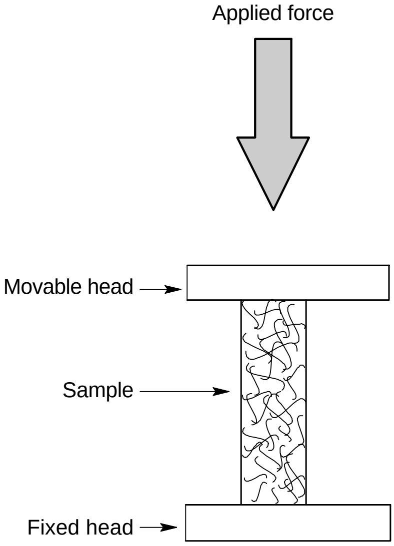


FIGURE 14.14 Representation of test apparatus for measurement of compression-related properties.

are required. Organics offer weight advantages, typically being less dense than most inorganic and metallic fibers. They are used in dental filings, the aircraft industry, production of lightweight fishing poles, automotive antennas, lightweight strong bicycles, turbine blades, heat-resistant reentry vessels, golf club shafts, etc. Many are also used as reinforcing agents in composites.

14.4.3 COMPRESSIVE STRENGTH

Compressive strength is the pressure required to crush a material defined as

$$\text{Compressive strength (Pa)} = \text{force } (N)/\text{cross-sectional area } (\text{m}^2) \qquad (14.19)$$

Compressive strength, or ability of a specimen to resist a crushing force, is measured by crushing a cylindrical specimen (ASTM-D-695) as shown in Figure 14.14. Here a sample of specified dimensions is placed between two heads, one movable and one set. Force is applied to the movable head moving it at a constant rate. The ultimate compression strength is equal to the load that causes failure divided by the minimal cross-sectional area. Since many materials do not fail in compression, strength reflective of specific deformation is often reported.

14.4.4 IMPACT STRENGTH

Impact strength is a measure of the energy needed to break a sample—it is not a measure of the stress needed to break a sample. The term *toughness* is typically used in describing the impact strength of a material but does not have a universally accepted definition although it is often described as the area under stress–strain curves.

There are a number of impact-related tests. Impact tests fall into two main categories: (1) falling-mass tests and (2) pendulum tests. Figure 14.15 shows an assembly suitable for determining impact strength of a solid sample by dropping a material of specified shape and weight at a given distance.

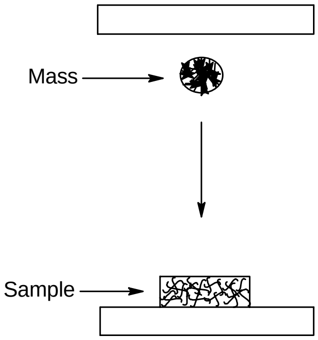


FIGURE 14.15 Assembly used to measure the impact strength of solid samples.

Impact resistance is related to impact strength. Two of the most utilized tests are the Izod (ASTM D-256) and Charpy (ASTM D-256) tests illustrated in Figure 14.16.

The Izod impact test measures the energy required to break a notched sample under standard conditions. A sample is clamped at the base of a pendulum testing apparatus so that it is cantilevered upward with the notch facing the direction of impact. The pendulum is released from a specified height. The procedure is repeated until the sample is broken. The Izod value is useful when comparing samples of the same polymer but is not a reliable indicator of toughness, impact strength, or abrasive resistance. The Izod test may indicate the need to avoid sharp corners in some manufactured products. Thus, nylon is a notch-sensitive material and gives a relatively low Izod impact value, but it is considered a tough material.

Unnotched or oppositely notched specimens are employed in the Charpy test.

Overall, impact strength tests are measures of toughness or the ability of a sample to withstand sharp blows, such as being dropped.

14.4.5 HARDNESS

The term *hardness* is a relative term. Hardness is the resistance to local deformation that is often measured as the ease or difficulty for a material to be scratched, indented, marred, cut, drilled, or abraded. It involves a number of interrelated properties such as yield strength and elastic modulus. Because polymers present such a range of behavior, as they are viscoelastic

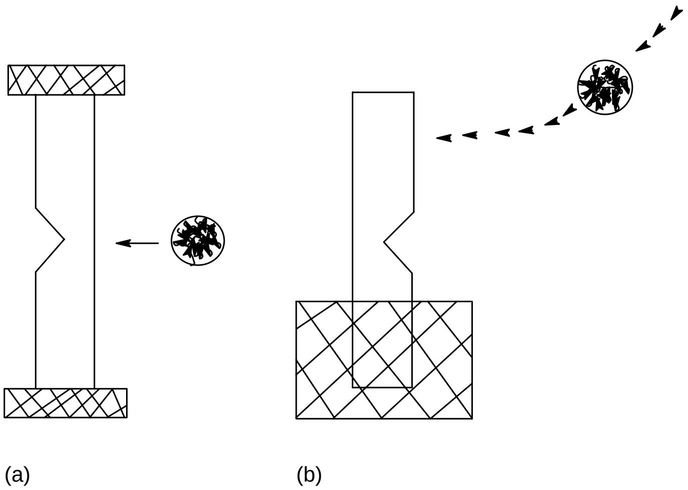


FIGURE 14.16 Pictorial description of Charpy (a) and Izod (b) pendulum impact tests.

materials, the test conditions must be carefully described. For instance, elastomeric materials can be easily deformed, but this deformation may be elastic with the indentation disappearing once the force is removed. While many polymeric materials deform in a truly elastic manner returning to the initial state once the load is removed, the range of total elasticity is often small resulting in limited plastic or permanent deformation. Thus, care must be taken in measuring and drawing conclusions from results of hardness measurements.

Static indention is the most widely employed measurement of hardness. Here, permanent deformation is measured. Hardness is often computed by dividing the peak contact load by the projected area of impression. The indention stresses, while concentrated within the area of impact, are generally more widely distributed to surrounding areas. Because of the presence of a combination of elastic and plastic or permanent deformation, the amount of recovery is also measured. The combination of plastic (permanent deformation) and elastic (noncreep associated reversible changes) deformation are determined by noting the recovery of the material after impact. The indention is then a measure of a complex of structure dependent on chain length, orientation, amounts and distributions of amorphous and crystalline combinations, etc.

Following is a description of some of the most used hardness tests.

14.4.6 BRINELL HARDNESS

Here, a steel ball is pushed against the flat surface of the test specimen. The standard test uses a ball of specific size pushed against the test surface with a given force.

14.4.7 ROCKWELL HARDNESS

Rockwell hardness tests (ASTM-D785-65 [1970]), depicted in Figure 14.17, measures hardness in progressive numbers on different scales corresponding to the size of the ball indenter and force of the load. Thus, varying loads are applied. Depth AB corresponds to the depth the indicator penetrates with a heavy load. The difference between A and B, i.e., AB, is used to calculate the Rockwell hardness values. While Rockwell hardness allows differentiation between materials, factors such as creep and elastic recovery are involved in determining the overall Rockwell hardness. Rockwell hardness may not be a good measure of wear qualities or abrasion resistance. For instance, PS has a relatively high Rockwell hardness value, yet it is easily scratched.

In the most used Rockwell tests, the hardness number does not measure total indentation but only the irreversible portion after a heavy load is applied for a given time and reduced to a

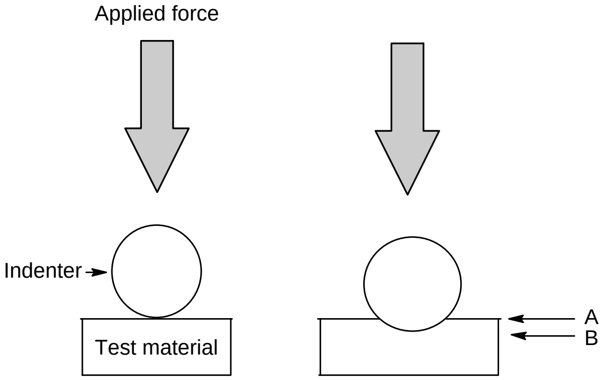


FIGURE 14.17 Description of the Rockwell hardness test.

TABLE 14.3
Comparative Hardness Scales

		Hardness Scale				
		Rockwell				
Mohs	Brindell	*M*	*R*	Shore	Barcol	Type of Material
2 (Gypsum)	25	100			55	Hard
	16	80			40	Plastics
	12	70	100	90	30	
	10	65	97	86	20	
	8	60	93	80		
	6	54	88	74		
1 (Talc)	5	50	85	70		
	2	32	~50	89		Soft plastics
	1	23		42		
	0.8	20		38		Rubbery
	0.5	15		30		

minor load for a given time. In Table 14.3 the "*M*" value is for a major load of 980 N (100 kgf) and a minor load of 98 N (10 kgf) using an indenter with a 6.25 mm diameter. The values given in the *R* column are for a lower initial load of 588 N (60 kgf) and a minor load of 98 N employing a larger indenter with a diameter of 12.5 mm.

Hardness may also be measured by the number of bounces of a ball or the extent of rocking by a Sward hardness rocker. Abrasion resistance may be measured by the loss in weight caused by the rubbing of the wheels of a Tabor abrader (ASTM-D-1044).

The shore durometer is a simple instrument used to measure the resistance of a material to the penetration of a blunt needle. In the Barcol approach, a sharp indentor is used to measure the ability of a sample to resist penetration by the indentor (Figure 14.18). The values given in Table 14.3 are for one specific set of conditions and needle area for the Barcol and Brinell hardness tests.

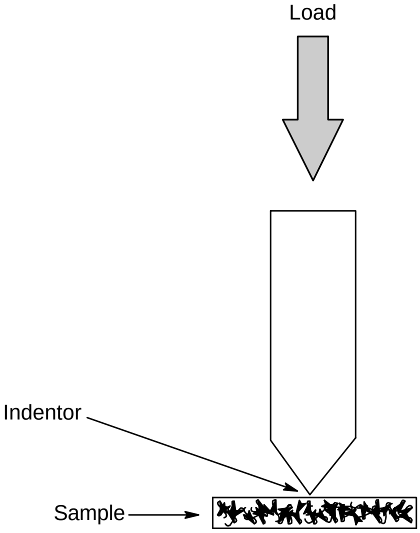


FIGURE 14.18 Barcol instrument employing a sharp indentor.

Table 14.3 contains comparative hardness values for five hardness scales including the classical Mohs scale, which ranges from the force necessary to indent talc given a value of 1 to that needed to scratch diamond given a Mohs value of 10. In the field, a number of relative tests have been developed to measure relative hardness. The easiest test for scratch hardness is to simply see how hard you have to push your fingernail into a material to indent it. A more reliable approach involves scratching the material with pencils of specified hardness (ASTM-D-3363) and noting the pencil hardness necessary to indent the material.

14.4.8 SHEAR STRENGTH

The measure of shear strength typically utilizes a punch-type shear fixture (Figure 14.19). The shear strength is equal to the load divided by the area. Thus, the sample is mounted in a punch-type shear fixture and punch-pushed down at a specified rate until shear occurs. This test is important for sheets and films but is not typically employed for extruded or molded products.

14.4.9 ABRASION RESISTANCE

Abrasion is the wearing away of a materials surface by friction. The most widely used tests to measure abrasion resistance employs Williams, Lamborn, and Tabor abraders (ASTM D-1044). In each test the abrader is rubbed on the material's surface and the material loss is noted.

14.4.10 FAILURE

The failure of materials can be associated with a number of parameters. Two major causes of failure are creep and fracture. The tensile strength is the nominal stress at the failure of a material. Toughness is related to ductility. For a material to be tough, it often takes a material having a good balance of stiffness and give.

Calculations have been made to determine the theoretical upper limits with respect to the strength of polymers. Real materials show behaviors near to those predicted by the theoretical calculations during the initial stress–strain determination, but vary greatly near the failure of the material. It is believed that the major reasons for the actual tensile strength at failure being smaller than calculated are related to imperfections, the nonhomogeneity of the polymeric structure. These flaws, molecular irregularities, act as the weak link in the polymer's behavior. These irregularities can be dislocations, voids, physical crack, and energy concentrations.

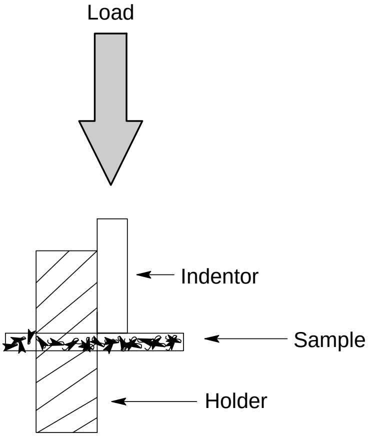


FIGURE 14.19 Assembly employed to measure shear strength.

Even with these imperfections, they have high strength/mass ratios (Table 14.2) with the highest tensile strength/density value for UHMWPE.

The fracture strengths of polymers are generally lower than those of metals and ceramics. The mode of failure for thermosets is generally referred to as the materials being brittle. Cracks, related to bond breakage, occur at points of excess stress. These create weak spots and may lead to fracture if the applied stress, appropriate to create bond breakage, continues.

Fracture of thermoplastics can occur either by a ductile or brittle fashion, or by some combination. Rapid application of stress (short reaction time), lower temperatures, application of the stress by a pointed or sharpened object, all increase the chances that failure will occur by a brittle mechanism as expected. For instance, below the T_g thermoplastics behave as solids, and above T_g polymer fracture increasingly moves to a ductile mode. Above the T_g thermoplastics display some plastic deformation before fracture; for some, crazing occurs before to fracture. These crazes are a form of defect and are associated with some yielding or void formation either through migration or elimination of some part of the polymer mix or because of chain migration through chain re-alignment or other mechanism. Fibrillar connections, from aligned chains, often form between void sides. If sufficient application of stress is continued, these fibrillar bridges are broken and the microvoids enlarge eventually leading to crack formation. Crazes can begin from scratches, flaws, molecular inhomogeneities, and molecular-level voids formed from chain migration (such as through crystallization) or small molecule migration from a site, as well as application of stress.

14.5 SUMMARY

1. Rheology is the study of deformation and flow of materials. Polymers are viscoelastic materials, meaning they can act as liquids and as solids.
2. Many of the rheological properties of materials are determined using stress–strain measurements.
3. Models are used to describe the behavior of materials. The fluid or liquid part of the behavior is described in terms of a Newtonian dashpot or shock absorber, while the elastic or solid part of the behavior is described in terms of a Hookean or ideal elastic spring. The Hookean spring represents bond flexing, while the Newtonian dashpot represents chain and local segmental movement.
4. In general, the springlike behavior is more important for polymers below their T_g, whereas the dashpot behavior is more important for polymers above their T_g.
5. Mathematical relationships have been developed to relate models composed at varying degrees of these two aspects of behavior to real materials.
6. Stress–strain behavior is closely dependent upon the particular conditions under which the experiment is carried out.
7. There are a number of specific tests that are used to measure various physical properties of materials. Many of these tests are described in detail by the various governing bodies that specify testing procedures and conditions.

GLOSSARY

barcol impressor Instrument used to measure the resistance of a polymer to penetration or indentation.
biaxially stretching Stretching in two directions perpendicular to each other.
Bingham, E.C. Father of rheology.
Bingham plastic Plastic that does not flow until the external stress exceeds a critical threshold value.
coefficient of expansion Change in dimensions per degree of temperature.
compression strength Resistance to crushing forces.

creep Permanent flow of polymer chains.

dashpot Model for Newtonian fluids consisting of a piston and a cylinder containing a viscous liquid.

dilatant Shear thickening agent; describes a system where the shear rate does not increase as rapidly as the applied stress.

elastic range Area under a stress–strain curve to the yield point.

flexural strength Resistance to bending.

Hooke's law Stress is proportional to strain.

impact strength Measure of toughness.

isotropic Having similar properties in all directions.

Maxwell element or model Model in which an ideal spring and dashpot are connected in series; used to study the stress relaxation of polymers.

modulus Stress per unit strain; measure of the stiffness of a polymer.

newtonian fluid Fluid whose viscosity is proportional to the applied viscosity gradient.

Newton's law Stress is proportional to flow.

Poisson's ratio Ratio of the percentage change in length of a sample under tension to its percentage change in width.

pseudoplastic Shear thinning agent: system where the shear rate increases faster than the applied stress.

relaxation time Time for stress of a polymer under constant strain to decrease to 1/e or 0.37 of its original value.

retardation time Time for the stress in a deformed polymer to decrease to 63% of the original value.

rheology Science of flow.

rheopectic Liquid whose viscosity increases with time.

shear Stress caused by planes sliding by each other.

shear strength Resistance to shearing forces.

stress (s) Force per unit area.

stress relaxation Relaxation of a stressed sample with time after the load is removed.

tensile strength Resistance to pulling stresses.

thixotropic Liquid whose viscosity decreases with time.

velocity gradient Flow rate.

viscoelastic Having the properties of a liquid and a solid.

Voigt–Kelvin model or element Model consisting of an ideal spring and dashpot in parallel in which the elastic response is retarded by viscous resistance of the fluid in the dashpot.

Williams, Landel, and Ferry equation (WLF) Used for predicting viscoelastic properties at temperatures above T_g when these properties are known for one specific temperature.

yield point Point on a stress–strain curve below which there is reversible recovery.

EXERCISES

1. What is the difference between morphology and rheology?
2. Which of the following is viscoelastic: (a) steel, (b) PS, (c) diamond, or (d) neoprene?
3. Define G in Hooke's law.
4. Which would be isotropic: (a) a nylon filament, (b) an extruded pipe, or (c) ebonite?
5. What are the major types of stress tests?
6. Describe in molecular terms what a dashpot represents.
7. Which will have the higher relaxation time: (a) unvulcanized rubber or (b) ebonite?
8. Describe in molecular terms what a spring represents.
9. Define what compliance is.
10. What does viscoelastic mean?
11. Below the glass transition temperature a material should behave in what manner?
12. At what temperature would the properties of PS resemble those of hevea rubber at 35 K above its T_g?
13. Define Young's modulus. Should it be high or low for a fiber?
14. Define the proportionality constant in Newton's law
15. What term is used to describe the decrease of stress with time at constant length?

16. In which element or model for a viscoelastic body will the elastic response be retarded by viscous resistance: (a) Maxwell or (b) Voigt–Kelvin?
17. What is the most important standards organization in the United States?
18. For most polymeric materials is failure abrupt or continuous?
19. Is it safe to predict long-range properties from short time period results for plastics?
20. Describe the importance of relating models to stress–strain results.
21. If a sample of PP measuring 5 cm elongates to 12 cm, what is the percentage of elongation?
22. If the tensile strength is 705 kg/cm^2 and the elongation is 0.026 cm, what is the tensile modulus?
23. Define creep.
24. Briefly describe a Voigt–Kelvin model.
25. What changes occur in a polymer under stress before the yield point?
26. What changes occur in a stress polymer after the yield point?
27. How can you estimate relative toughness of polymer samples from stress–strain curves?
28. What effect will a decrease in testing temperature have on tensile strength?
29. What effect will an increase in the time of testing have on tensile strength?
30. Describe a Maxwell model.

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15

Additives

Most polymeric materials are not a single polymer, but they contain chemicals that modify some physical and/or chemical behavior. These additives are generally added to modify properties, assist in processing, and introduce new properties to a material. Coloring agents, colorants, are added giving a product or component with a particular color often for identification or ecstatic purposes. Antibacterial agents are added to protect the material from certain microbial attack. Composites contain a fiber and continuous polymer phase resulting in a material that has a greater flexibility and strength than either of the two components. Some of these additives are polymeric while others are not. They may be added as gases, liquids, or solids. Often, some combination of additives is present. A typical tire tread recipe has a processing aid, activator, antioxidant, reinforcing filler, finishing aid, retarder, vulcanizing agent, and accelerator as additives (Table 15.1). A typical water-based paint has titanium dioxide as the white pigment, China clay as an extender, a fungicide, a defoaming agent, a coalescing liquid, a surfactant-dispersing agent, and calcium carbonate as another extender. In total, additives are essential materials that allow the polymeric portion(s) to perform as needed. Some of these additives are present in minute amounts and others are major amounts of the overall composition. Some additives are expensive, whereas others that are added simply to give bulk are inexpensive. While the identity, amount, and action of many additives were not totally developed on a scientific basis, adequate scientific knowledge is available so that there exists a rational for the use of essentially all additives.

Typical additives include:

Antiblocking agents
Antifoaming agents
Antifogging agents
Antimicrobial agents
Antioxidants
Antistatic agents
Blowing agents
Coloring agents
Coupling agents
Curing agents
Fillers
Flame retardants
Foaming agent
Impact modifiers
Low-profile materials
Lubricants
Mold release agents
Odorants or fragrances
Plasticizers
Preservatives
Reinforcements
Slip agents
Stabilizers, including
  Radiation (UV, VIS)
  Heat
Viscosity modifiers
  Flow enhancers
Thickening agents
  Antisag agents

In this chapter, we will look at a variety of additives.

TABLE 15.1
Typical Contents of a Modern Tire Tread

Material	% (by Weight)	Purpose
Natural rubber	30	Elastomer
Styrene–butadiene rubber	30	Elastomer
Carbon black	27	Reinforcing filler
Aromatic oil	5	Extender
Stearic acid	2	Accelerator
Aryl diamine	2	Antioxidant
Zinc oxide	2	Accelerator
Sulfur	1	Vulcanizing agent
Antiozonate	0.5	Antioxidant
Parafin wax	0.5	Processing aid
N,*N*-diphenyl guanidine	0.1	Delayed accelerator

15.1 PLASTICIZERS

Flexibilizing of polymers can be achieved through internal and external plasticization. Internal plasticization can be produced through copolymerization giving a more flexible polymer backbone or by grafting another polymer onto a given polymer backbone. Thus, poly(vinylchloride-co-vinyl acetate) is internally plasticized because of the increased flexibility brought about by the change in structure of the polymer chain. The presence of bulky groups on the polymer chain increases segmental motion and placement of such groups through grafting acts as an internal plasticizer. Internal plasticization achieves its end goal at least in part by discouraging association between polymer chains. However, grafted linear groups with more than 10 carbon atoms reduce flexibility because of side-chain crystallization when the groups are regularly spaced.

External plasticization is achieved through incorporation of a plasticizing agent into a polymer through mixing and/or heating. The remainder of this section focuses on external plasticization.

Plasticizers should be relatively nonvolatile, nonmobile, inert, inexpensive, nontoxic, and compatible with the system to be plasticized. They can be divided based on their solvating power and compatibility. Primary plasticizers are used as either the sole plasticizer or the major plasticizer with the effect of being compatible with some solvating nature. Secondary plasticizers are materials that are generally blended with a primary plasticizer to improve some performance such as flame or mildew resistance, or to reduce cost. The division between primary and secondary plasticizers is at times arbitrary. Here we will deal with primary plasticizers.

According to the ASTM D-883 definition, a plasticizer is a material incorporated into a plastic to increase its workability and flexibility or dispensability. The addition of a plasticizer may lower the melt viscosity, elastic modulus, and T_g.

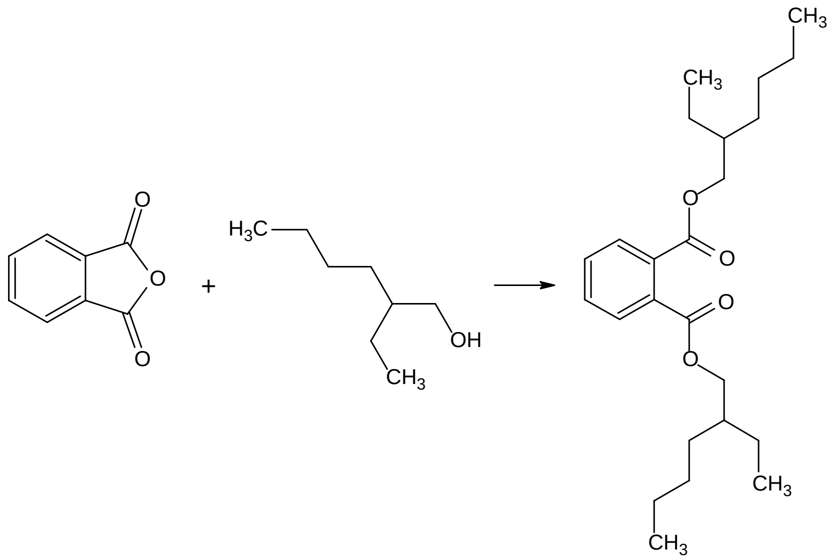
Waldo Semon patented the use of tricresyl phosphate as a plasticizer for PVC in 1933. This was later replaced by the less toxic di-2-ethylhexyl phthalate (DOP), which is now the most widely used plasticizer. The worldwide production of plasticizer is on the order of 3.2 million tons annually. Volume-wise, about 90% of the plasticizers are used with PVC and PVC-containing systems.

The effect of plasticizers has been explained by the lubricity, gel, and free volume theories. The lubricity theory states that the plasticizer acts as an internal lubricant and permits the polymers to slip past one another. The gel theory, which is applicable to amorphous polymers, assumes that a polymer, such as PVC, has many intermolecular attractions that are weakened by the presence of a plasticizer. In free volume theories, it is assumed that the addition of a plasticizer increases the free volume of a polymer and that the free volume is identical for polymers at T_g. There may be some truth in most of these theories. It is believed that a good plasticizer solubilizes segments allowing them some degree of mobility creating free volume through Brownian movement. In turn, this lowers the temperature where segmental mobility can occur making the material more flexible.

Most plasticizers are classified as general-purpose, performance, or specialty plasticizers. General-purpose plasticizers are those that offer good performance inexpensively. Most plasticizers belong to this group. Performance plasticizers offer added performance over general-purpose plasticizers generally with added cost. Performance plasticizers include fast solvating materials such as butyl benzyl phthalate and dihexyl phthalate; low temperature plasticizers such as di-n-undecyl phthalate and di-2-ethylhexyl adipate (DOA); and so-called permanent plasticizers such as tri-2-ethylhexyl trimellitate (TOTM), triisononyl trimellitate, and diisodecyl phthalate. Specialty plasticizers include materials that provide important properties such as reduced migration, improved stress–strain behavior, flame resistance, and increased stabilization.

The three main chemical groups of plasticizers are phthalate esters, trimellitate esters, and adipate esters. In all three cases, performance is varied through the introduction of different alcohols into the final plasticizer product. There is a balance between compatibility and migration. Generally, the larger the ester group is, the lesser the migration, up to a point where compatibility becomes a problem and a limiting factor.

The most used phthalate ester is DOP (Equation 15.3), made from the reaction of 2-ethyl hexanol (Equation 15.1) with phthalic anhydride (Equation 15.2).

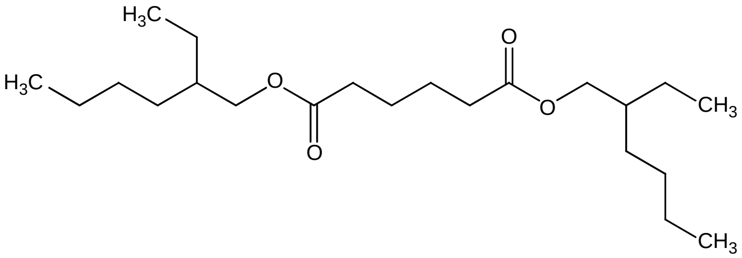


Phthalic anhydride
(15.1)

1-Ethyl hexanol
(15.2)

DOP
(15.3)

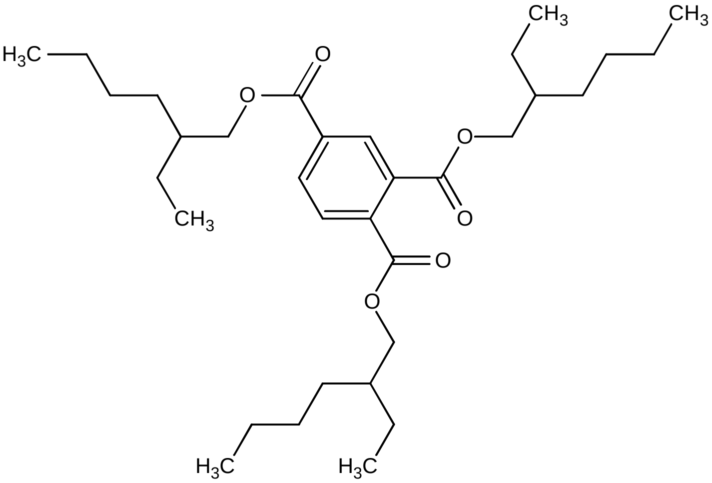
The most important adipate ester is also the di-2-ethylhexyl ester, DOA (Equation 15.4).



(15.4)

DOA

There are several widely used trimellitate esters including TOTM (Equation 15.5).



(15.5)

TOTM

Compatibility is the ability to mix together without forming different phases. A good approach to measure the likelihood of compatibility is solubility parameters (Section 3.2). Plasticizers with solubility parameters and type of bonding similar to those of polymers are more apt to be compatible than when the solubility parameters are different. The solubility parameter for PVC (9.66) is near that of good plasticizers such as DOP (8.85). Table 15.2 contains solubility parameters for typical plasticizers.

The development of plasticizers has been plagued with toxicity problems. Thus, the use of highly toxic polychlorinated biphenyls (PCBs) has been discontinued. Phthalic acid esters, such as DOP, may be extracted from blood stored in plasticized PVC blood bags and tubing. These aromatic esters are also distilled from PVC upholstery in closed automobiles in hot weather. These problems have been solved by using oligomeric polyesters as nonmigrating plasticizers in place of DOP for appropriate situations. Recently, some limited tests have indicated a relationship of prenatal exposure to phthalates and reproductive abnormalities of male babies. The chemical industry is monitoring these results, taking appropriate steps to limit or eliminate exposure to dangerous materials.

Experimental investigations and assessments show that the average person takes in about 2 g a year of external plasticizers. Most of this is from traces of DOA migrating from food packaging. The so-called no observed effect level (NOEL) for DOA in rodents is about 40 mg/kg of body weight per day. Extrapolation for a person equates to 1000 g of plasticizer

TABLE 15.2
Solubility Parameters of Typical Plasticizers

Plasticizer	Solubility Parameter (H)
Paraffinic oils	7.5
Dioctyl phthalate	7.9
Dibutoxyethyl phthalate	8.0
Tricresyl phosphate	8.4
Dioctyl sebacate	8.6
Triphenyl phosphate	8.6
Dihexyl phthalate	8.9
Hydrogenated terphenyl	9.0
Dibutyl sebacate	9.2
Dibutyl phthalate	9.3
Dipropyl phthalate	9.7
Diethyl phthalate	10.0
Glycerol	16.5

for a "safety factor" of about 500. Even so, increased efforts to evaluate the safety of plasticizers continue.

Plasticizers extend the lower temperature range for use of materials since they discourage polymer chain associative behavior and encourage segmental flexibility, thus increasing the rotational freedom and effectively decreasing the material's typical T_g.

When present in small amounts, plasticizers can act as antiplasticizers, increasing the hardness and decreasing the elongation of the material partly due to their ability to fill voids. Inefficient plasticizers require larger amounts of plasticizers to overcome the initial antiplasticization. However, good plasticizers such as DOP change from being antiplasticizers to plasticizers when less than 10% of the plasticizer is added to PVC.

External plasticizers are not permanent. Plasticizer molecules associate with one another eventually creating "preferred" migration routes to the material's surface where the plasticizer is rubbed or washed away. The preferential association of plasticizers also leaves some sites less flexible and creates variations in the material's stress–strain and expansion–contraction behaviors.

15.2 ANTIOXIDANTS

Antioxidants retard oxidative degradation. Heat, mechanical shear, and UV radiation can be responsible for the formation of free radicals, which, in turn, can act to shorten polymer chains and increase cross-linking, both leading to a deterioration in material properties. Free radical production often begins a chain reaction. Primary antioxidants donate active hydrogen atoms to free radical sites thereby quenching or stopping the chain reaction. Secondary antioxidants or synergists act to decompose free radicals to more stable products.

Polymers such as PP are not usable outdoors without appropriate stabilizers because of the presence of readily removable hydrogen atoms on the tertiary carbon atoms. PP and many other polymers (R—H) are attacked during processing or outdoor use in the absence of stabilizers because of chain degradation reactions as shown in the following equations:
By initiation:

$$\begin{array}{ccc} \text{R–H} & \longrightarrow & \text{R}^\bullet + \text{H}^\bullet \\ \text{Polymer} & \longrightarrow & \text{Free radicals} \end{array} \tag{15.6}$$

By propagation:

$$\underset{\text{Free radical}}{R^\bullet} + \underset{\text{Oxygen}}{O_2} \longrightarrow \underset{\text{Peroxy free radical}}{ROO^\bullet} \tag{15.7}$$

$$\underset{\text{Peroxy free radical}}{ROO^\bullet} + \underset{\text{Polymer}}{R\text{–}H} \longrightarrow \underset{\text{Dead polymer}}{ROOH} + \underset{\text{Free radical}}{R^\bullet} \tag{15.8}$$

By termination:

$$R^\bullet + R^\bullet \longrightarrow \underset{\text{Dead polymer}}{R\text{–}R} \tag{15.9}$$

$$R^\bullet + ROO^\bullet \longrightarrow \underset{\text{Dead polymer}}{ROOR} \tag{15.10}$$

$$ROO^\bullet + ROO^\bullet \longrightarrow \underset{\text{Dead polymer}}{ROOR} + \underset{\text{Oxygen}}{O_2} \tag{15.11}$$

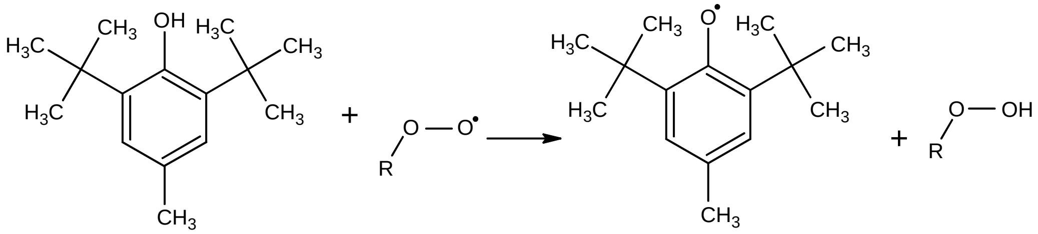
These degradation reactions are retarded by the presence of small amounts of antioxidants, but they are accelerated by the presence of heavy metals such as cobalt (II) ions as follows:

$$\mathrm{ROOH} + \mathrm{CO}^{+2} \rightarrow \mathrm{CO}^{+3} + \mathrm{RO}^\bullet + \mathrm{OH}^{-1} \tag{15.12}$$

$$\mathrm{ROOH} + \mathrm{CO}^{+3} \rightarrow \mathrm{CO}^{+2} + \mathrm{H}^{+1} + \mathrm{ROO}^\bullet \tag{15.13}$$

Naturally occurring antioxidants are present in many plants and trees such as hevea rubber. The first synthetic antioxidants were synthesized independently by Caldwell and by Winkelman and Gray by the condensation of aromatic amines with aliphatic aldehydes.

Many naturally occurring antioxidants are derivatives of phenol and hindered phenols, such as di-tert-butyl paracresol (Equation 15.14). It has the ability to act as a chain transfer agent forming a stable free radical that does not initiate chain radical degradation. However, the phenoxy free radical may react with other free radicals producing quinone derivatives.



(15.14)

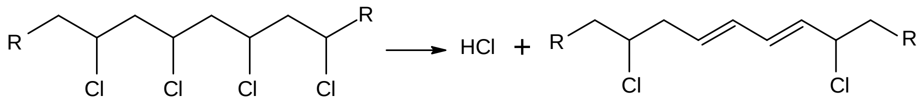
Since carbon black has many stable free radicals, it may be added to polymers such as polyolefins to retard free radical by attracting and absorbing other free radicals. It is customary to add small amounts of other antioxidants to enhance the stabilization by a "synergistic effect" whereby many antioxidant combinations are more stable than using only one antioxidant.

15.3 HEAT STABILIZERS

Heat stabilizers are added to materials to impart protection against heat-induced decomposition. Such stabilizers are needed to protect a material when it is subjected to a thermal-intense process (such as melt extrusion) or when the material is employed under conditions where increased heat stability is needed.

In addition to the free radical chain degradation described for polyolefins, other types of degradation occur including dehydrohalogenation for PVC. When heated, PVC may lose hydrogen chloride, forming chromophoric conjugated polyene structures, eventually yielding fused aromatic ring systems.

This type of degradation is accelerated in the presence of iron salts, oxygen, and hydrogen chloride. Toxic lead and barium and cadmium salts act as scavengers for hydrogen chloride and may be used for some applications such as wire coating. Mixtures of magnesium and calcium stearates are less toxic and effective. Among the most widely used heat stabilizers for PVC are the organotin products. Many of these are based on organotin polymers discovered by Carraher.



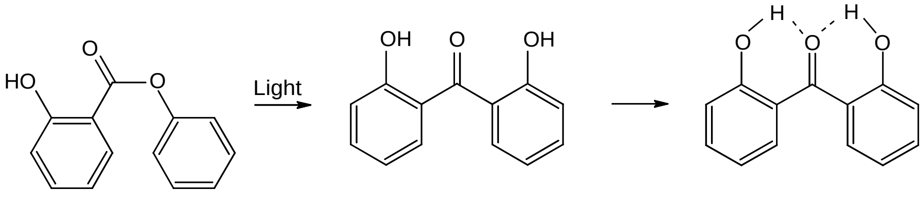
(15.15)

15.4 ULTRAVIOLET STABILIZERS

UV stabilizers act to quench UV radiation. While much of the sun's high-energy radiation is absorbed by the atmosphere, some radiation in the 280–400 nm (UV) range reaches the earth's surface. Since the energy of this radiation is on the order of 70–100 kcal/mol (280–400 kJ/mol), UV radiation is sufficient to break many chemical bonds, and thus cause polymer chains to break. This breakage generally does one of the two things: (1) It can increase the amount of cross-linking through subsequent formation of bonds after the initial bond breakage; or (2) bond breakage can result in a decreased chain length. Either of these results in a decreased overall strength of the polymeric material, and often the yellowing of many organic polymers. Cross-linking also results in the embrittlement of these polymers.

PE, PVC, PS, PET, and PP are degraded at wavelengths of 300, 310, 319, 325, and 370 nm, respectively. The bond energy required to cleave the tertiary carbon hydrogen bond in PP is only 320 kJ/mol, which corresponds to a wavelength of 318 nm.

Since the effect of UV radiation on synthetic polymers is similar to its effect on the human skin, it is not surprising that UV stabilizers such as phenyl salicylate have been used for commercial polymers and in suntanning lotions for many years. Phenyl salicylate rearranges in the presence of UV radiation forming 2,2′-dihydroxybenzophenone. The latter and other 2-hydroxybenozophenones act as energy transfer agents, i.e., they absorb energy forming chelates, which release energy at longer wavelengths by the formation of quinone derivatives.



(15.16)

Over 100,000 t of UV stabilizers are used by the U.S. polymer industry annually.

15.5 FLAME RETARDANTS

Although some polymers such as PVC are not readily ignited, most organic polymers, like hydrocarbons, will burn. Some will support combustion, such as polyolefins, SBR, wood, and paper, when lit with a match or some other source of flame. The major products for much of this combustion are carbon dioxide (or carbon monoxide if insufficient oxygen is present) and water.

Since many polymers are used as shelter and clothing and in household furnishing, it is essential that they have good flame resistance. Combustion is a chain reaction that may be initiated and propagated by free radicals. Since halides and phosphorus radicals couple with free radicals produced in combustion terminating the reaction, many flame retardants are halide (halogen) or phosphorus-containing compounds. These may be additives; external retardants sprayed onto the material such as antimony oxide and organic bromides; or internal retardants such as tetrabromophthalic anhydride that are introduced during the polymerization process so that they are part of the polymer chain.

Fuel, oxygen, and high temperature are essential for the combustion process. Thus, polyfluorocarbons, phosphazenes, and some composites are flame-resistant because they are not good fuels. Fillers such as alumina trihydrate (ATH) release water when heated and hence reduce the temperature of the combustion process. Compounds such as sodium carbonate, which releases carbon dioxide when heated, shield the reactants from oxygen. Char, formed in some combustion processes, also shields the reactants from a ready source of oxygen and retards the outward diffusion of volatile combustible products. Aromatic polymers, such as PS, tend to char and some phosphorus and boron compounds catalyze char formation aiding in controlling the combustion process.

Synergistic flame retardants such as a mixture of antimony trioxide and an organic bromo compound are more effective that single flame retardants. Thus, mixtures are often employed to protect materials and people.

Since combustion is subject to many variables, tests for flame retardancy may not correctly predict flame resistance under unusual conditions. Thus, a disclaimer stating that flame retardancy tests do not predict performance in an actual fire must accompany all flame-retardant products. Flame retardants, like many organic compounds, may be toxic or may produce toxic gases when burned. Hence, care must be exercised when using fabrics or other polymers treated with flame retardants.

Combustion is a chain reaction that can be initiated and propagated by free radicals such as the hydroxyl free radical. The hydroxyl radical may be produced by reaction of oxygen with macroalkyl radicals as shown below:

$$\underset{\substack{\text{Macroalkyl}\\\text{radical}}}{\text{R–CH}_2^{\bullet}} + \underset{\text{Oxygen}}{\text{O}_2} \longrightarrow \underset{\text{Dead polymer}}{\text{R–CHO}} + \underset{\substack{\text{Hydroxyl}\\\text{radical}}}{\text{HO}^{\bullet}} \tag{15.17}$$

$$\underset{\text{Hydroxyl}}{\text{HO}^{\bullet}} + \underset{\text{Polymer}}{\text{R–CH}_3} \longrightarrow \underset{\text{Macroradical}}{\text{R–CH}_2^{\bullet}} + \underset{\text{Water}}{\text{H}_2\text{O}} \tag{15.18}$$

Halide-containing compounds have often been used to suppress flame propagation by reduction of free radical concentration as follows:

$$\underset{\substack{\text{Hydrogen}\\\text{halide}}}{\text{HX}} + \underset{\substack{\text{Hydroxyl}\\\text{radical}}}{\text{HO}^{\bullet}} \longrightarrow \underset{\text{Water}}{\text{H}_2\text{O}} + \underset{\substack{\text{Halogen}\\\text{radical}}}{\text{X}^{\bullet}} \tag{15.19}$$

$$\underset{\text{Halogen radical}}{X^{\bullet}} + \underset{\text{Macroradical}}{R{-}CH_2^{\bullet}} \rightarrow \underset{\text{Dead polymer}}{R{-}CH_2X} \tag{15.20}$$

15.6 COLORANTS

Color is a subjective phenomenon whose esthetic value has been recognized for centuries. Since it is dependent on the light source, the object, and the observer, color is not subject to direct measurement, though instruments can measure a color for reproducibility. Colorants that provide color in polymers may be soluble dyes or comminuted pigments.

Some polymeric objects, such as rubber tires, are black because of the presence of high proportions of carbon black filler. Many other products, including some paints, are white because of the presence of titanium dioxide (titanium (IV) oxide), the most widely used inorganic pigment. Over 50,000 t of colorants are used annually by the polymer industry.

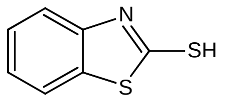
Pigments are classified as organic or inorganic. Organic pigments are brighter, less dense, and smaller in particle size than the more widely used, more opaque, inorganic colorants. Iron oxides or ochers are available as yellow, red, black, brown, and tan.

Carbon black is the most widely used organic pigment, but phthalocyanine blues and greens are available in many shades and are also widely used.

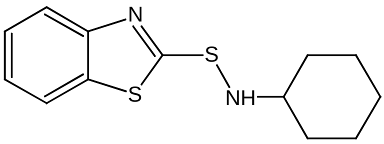
15.7 CURING AGENTS

The use of curing agents began with the serendipitous discovery of vulcanization of hevea rubber with sulfur by Charles Goodyear in 1838. The conversion of an A- or B-stage phenolic novolac resin with hexamethyalenetetramine in the early 1900s was another relatively early use of curing (cross-linking) agents. Organic accelerators, or catalysts, for the sulfur vulcanization of rubber were discovered by Oenslager in 1912. While these accelerators are not completely innocuous, they are less toxic than aniline, used before the discovery of accelerators. Other widely used accelerators are thiocarbanilide and 2-mercaptobenzothiazole (Captax).

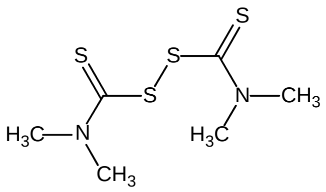
Captax (Structure 15.21) is used to the extent of 1% with hevea rubber and accounts for the major part of the over 30,000 t of accelerators used annually in the United States. Other accelerators widely used include 2-mercaptobenzothiazole sulfenamide (Santocure; Structure 15.22), used for the vulcanization of SBR; dithiocarbamates; and thiuram disulfides. Thiuram disulfide (Structure 15.23) is a member of a group called ultra-accelerators, which allow the curing of rubber at moderate temperatures and may be used in the absence of sulfur.



2-Mercaptobenzothiazole
(15.21)



2-Mercaptobenzothiazole
sulfenamide (15.22)



Tetramethyl thiuram
disulfide (15.23)

Initiators such as BPO are used not only for the initiation of chain reaction polymerization, but also for the curing of polyesters and ethylene–propylene copolymers, and for the grafting of styrene on elastomeric polymer chains.

Unsaturated polymers such as alkyd resins can be cured or "dried" in the presence of oxygen, a heavy metal, and an organic acid called a drier. The most common organic acids are linoleic, abietic, naphthenic, octoic, and tall oil fatty acids.

15.8 ANTISTATIC AGENTS—ANTISTATS

Antistatic agents (antistats) dissipate static electrical charges. Insulating materials, including most organic plastics, fibers, films, and elastomers, can build up electrical charge. Because these largely organic materials are insulators, they are not able to dissipate the charge. Such charge buildup is particularly noticeable in cold, dry climates and leads to dust attraction and sparking.

External antistats are applied to the surface by wiping, spraying, etc. These surface treatments act to prevent static charge buildup. Internal antistats are added during the processing and become an integral part of the bulk composition of the material. Because surface treatments are often worn away through washing, waxing, and handling, the external antistats must be replenished. Internal antistats are added to allow the antistats to come (bleed) to the surface over a long time, giving the material long-term protection.

15.9 CHEMICAL BLOWING AGENTS

Chemical blowing agents (CBAs) are employed to create lighter weight material through formation of foam. Physical CBAs are volatile liquids and gases that expand and volatilize during processing through control of the pressure and temperature.

Cellular polymers not only provide insulation and resiliency, but are also usually stronger on a weight basis than solid polymers. Fluid polymers may be foamed by the addition of low-boiling liquids such as pentane or fluorocarbons by blowing with compressed nitrogen gas, by mechanical heating, and by the addition of foaming agents. While some carbon dioxide is produced when PUs are produced in the presence of moisture, auxiliary propellants are also added to the prepolymer mixture to give the desired amount of foaming. The most widely used foaming agents are nitrogen-producing compounds such as azobisformamide. Other foaming agents that decompose at various temperatures are also available.

15.10 COMPATIBILIZERS

Compatibilizers are compounds that provide miscibility or compatibility to materials that are otherwise immiscible or only partially miscible yielding a homogeneous product that does not separate into its components. Typically, compatibilizers act to reduce the interfacial tension and are concentrated at phase boundaries. Reactive compatibilizers chemically react with the materials they are to make compatible. Nonreactive compatibilizers perform their task by physically making the various component materials compatible.

15.11 IMPACT MODIFIERS

Impact modifiers improve the resistance of materials to stress. Most impact modifiers are elastomers such as ABS, BS, methacrylate–butadiene–styrene, acrylic, ethylene–vinyl acetate, and chlorinated PE.

15.12 PROCESSING AIDS

Processing aids are added to improve the processing characteristics of a material. They may increase the rheological and mechanical properties of a melted material. Acrylate copolymers are often utilized as processing aids.

15.13 LUBRICANTS

Lubricants are added to improve the flow characteristics of a material during its processing. They operate by reducing the melt viscosity or by decreasing adhesion between the metallic surfaces of the processing equipment and the material being processed. Internal lubricants reduce molecular friction consequently decreasing the material's melt viscosity allowing it to flow more easily. External lubricants act by increasing the flow of the material by decreasing the friction of the melted material as it comes in contact with surrounding surfaces. In reality, lubricants such as waxes, amides, esters, acids, and metallic stearates act as both external and internal lubricants.

15.14 MICROORGANISM INHIBITORS

Although most synthetic polymers are not directly attacked by microorganisms such as fungi, yeast, and bacteria, they often allow growth on their surfaces. Further, naturally occurring polymeric materials such as cellulosics, starch, protein, and vegetable oil–based coatings are often subject to microbiologic deterioration. Finally, some synthetics containing linkages that can be "recognized" by enzymes within microorganism (such as amide and ester linkages) may also be susceptible to attack.

One major antimicrobial grouping was once organotin-containing compounds. These monomeric organotin-containing compounds are now outlawed because of the high "leaching" rates of these material affecting surrounding areas. Even so, polymeric versions are acceptable and can be considered "nonleaching" or slowly leaching.

Organic fungistatic and bacteriostatic additives are currently employed, but in all cases, formation of resistant strains and the toxicity of the bioactive additive must be considered.

15.15 SUMMARY

1. Most polymers contain materials added to modify some physical and/or chemical property that allows them to better fulfill their intended use. These added materials are called additives.
2. Plasticizers allow polymer chains to move past one another allowing wholesale flexibility. They can enhance flexibility above and below the glass transition temperature of a polymer. Plasticization can occur through addition of an external chemical agent or may be incorporated within the polymer itself.
3. Antioxidants retard oxidative degradation.
4. Heat stabilizers allow some protection to heat-induced decomposition.
5. UV stabilizers act to quench UV radiation. UV radiation is strong enough to break chemical bonds, and thus cause polymer chains to break, either increasing the amount of cross-linking through subsequent formation of bonds, or resulting in a decreased chain length. Either of these results in a decreased overall strength of the polymeric material.
6. Flame retardants impart to the polymers some ability to resist ready combustion. Since fuel, oxygen, and high temperature are essential for the combustion of polymers, the removal of any of these prerequisites retards combustion. Flame retardants act through a variety of mechanisms including char formation and combination with free radical species that promote further combustion, through release of water.
7. A variety of inorganic and organic compounds are used to color polymers.
8. The rate of cross-linking of polymers, such as NR, is increased through the use of accelerators, often misnamed as catalysts.
9. Antistats reduce the electrostatic charge on the surface of polymers.
10. Gas-producing additives are essential for the formation of cellular products such as foam cushions.

11. Biocides are used to prevent or retard attack on polymers by microorganisms.
12. Lubricants serve as processing aids that discourage the sticking of polymers to metal surfaces during processing.
13. Other important additives are coloring agents, curing agents, antistatic agents, chemical blowing agents, and microorganism inhibitors.
14. Each of these additives performs a critical role in allowing polymers to be processed and utilized giving the variety of useful products we have today.

GLOSSARY

accelerator Catalyst for the vulcanization of rubber.
acicular Needle-shaped.
antioxidant Additive that retards polymer degradation by oxidative modes.
antiplasticization Hardening and stiffening effect observed when small amounts of a plasticizer are added to a polymer.
antistat Additive that reduces static charges on polymers.
aspect radio Ratio of length to diameter.
biocide Additive that retards attack by microorganisms.
blocking Sticking of sheets of film to one another.
bulk molding compound (bmc) Resin-impregnated bundles of fibers.
bound rubber Rubber adsorbed on carbon black and that is insoluble in benzene.
carbon black Finely divided carbon made by the incomplete combustion of hydrocarbons.
cellular polymers Foams.
chemical blowing agent Volatile liquids and gases that expand and/or volatilize during processing of a material creating pockets leading to lighter weight materials.
comminuted Finely divided.
colorant Color causing material; usually a dye or pigment.
compatibilizers Chemicals that provide miscibility or compatibility to materials that are otherwise immiscible or only partially miscible, giving a more homogeneous material.
coupling agents Products that improve the interfacial bond between the filler and resin.
curing agent Additive that causes cross-linking.
drier Catalyst that aids the reaction of polymers with oxygen.
drying Cross-linking of an unsaturated polymer chain.
energy transfer agent Molecule that absorbs high energy and re-radiates it in the form of lower energy.
extender Term sometimes applied to an inexpensive filler.
filler Usually a relatively inert material used as the discontinuous additive; generally inexpensive.
flame retardant Additive that increases the flame resistance of a polymer.
foaming agent Gas producer.
free volume Volume not occupied by polymer chains.
gel theory Theory that assumes that in the presence of a pseudo-three-dimensional structure intermolecular attractions are weakened by the presence of a plasticizer.
heat stabilizers Additives that retard the decomposition of polymers at elevated temperatures.
impact modifiers Materials that improve the resistance of materials to stress.
low-profile resins Finely divided incompatible resins that made a rough surface smooth.
lubricants Materials that improve the flow characteristics of materials, generally during processing.
lubricity theory Theory that plasticization occurs because of increased polymer chain slippage.
microballoons Hollow glass spheres.
mold release agent Lubricant that prevents polymers form sticking to mold cavities.
novaculite Finely ground quartzite rock.
plasticizer Material that increases the flexibility of a material.
plastisol Suspension of finely divided polymer in a liquid plasticizer with the plasticizer penetrating and plasticizing the polymer when heated.
promotor Coupling agent.

side-chain crystallization Stiffening effect noted when long, regularly spaced pendent groups are present on a polymer chain.

synergistic effect Enhanced effect beyond that expected by simply an additive effect.

ultra-accelerator Catalyst that cures rubber at low temperatures.

UV stabilizer Additive that retards degradation caused by UV radiation.

vulcanization Cross-linking with heat and sulfur.

EXERCISES

1. Which would be stronger: (a) a chair made from PP or (b) one of equal weight made from cellular PP?
2. What advantage would a barium ferrite-filled PVC strip have over an iron magnet?
3. Providing that the volumes of the fibers are similar, which would give the stronger composite: fibers with (a) small or (b) large cross-sections?
4. How would you make abrasive foam from PU?
5. Why is a good interfacial bond between the filler surface and the resin important?
6. CN explodes when softened by heat. What would you add to permit processing at lower temperatures?
7. PVC was produced in the 1830s but not used until the 1930s. Why?
8. What was believed to be the source of "fog" on the inside of the windshield until the 1930s?
9. Can you propose a mechanism for antiplasticization?
10. What naturally occurring fiber is more resistant to microbiological attack than nylon?
11. The T_g decreases progressively as the size of the alkoxy group increases from methyl to decyl in polyalkyl methacrylates, but then increases. Explain.
12. PP is now used in indoor or outdoor carpets. However, the first PP products deteriorated rapidly when subjected to sunlight because of the presence of tertiary hydrogen atoms present. Explain.
13. Which is more resistant to attack by microorganisms: (a) PVC or (b) plasticized PVC?
14. Lead stearate is an effective thermal stabilizer for PVC, yet its use in PVC pipe is not permitted. Why?
15. PVC sheeting fails when exposed to long periods of sunlight and undergoes a series of color changes before becoming black. Explain.
16. What is the advantage of using epoxidized soybean oil as a stabilizer for PVC?
17. Why do PVC films deteriorate more rapidly when used outdoors in comparison to indoors?
18. Which of the following is more resistant to UV light: (a) PP, (b) PE, or (c) PVC?
19. Sometimes molded plastics have opaque material called "bloom" on the surface. Explain.
20. Why are static charges on polymer surfaces not desired?
21. Many ingredient combinations are called recipes. Why?
22. How were recipes developed?
23. Certain live animal testing has shown that certain additives may be harmful. If you headed a chemical company what would you do if one of the additives was suspected of being harmful?
24. Why is there an overlap between materials found in sun screens and those employed to help protect polymers from degradation from light?
25. Why are so many additives used in polymers?

FURTHER READING

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16 Reactions on Polymers

Reactions occurring on polymers in nature and industry are widespread. In nature, reactions on polymers serve as the basis for information transfer, synthesis of needed biomaterials, degradation of biomaterials, and in fact reactions of polymers are at the core of life itself. Nature also reacts with synthetic polymers as they age, degrade, and cross-link. Synthetic polymers also serve as the basic material for the production of many important fibers, elastomers, and plastics. The nature of these reactions is governed similarly, whether the source and site of the polymer is natural or man-made. There are some differences especially with respect to the precision of the interaction and predicted outcome. Some polymer interactions, such as those that transfer information, must occur with a very high degree of precision for each and every incident. By comparison, naturally induced degradation of natural and synthetic polymers through weathering occurs through general steps that can be described in some statistical manner.

Reactions on synthetic polymers often mimic similar reactions involving small molecules where size is the main difference. There are some exceptions where nearby groups may hinder or assist in the reaction in which differences occur. Here, the main differences are often kinetic, though some geometrical differences are found for specific cases. Reactions in which the rate of reaction in polymers is enhanced by the presence of neighboring groups are called anchimeric assistance.

While there are many possible routes, most degradations can be described as occurring through two general routes: unzipping and random scission. Polymers such as polysiloxanes and polysulfur undergo unzipping reactions forming preferred internal cyclic products unless the end group is capped in such a manner as to discourage unzipping. In unzipping, one end begins to "unzip" and this process continues down the chain until it is completed. Random scission is the normal degradation pathway for most natural (e.g., polycarbonates) and synthetic polymers. Here, a long chain is attacked at some site, normally one that is exposed and of the exposed sites, one that is stressed. Thus, while random scission implies a random statistical manner of chain breakage, superimposed on this are more complex considerations of exposure and stress and the likelihood that a particular site is susceptible to that particular type of bond breakage.

This chapter describes many of the important reactions of polymers. Synthesis and curing (cross-linking) of polymers and telomerization are chemical reactions of polymers that have been discussed in previous chapters.

16.1 REACTIONS WITH POLYOLEFINES AND POLYENES

As with other carbon, hydrogen, and oxygen-containing materials, the main products of combustion in the presence of oxygen are water and carbon dioxide. Such polymers can be reacted with various reactants giving products analogous to those obtained from small alkanes and alkane-intense compounds. The moderating conditions between reactions of small molecules and polymers involve contact between the polymer segments and the reactants.

Polyolefines, like simple alkanes, can be chlorinated by chlorine giving hydrogen chloride and chlorinated products such as Tyrin, used as plasticizers and flame retardants, and poly (vinyl dichloride), which has better heat resistance than PVC and is used for hot water piping.

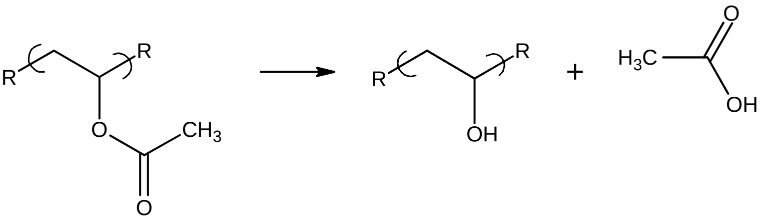
Reactions with polyenes are similar to the reactions of alkenes. Thus, Hermann Staudinger found that polyenes such as *Hevea brasiliensis* could be hydrogenated, halogenated, hydrohalogenated, and cyclized. This classic work was done in the early 1900s. In fact, Berthelot hydrogenated *H. brasiliensis* in 1869. Chlorinated rubber (Tornesit and Parlon) is produced by the chlorination of rubber giving products with varying amounts of chlorine and is used for the coating of concrete. Hydrohalogenation of *H. brasiliensis* gives a product (e.g., Pliofilm) that is a packaging film.

The product obtained by the partial hydrogenation of polybutadiene (Hydropol) has been used as a wire coating and a saturated ABA copolymer (Kraton) is produced by the hydrogenation of the ABA block copolymer of styrene and butadiene.

16.2 REACTIONS OF AROMATIC AND ALIPHATIC PENDANT GROUPS

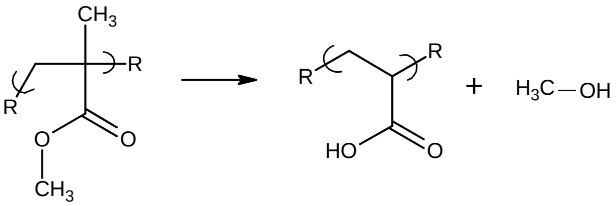
Polymers with aromatic pendant groups, such as PS, undergo all of the characteristic reactions of benzene including alkylation, halogenation, nitration, and sulfonation. PS has been sulfonated by fuming sulfuric acid with cross-linked products used as ion exchange resins. Living polymers (cation propagation) are used to form a variety of products with hydroxyl and dihydroxyl products forming telechelic and macromers. Polyaminostyrene is formed from the nitration of PS. These polyaminostyrene products can be diazotized giving polymeric dyes.

Esters such as PVAc may be hydrolyzed producing alcohols such as PVA (16.1), which will have the same DP as the ester. In fact, PVAc does not totally hydrolyze, but with reasonable effort the extent of hydrolysis is greater than 90%. Since PVAc is not water-soluble, but PVA, the extent of water solubility is dependent on the extent of hydrolysis.



(16.1)

Esters of poly(carboxylic acids), nitrites, and amides may be hydrolyzed to produce poly (carboxylic acids). Thus, polyacrylonitrile, polyacrylamide, or poly(methyl acrylate) may be hydrolyzed producing poly(acrylic acid) (equation 16.2).



(16.2)

Poly(acrylic acid) and partially hydrolyzed polyacrylamide are used for the prevention of scale in water used for boilers and for flocculating agents in water purification.

Neutralization of ionic polymers, such as poly(acrylic acid), causes the now fully negatively charged carboxylate groups to repel one another, resulting in the chain-changing conformation from that of a free-draining random shape to that approaching a rigid rod. This increase in length results in an increase in polymer viscosity with the extent of increasing viscosity related to the extent of ionic groups present. Addition of salts, such as sodium chloride, allows the negatively charged chains to return to a more random conformation and subsequent decrease in viscosity.

Some of the largest polymers, with molecular weights of the order of 10–15 million daltons, contain sodium acrylate and acrylamide groups. Simple stirring can result in chain breakage for these extremely high-molecular weight chains. Copolymers containing sodium acrylate and acrylamide groups are used in tertiary oil recovery and in water purification.

16.3 DEGRADATION

Some reactions on polymers are intended and give a material with different desired properties. The (positive) modification of polymers is an area of vigorous activity. Other reactions on polymers are unintended and generally result in a material with unfavorable properties. Included in the latter are a whole host of polymer degradation reactions. Some of these degradation reactions are covered elsewhere. Here, we will focus on some general concepts. Degradation can be promoted by many means and any combination of means. The major means of polymer degradation are given in Table 16.1.

Backbone chain scission degradation can be divided as occurring via depolymerization, random chain breakage, weak-link or preferential site degradation, or some combination of these general routes. In depolymerization, monomer is split off from an activated end group. This is the opposite of the addition polymerization and is often referred to as "unzipping."

$$\mathrm{P{-}MMMMMMMM} \xrightarrow{-\mathrm{M}} \mathrm{P{-}MMMMMMM} \xrightarrow{-\mathrm{M}} \mathrm{P{-}MMMMMM} \xrightarrow{-\mathrm{M}} \mathrm{P{-}MMMMM} \xrightarrow{-\mathrm{M}} \text{etc.} \tag{16.3}$$

Chain scission is similar to the opposite of stepwise polycondensation where units are split apart in a random manner.

$$\mathrm{P}_m - \mathrm{P}_n \rightarrow \mathrm{P}_m + \mathrm{P}_n \tag{16.4}$$

Depolymerization can result in backbone degradation and/or in the formation of cyclic or other products. The thermal degradation of PVA and PVC occurs with the splitting of water

TABLE 16.1
Major Synthetic Polymer Degradative Agents

Degradation Agent	(Most) Susceptible Polymer Types	Examples
Acids and bases	Heterochain polymers	Polyesters, polyurethanes
Moisture	Heterochain polymers	Polyesters, nylons, polyurethanes
High-energy radiation	Aliphatic polymers with quaternary carbons	Polypropylene, LDPE, PMMA, poly(alpha-methylstyrene)
Ozone	Unsaturated polymers	Polybutadienes, polyisoprene
Organic liquids/vapors	Amorphous polymers	
Biodegradation	Heterochain polymers	Polyesters, nylons, polyurethanes
Heat	Vinyl polymers	PVC, poly(alpha-methylstyrene)
Mechanical (applied stresses)	Polymers below T_g	

or HCl followed by a combination of further chain degradation to finally give small products and formation of complex cyclic products. Elimination of HCl further accelerates additional HCl elimination and increased property loss. PVC degradation is decreased by addition of agents that impede degradation such as those that neutralize HCl, trap free radicals and/or that react with the forming double bonds to impede further depolymerization. Commercial PVC often contains organotin or antimony mercaptide compounds that act as stabilizers.

In general, for vinyl polymers thermal degradation in air (combustion) produces the expected products of water, carbon dioxide, and char along with numerous hydrocarbon products. Thermally, simple combustion of polymeric materials gives a complex of compounds that vary according to the particular reaction conditions. Application of heat under controlled conditions can result in true depolymerization generally occurring via an unzipping. Such depolymerization may be related to the ceiling temperature of the particular polymer. Polymers such as PMMA and poly(alpha-methylstyrene) depolymerize to give large amounts of monomer when heated under the appropriate conditions. Thermal depolymerization generally results in some char and formation of smaller molecules including water, methanol, and carbon dioxide.

Most polymers are susceptible to degradation under natural radiation, sunlight, and high temperatures even in the presence of antioxidants. Thus, LDPE sheets, impregnated with carbon black, become brittle after exposure to 1 year's elements in South Florida. HDPE, while more costly, does stand up better to these elements, but again after several seasons, the elements win and the HDPE sheets become brittle and break. Long-term degradation is often indicated in clear polymers by a yellowing and a decrease in mechanical properties.

Most polymers are subject to oxidative degradation, particularly in the presence of other "enticers" such as heat, a good supply of air, various catalysts, high-energy radiation including UV and higher-energy visible light, and mechanical stressing that not only exposes additional polymer to the "elements," but also brings about the actual breakage of bonds subsequently leading to additional breakdown.

While polymers that contain sites of unsaturation, such as polyisoprene and the polybutadienes, are most susceptible to oxygen and ozone oxidation, most other polymers also show some susceptibility to such degradation including NR, PS, PP, nylons, PEs, and most natural and naturally derived polymers.

Because of the prevalence of degradation by oxidation, antioxidants are generally added. These antioxidants are generally compounds that readily react with free radicals or those that may act to lessen the effects of enticers such as UV radiation.

Mechanical degradation, while applied on a macrolevel, can result not only in chain rearrangement, but also in chain degradation. Such forces may be repetitive or abrupt and may act on the polymer while it is in solution, melt, elastic, or below its T_g. Passage of polymer melts through a tiny orifice for fabrication purposes can result in both chain alignment and chain breakage. In the case of rubber, mastication of the elastomer, breaking polymer chains, is intentional allowing easier deformation and processability. Shearing itself can result in chain breakage, which is often associated with localized heat buildup that is a consequence of chains "rubbing" together (molecular friction).

Most heterochained polymers, including condensation polymers, are susceptible to aqueous-associated acid or base degradation. This susceptibility is due to a combination of the chemical reactivity of heteroatom sites and the materials being at least wetted by the aqueous solution allowing contact between the proton and hydroxide ion. Both these factors are related to the difference in the electronegatives of the two different atoms resulting in the formation of a dipole that acts as a site for nucleophilic or electrophilic chemical attack and that allows polar materials to come in contact with it. Such polymers can be partially protected by application of a thin film of hydrocarbon polymer that acts to repel the aqueous solutions.

Enzymatic degradation is complex and not totally agreed upon. Microbes have enzymes, some of which are capable of breaking selected bonds such as those that appear naturally—including amide, ester, and ether linkages—and including natural, naturally derived, and synthetic materials. Although the purpose of these enzymes is to digest nutrients for the host, when polymers with susceptible linkages come in contact with a microbe that contains appropriate enzymes, polymer degradation can occur. While often similar to acid- and base-associated degradations, enzymatic degradations are more specific, bringing about only specific reactions. Even so, it is often difficult to differentiate between the two and both may occur together.

Some polymer deterioration reactions occur without loss in molecular weight. These include a wide variety of reactions where free radicals (most typical) or ions are formed and cross-linking or other nonchain session reaction occurs. Cross-linking discourages chain and segmental chain movement. At times this cross-link is desired such as in permanent press fabric and in elastomeric materials. Often the cross-links bring about an increased brittleness beyond that desired.

Some degradation reactions occur without an increase in cross-linking or a lessening in chain length. Thus, with minute amounts of HCl, water, ester, etc. elimination can occur with vinyl polymers giving localized sites of double bond formation. Because such sites are less flexible and more susceptible to further degradation, these reactions are generally considered as unwanted.

Cross-linking reactions can give products with desired increased strength, memory retention, etc. but accompanying such cross-linking can be unwanted increases in brittleness. Throughout the text, cross-linking is an important reaction that allows the introduction of desirable properties. For instance, it is the basis for many of the elastomeric materials.

16.4 CROSS-LINKING

Cross-linking reactions are common for both natural and synthetic polymers including vinyl and condensation polymers. These cross-links can act to lock in "memory" preventing free-chain movement. Cross-linking can be chemical or physical. Physical cross-linking occurs in two major modes. First, chain entanglement acts to cause the tangled chains to act as a whole. Second, crystalline formations, large scale or small scale, act to lock in particular structures. This crystalline formation typically increases the strength of a material as well as acts to reduce wholesale chain movement.

Chemical cross-linking often occurs through the use of double bonds that are exploited to be the sites of cross-linking. Cross-linking can be effected either through the use of such preferential sites as double bonds, or through the use of other especially susceptible sites such as tertiary hydrogens. It can occur without the addition of an external chemical agent or, as in the case of vulcanization, when an external agent, a cross-linking agent such as sulfur, is added. Cross-linking can be effected through application of heat, mechanically, through exposure to ionizing radiation and nonionizing (such as microwave) radiation, through exposure to active chemical agents, or through any combination of these.

Cross-linking can be positive or negative depending on the extent and the intended result. Chemical cross-linking generally renders the material insoluble. It often increases the strength of the cross-linked material, but decreases its flexibility and increases its brittleness. Most chemical cross-linking is not easily reversible. The progress of formation of a network polymer has been described in a variety of ways. As the extent of cross-linking increases, there is a steady increase in the viscosity of the melt. At some point, there is a rapid increase in viscosity and the mixture becomes elastic and begins to feel like a rubber. At this point, the mixture is said to be "gelled." Beyond this point the polymer is insoluble. The extent of cross-linking can continue beyond this gel point.

Flory and others derived expressions describing the extent of reaction at the gel point using statistical methods. In general, the M_w at an extent reaction p can be described by the expression

$$\overline{M}_{w,p} = \frac{M_{w,o}(1+p)}{(1-p)(f-1)} \tag{16.5}$$

where $M_{w,o}$ is the weight-average molecular weight at no reaction, $\overline{M}_{w,p}$ is the weight-average molecular weight at an extent of reaction p, and f is the functionality. At the gel point, molecular weight becomes quite large approaching infinity, giving eventually

$$p_{\text{gel}} = 1/(f-1) \tag{16.6}$$

For a system containing two types of functional groups

$$(p_{\text{gel}})^2 = \frac{1}{\mathrm{r}(f'-1)(f''-1)} \tag{16.7}$$

where r is the ratio of the two types of functionality f' and f''.

This equation is valid when the ratio of the two types of reactant groups is almost equal and where the reactivity of members within each of the two types is almost the same, and finally, when the reactivity of the two types of sites does not change during the process.

For the case where cross-linking occurs with the cross-linking sites contained in already formed polymer chains, average functionalities can be calculated in terms of the weight-average or number-average molecular weight. For the weight-average molecular weight the average degree of polymerization, DP_w, can be described where M_c is the weight-average molecular weight between cross-linkable sites and p is the fraction of repeat units reacted, i.e., the degree of conversion.

$$DP_w = \frac{M_w}{M_c} - \frac{f(1+p)}{(1-p)(1-f)} \tag{16.8}$$

If $DP_{w,o}$ is the weight-average degree of polymerization of the initial mixture of long chains then

$$DP_w = \frac{DP_{w,o}(1+p)}{(1-p)(DP_{w,o}-1)} \tag{16.9}$$

and at the gel point the degree of polymer approaches infinity giving

$$p_{\text{gel}} = 1/(DP_{w,o}-1) \tag{16.10}$$

Equating the two equations for p_{gel} gives

$$DP_{w,o} - 1 = f - 1 \tag{16.11}$$

Similar expressions can be derived based on the number-average molecular weight so that at the gel point

$$p_{\text{gel}} = 1/DP_{n,o} \tag{16.12}$$

The degree of cross-linking can be expressed in terms of cross-links per gram or per unit volume. If C is the moles of cross-links per unit volume, n the number of network chains per unit volume, d the density of cross-linked polymer, and M_c the number-average molecular weight of the polymer segments between cross-links, then

$$C = n/2 = d/2M_c \tag{16.13}$$

such that the number of moles of cross-links per gram of network polymer is $1/2M_c$.

Swelling and mechanical measurements are generally employed to experimentally determine the degree of cross-linking.

16.5 REACTIVITIES OF END GROUPS

Polymers containing one reactive end group are often referred to as macromolecular monomers or *macromers*. They can be represented as

$$\mathrm{M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}Reactive\ group} \tag{16.14}$$

They are used in the formation of a number of products including star polymers, and some graft polymers.

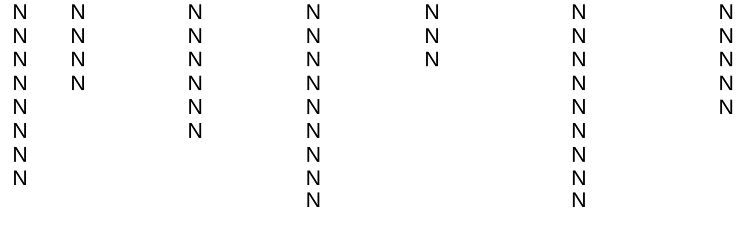
Polymers that contain two active end groups are referred to as *telechelic* polymers. These are of the form

$$\mathrm{Reactive\ group{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}M{-}Reactive\ group} \tag{16.15}$$

Telechelic polymers are also used in the synthesis of many products including segmented PU and polyester products.

Macromers are then "short" polymers, which contain an active end group. This end group can be a site of unsaturation, heterocycle, or other group that can further react. Macromers are usually designed as intermediates in the complete synthesis of a polymeric material. These macromers can be introduced as side chains (grafts) or they may serve as the backbones (comonomer) of polymers. The macromers can also act as separate phases.

Macromers have been used to produce thermoplastic elastomers. Generally, the backbone serves as the elastomeric phase while the branches serve as the hard phases. These structures are often referred to as "comb"-shaped because of the similarity between the rigid part of the comb and its teeth and the structure of these graft polymers.



$$\begin{array}{*{26}{c}}
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\end{array} \tag{16.16}$$

Block copolymers are also produced using such macromers. Again, the various units of the polymer can be designed to act as needed with hard or/soft, or hydrophilic or hydrophobic, or other combinations. In addition, these macromers generally have two active functional groups that allow polymerization to occur.

Macromers can also be used as cross-linkers between already formed polymers when both ends are active. These functional groups could be either two vinyl ends or two Lewis acids or bases such as two hydroxyl or amine groups. Interpenetrating polymer networks (IPNs) and related structures such as dendrites and stars can also be formed using macromers.

The use of placing specific end groups onto polymers and oligomers is widespread and will be illustrated here for dimethylsiloxanes, the most widely used siloxanes. These end groups are given various names, based on their intended use, e.g., capping agents, blocking agents, chain length modifiers, and coupling agents. Typical siloxane end groups include trimethylsiloxyls, acyloxyls, amines, oximes, alcohols, and alkoxyls. These reactive end groups are reacted forming a wide variety of useful materials. Most silicone RTV adhesives, sealants, and caulks are moisture curing, i.e., they contain hydroxyl-capped siloxyls that are reacted with acyloxyls, amines, oximes, or alkoxyls moisture-sensitive compounds.

16.6 SUPRAMOLECULES AND SELF-ASSEMBLY

The terms self-assembly, self-organization, and self-synthesis are closely related and sometimes used interchangeably. *Self-assembly* involves the aggregation of molecules, including macromolecules, into thermodynamically stable structures that are held together often using secondary bonding including hydrogen bonding, van der Waals and electrostatic forces, pi–pi interactions, and hydrophobic and hydrophilic interactions. The term *self-organization* is used for situations where the secondary bonding interactions are more specific and directional giving a higher degree of order to the self-assembled molecules. Finally, the term *self-synthesis* includes self-assembly and self-organization, and also includes situations where self-replication and template-type synthesis occurs.

Self-assembly is the spontaneous organization of molecules into stable, well-defined structures with the driving forces being noncovalent associations. The final structure is normally near or at the thermodynamic equilibrium arrangement allowing it to form spontaneously. Such formations can be done under conditions where defects are either minimized or eliminated. In nature, self-assembly is common as in the folding of proteins, formation of the DNA double helix, etc.

Self-assembled monolayers (SAMs) are the most widely studied nonnatural self-assembly systems. They are generally spontaneously formed from chemisorption and self-organization of organic molecules onto appropriate surfaces.

Natural polymers utilize a combination of primary and secondary forces, bond angles, and distances to form polymers with both long-range (multimacromolecular) and short-range structures, which are essential for the "proper" functioning of the macromolecular structure. While most synthetic polymer chemists have focused on what are referred to as primary and secondary structures (short-order structure control), work is just beginning on developing the appropriate structure control to allow tertiary and quaternary structural control (long-range control). While the "backbones" of these structures are held together with primary bonds, the secondary, tertiary, and quaternary structures are generally "driven" by secondary forces with the resulting tertiary and quaternary structures fixed in place through a combination of these secondary forces and small amounts of covalent cross-linking.

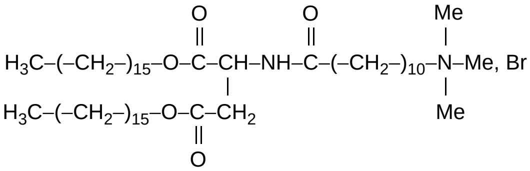
Several strategies are being developed, which allow this long-range control including the use of secondary forces to "hold" in place monomers that subsequently will be polymerized "in place." In another approach, already molecular "architectured" templates are employed to hold the polymer, prepolymer, or monomers in the desired shape with subsequent reactions and interactions enacted producing a material with a somewhat "robust" tertiary and quaternary structure. Some of these "molecular molds" are being produced using nanotechnology.

Self-assembly tendencies are apparent in the simple crystallization of inorganics and organics. Structure, size, and chemical tendencies (e.g., "like-liking-like" and "unlikes" repelling, secondary and primary bonding tendencies) are all involved. Proteins "self-assemble" in a much more diverse manner than "simple" crystallization of common organics and inorganics. As noted earlier, we are just beginning to understand the nuances involved with the self-assembling, formation of giant macromolecules including organizations such as those present in the cells of our bodies. We are beginning to understand the major factors involved in making the cell membranes and are starting to mimic these features to form synthetic biological-like membranes. We are using self-assembling concepts and approaches to develop a large number of interesting and potentially useful macromolecular materials.

One of the applications of molecular self-assembling is the formation of ultrathin films using both synthetic and natural surfaces as two-dimensional templates. As noted earlier, the same chemical and physical factors that we recognize in other areas are at work here. We will begin considering the formation of a simple bilayer membrane such as that present in natural cell membranes. Using the concept of like-liking-like and unlikes, rejecting one another, the orientation of molecules with two different polar environments will vary depending upon the particular environment in which they are placed. For a common soap molecule with hydrophilic and hydrophobic ends, the like ends will congregate together and will reside either internally or externally together. This is exactly the same concept as given in most general chemistry texts when considering the formation of micelles in commercial detergents. In the presence of water, the hydrophilic ends will face outward and in a nonpolar organic solvent the polar ends will face inward. Researchers have extended these simple concepts to include specially designed molecules that contain not only the heads and tails, but also spacers and conductors, and to vary the flexibility of the various parts of the molecule, spacing and number of heads and tails, etc.

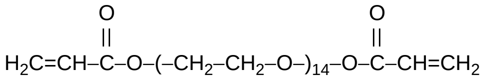
An important concept in the creation of some of these structures is that a primary driving force is the solute–solvent immiscibilities (energy; enthalphic). Thus, the magnitude of the cohesive energy of the solute may be a secondary factor in determining these supermolecular or supramolecular structures for such systems.

The self-assembling character of bilayer membranes is demonstrated by the formation of free-standing cast films from aqueous dispersions of synthetic bilayer membranes. The tendencies for association are sufficiently strong to allow the addition of "guest" molecules (nanoparticles, proteins, and various small molecules) to these films where the connective forces are secondary in nature and not primary. Synthetic polymer chemists have made use of these self-assembling tendencies to synthesize monolayer films. In particular, a monomer that contains both reactive groups and hydrophobic and hydrophilic areas is "cast" onto an appropriate template that "self-assembles" the monomer, holding it for subsequent polymerization. Thus, a bilayer structure is formed by



$$\begin{array}{l} H_3C{-}({-}CH_2{-})_{15}{-}O{-}\overset{\overset{O}{\|}}{C}{-}\underset{|}{CH}{-}NH{-}\overset{\overset{O}{\|}}{C}{-}({-}CH_2{-})_{10}{-}\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{N}}{-}Me,\ Br \\ H_3C{-}({-}CH_2{-})_{15}{-}O{-}\underset{\underset{O}{\|}}{C}{-}CH_2 \end{array} \qquad (16.17)$$

The bis-acrylate monomer (structure 16.18)



$$H_2C{=}CH{-}\overset{\overset{O}{\|}}{C}{-}O{-}(-CH_2{-}CH_2{-}O{-})_{14}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2 \qquad (16.18)$$

is accommodated by this bilayer. The bis-acrylate is photopolymerized. Although there is some change in the particular bond lengths, the bilayer still holds on and a coherent film is formed. The bilayer template is subsequently washed away by the addition of methanol leaving a flexible, self-supporting film. Polymerization can also result in the creation of different bond lengths that can act to "release" the newly formed monolayer. Multilayered structures can be made by simply allowing the outer surface of one monolayer to act as the template for the next monolayer.

Inorganics can also be synthesized and used as templates. Thus, controlled siloxane networks were formed when dispersions of alkoxysilanes (such as $(MeO)_3SiMe$) are mixed with the suitable template matrixes. Ultrafine particles of metal oxides can be used as starting materials for the formation of metal oxide films. For instance, a mixture of a double-chained ammonium amphiphile and an aqueous solution of aluminum oxide particles (diameter about 10–100 nm) gives a multilayered aluminum oxide film when calcinated at over 300°C.

Metal–ligand structures, such as porphyrin-based structures, are able to "control" the geometry of forming superstructures. The interactions between the various internally chelated porphyrin metal and a combination of the planarity and pi–pi interactions between the porphyrin rings drive the resulting structures. Connecting groups can act as spacers or as additional geometry-determining features. Smaller metal-based groups have been used to self-assemble structures such as nanocages that can have within them molecules that give the combination cage and captive molecule unique chemical and electrical environments. A nanocage has been formed using six *cis*-protected palladium II nitrate molecules and four tridendate tripyridyl molecules. These structures, unlike other self-assembly molecules considered here, have primary bonds as major contributors to the self-assembly process. Many of these excursions are the exercise of combining organometallic chemistry with structural knowledge and purpose.

Graphite and carbon fibers have been used at templates. Thus, nylon 6 has been polymerized on a graphite matrix. Such syntheses of polymers in the presence of a solid template, where the solid acts as a template have been described as polymerization-induced epitaxy (PIE). The monomer and resulting film is adsorbed on the template surface through only van der Waals forces. After polymerization, the polymer is washed from the template. The recovered polymer retains "special" structural features introduced by the template.

Block copolymers with amphilic groups have been used to give molecules with several "levels" of molecular architecture. Thus, a block copolymer of styrene and 4-vinylpyridine and long-tailed alkylphenols contains polar groups in the backbone that associate with the alkylphenol chains forming hydrogen bonds resulting in a bottlebrush-like structure. If the alkyl tails on the polymer are strongly repulsed by the amphiphilic portions, microphase separation between the tails and the rest of the copolymer results. Here, the alkylphenol portion, which is hydrogen bonded to the vinylpyridine blocks, separates as a microphase inside the poly(4-vinylpyridine) block domains. If the copolymer is heated, the bottlebrush structure undergoes an order–disorder transition at around 100°C and a second order–order transition at about 150°C as the amphiphilic alkylphenol chains diffuse into the PS-rich domains and cylindrical structures are formed.

While much of the emphasis on inter- and intramolecular interactions, secondary bonding, and forces associated with association and dissociation involve attractive forces, we are finding that phobic effects are also important and for some systems are actually the major factors. Briefly, this can be described by the sayings ‘‘the enemy of my enemy is my friend,’’ or ‘‘given the choice between bad and worse, bad wins out.’’ Formation of many self-assemblies is due in large measure to such phobic factors.

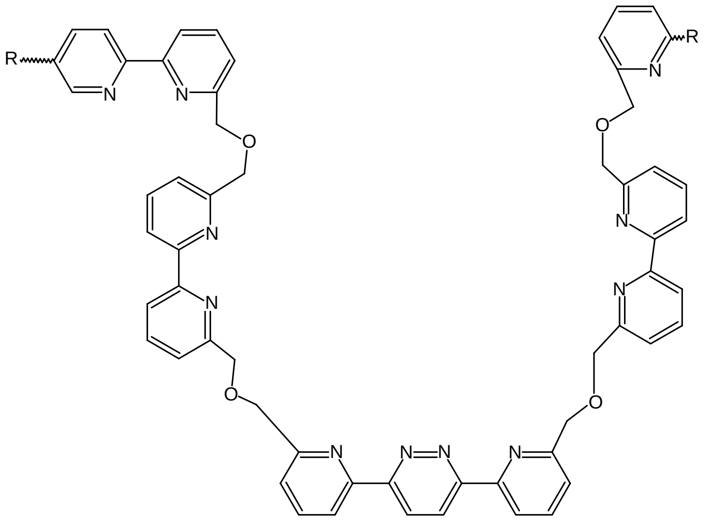
As we learn more about what drives molecular shapes, we are finding more applications utilizing this information in designing, on a molecular level, oligomeric and polymeric chains. It is also becoming more apparent to us that we have been forming organized structures without knowing it. While simple-layered and linear structures are generally employed to describe the concept, the self-assembling approach holds for any two- or three-dimensional structure under the appropriate conditions. As in many areas of research, the potential is only limited by our imagination, fueled by our understanding and use of available and newly created tools.

Considering only Lewis acid–base or donor–acceptor interactions we can envision a hydrogen bond donor site such as an alcohol, acid, thiol, or amine and an acceptor site such as a carbonyl oxygen on another molecule or part of the molecule. These components will bind with one another, acting to bind either the molecules containing the two differing bonding sites, or if the two sites are on the same molecule, will attempt to contort, or twist the molecule allowing the preferred bonding to occur.

Synthetic shapes are generally limited to sheets and polyhedral structures. Yet nature produces a much wider variety of shapes including curves, spirals, ripples, bowls, pores, tunnels, spheres, and circles. We are beginning to master these shapes based on especially ‘‘grown’’ shapes that act as templates for further growth. For instance, Geofreey Ozin and coworkers mixed together alumina, phosphoric, and decylamine in an aqueous solution of tetraethylene glycol. After a few days, millimeter-sized aluminophosphate solid spheres and hollow shells were formed with the surfaces sculpted into patterns of pores, meshes, ripples, bowls, etc. A decylammonium dihydrogenphosphate liquid-crystal phase was formed and this surfactant, along with the glycol, was forming bilayer vesicles. The vesicles acted in different ways with some fusing into one another and others splitting apart or collapsing giving a variety of structures. Thus, appropriate conditions can be selected, which favor certain template structures producing an array of geometric structures. Further, the templates themselves can be used to make selective separations. In a related study, the group employed a silica precursor, tetraethyl orthosilicate. Here, the orthosilicate units assembled together forming micelles that in turn acted as liquid-seed crystals growing other assemblies with varying shapes. Rapid growth in the axial direction produces ropelike structures that can be made to form circles and loops through application of external forces. Other structures included egg shapes, disks, spirals, knots, and spheres.

Metal coordination is another important bonding opportunity with respect to self-assembly. This is important in many natural molecules such as hemoglobin and chlorophyll, where the metal atom acts both as the site of activity and as a ‘‘centralizing’’ agent with respect to shape and thus acts as a nucleating agent for self-assembly.

Numerous metal-chelating designs can be envisioned. Structure 16.19 is one made by Daniel Funeriu and coworkers. The end structure is dependent upon the nature of the metal. For instance, a wreath-shaped double-helical complex is formed when $FeCl_2$ is added with each wreath containing five iron ions with each iron having three bonding sites. Further, the wreath size is such that it will selectively bind the chloride or other similar-sized ions because the source of iron is iron chloride. The ratio of reactants is also important and by varying the ratio different structures such as wire and tape-like forms can be formed. Again, it is up to the researcher to utilize information at hand to construct these self-assemblies.



(16.19)

There are many potential and real applications of self-assembly.

Pharmaceutical chiral drug sales top $100 billion yearly worldwide. More than half of the drugs in the market are asymmetric molecules with about 90% administered as racemates. Generally, one optical center of a drug will have the desired activity, while the other often produces negative side effects. Because of this the Food and Drug Administration (FDA), in 1992, issued a statement saying that for every new racemic drug, the two enantiomers must be treated as separate substances that are required to undergo pharmacokinetic and topological studies.

One direct approach to the separation of chiral compounds is called molecular imprint polymers (MIPs) that involves the formation of a three-dimensional cavity with the shape and electronic features that are complementary to the imprinted or target molecule.

While MIPs are part of the current nanorevolution, its roots are found in Pauling's theory of antibody formation. Although the particulars were wrong, the general concept is good.

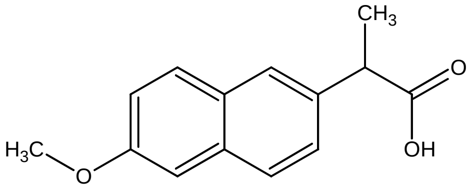
In the formation of MIPs, the target drug is added to a solvent along with selected polymers. It is important that the liquid, self-assembling polymer(s), and template molecule complement one another. The specific bonding can be a combination of covalent and noncovalent bonding. Here, we will consider an instance involving only noncovalent bonding. The main secondary bonding interactions include metal–ligand complexations, hydrogen bonding, and ionic, dipolar, hydrophobic, and pi–pi interactions.

Because most drugs have both polar and nonpolar regions, solvents and vinyl monomers that contain both polar and nonpolar regions are often employed. Where aromatic rings are present, polymers such as 4-vinylpyridine and styrene are often utilized because of their ability to "fit" such structures, bond through overlap of pi systems, and can be readily polymerized via a variety of methods (e.g., UV, heat, and use of free radical initiators). Hydrogen bonding solvents are generally discouraged because of their tendency to form strong bonds with the template molecule and after evacuation of the template site, with polar portions of the template site. Often dipolar aprotic solvents are employed that offer both polar and nonpolar sites.

In general the sequence is

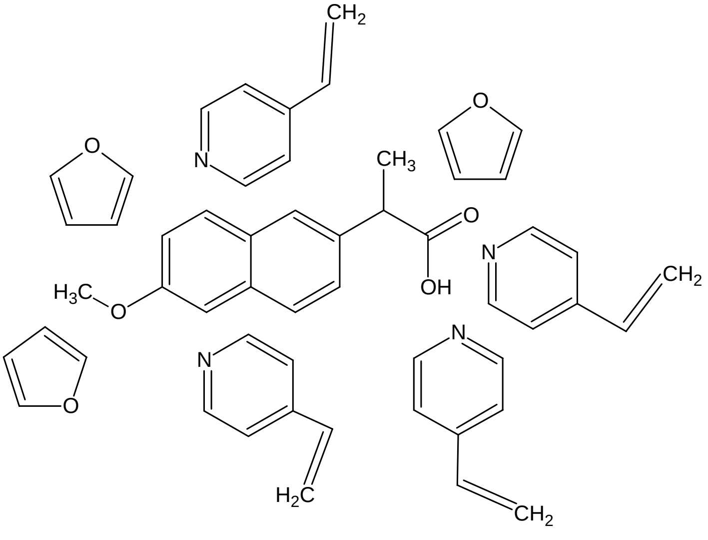
mixing together of the template, polymer, and solvent → self-assembly about the template →
polymerization → extraction of template molecule → grinding, sieving, and column packing

A number of drugs have been successfully separated using MIPs. Naproxen™, (S)-6-methoxy-α-methyl-2-naphthaleneacetic acid, is a nonsteroidal anti-inflammatory drug (NSAID) that is administered as the "S" enantiomer. Naproxen (structure 16.20) will be used to illustrate the MIP sequence. Naproxen has both polar and nonpolar domains. It also has a fused-ring aromatic site.



(16.20)

Solvents and self-assembling polymer(s) are chosen, which have both polar and nonpolar portions. The polymers and solvents then self-assemble around the target molecule. This arrangement is then exposed to UV radiation, heat, and/or catalysts that effectively form a polymeric "cocoon" around the target molecule. After polymerization and the formation of the cocoon around the target molecule, the solvent and target molecules are removed exposing a partially completed cavity with both structural (both shape and spatial configuration) and electronic characteristics complementing the target molecule. For naproxen, the solvent is THF and the monomer is 4-vinylpyridine.

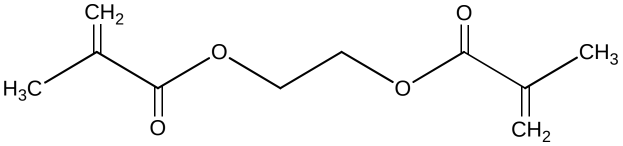


(16.21)

An illustration of a possible self-assembly arrangement involving only the vinylpyridine and THF is given in structure 16.21. Around the acid group there are two vinylpyridines both with the nitrogens pointed toward the naproxen template molecule, one making use of hydrogen bonding and the other bonded through dipolar interactions to the electron-deficient "acid" carbon. This gives an electron-rich region. Around the naphthalene-ring portion are also located vinylpyridine molecules except that they have the nitrogens "pointed" away creating a nonpolar region. These self-assemblies vary from one template site to the other and this variation in specific site structure is at least partially responsible for the broadening of the chromatography peak associated with the template molecule. Assembly also occurs above and below the naproxen with appropriate secondary bonding such as pi-bonding interactions between the aromatic sites on the naproxen and the furane and vinylpyridine.

The ratio of THF and 4-vinylpyridine is important because both assemble around the naproxen. If there are many solvent molecules present, the cocoon cavity will not be sufficient to retain the template molecule imprint. If the concentration of vinylpyridine is very high, the cocoon structure will be complete and prevent both the exit of the target molecule and entrance of other naproxen molecules during the separation procedure.

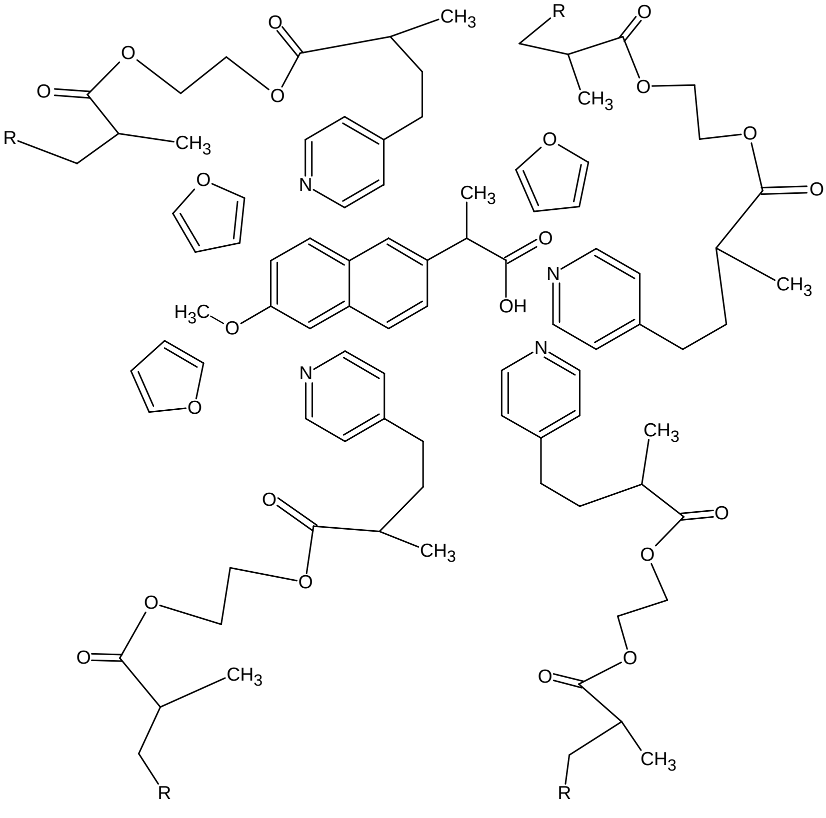
Added along with the "imprinting" vinylpyridine are cross-linkers, spacers, or "porogens." These cross-linkers or spacers should be miscible with the other ingredients, but have shapes that are dissimilar so that they do not become an integral part of the assembly around the template molecule. For naproxen, the cross-linker is ethylene glycol dimethylacrylate (EDMA).



(16.22)

The conditions, amounts, and identity of reactants are carefully selected to allow ready entrance and acceptance of the target molecules.

Eventually, a matrix is formed containing the molecularly imprinted sites locked into a matrix such as illustrated in the following structure:



(16.23)

After polymerization, the MIP or functionalized polymer matrix is dried, ground, sieved, and packed.

On the column, the eluding liquid is important. The liquid must dissolve the desired compound but it should not be good of a solvent or it will inhibit the release of the desired molecule, allowing it to interact with the template cavity. In the case of naproxen, there is a further consideration. Naproxen has an acid function that was ‘‘templated’’ in the protonated form. Thus, acetic acid, along with THF and heptane, is added to insure that the naproxen is present in the needed correct geometry.

As with most processes, MIPs have both positive and negative aspects. On the positive side, with the correct choice of original polymer and solvent almost any molecule can be employed as a template including much larger molecules. (This approach is not realistic for synthetic polymers where the short-range geometry is varied and the long-range geometry is not fixed. It might be feasible for natural polymers where the structures are fixed.) Further, since the desired compound is the one that is preferentially being attracted by the template site it is the last to be eluded from the column so that additional work is not needed to identify where the target molecules are. Increased temperatures can also be employed, presumably to the range of 180°C–200°C so that high-temperature isolations can be effected. In general, with the possible exception of the target compound, the reagents are inexpensive so that such selective molecular sieves are relatively inexpensive.

On the negative side, there is excessive broadening of the elution band caused by a number of features including the heterogeneity of the imprint as noted earlier.

One problem with nanomolecules is ready alignment. On a molecular level AFM and related tools can be used to align such individual or nanomolecules, but this is impractical on a large scale. Thus, strategics are being developed to accomplish this. One approach for single-walled carbon nanotubes (SWCNTs) is to physically or chemically anchor molecules onto tubes and to have these anchors direct the nanomolecules into desired arrays or organizations.

16.7 TRANSFER AND RETENTION OF OXYGEN

Today the polymer scientist should be aware of synthetic, inorganic, and biological macromolecules. The field of biological macromolecules is large and is one of the most rapidly expanding areas of knowledge. It involves gene splicing and other related biological aspects such as biological engineering, neurobiology, medicine, and drugs; the very elements of life and death, thought and caution, pain and health, biological transference, energy, and biological matter. The polymer scientist can learn from these advances but must also contribute to their understanding on a molecular and chain aggregate level. The investigation of these biological macromolecules is done using state-of-the-art instrumentation and techniques, and with scientific intuition. The world of the natural macromolecule is yielding information allowing an understanding on a molecular level. A striking example involves oxygen transfer and retention in mammals.

Oxygen retention and transfer involves the iron-containing organometallic planer porphyrin-containing structure called *heme* (Figure 16.1). The iron is bonded through classical coordination. The ferrous or iron (II) has six coordination sites. Four of these coordination sites are occupied by the nitrogen atoms of the four pyrrole-related rings of the porphyrin. The fifth site is occupied by one of the nitrogens of an imidazole side chain found as part of the protein structure and located just opposite to the planer porphyrin moiety. The sixth site acts to bind oxygen. The ion remains in the +2 oxidation state, whether oxygen is being bound or the site is vacant. An additional histidine is present, residing in the protein chain opposite to the sixth site of the iron atom. This second histidine does not bind iron, but serves to stabilize the binding site for oxygen. Experimentally, heme does not bind oxygen. Instead, a complex protein wrapping is necessary to both assist binding and protect

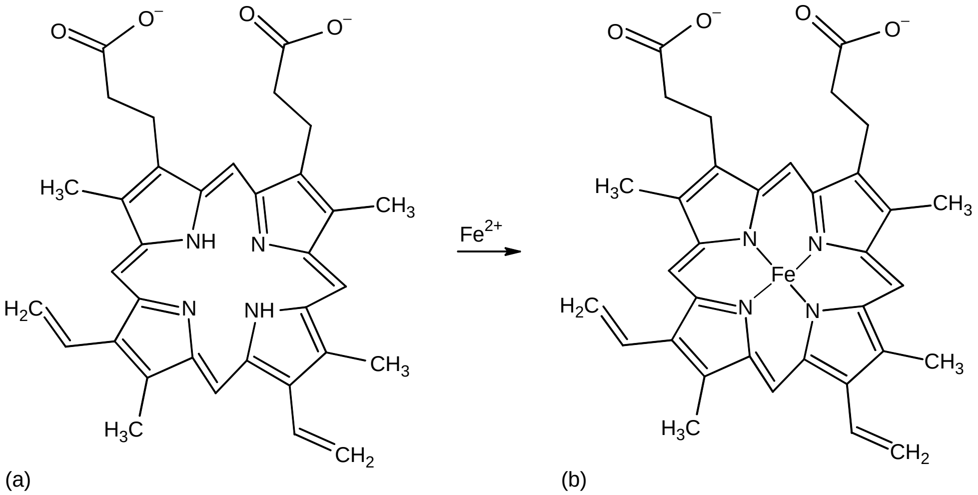


FIGURE 16.1 Porphyrin structures that serve as the basis of heme (a). Upon addition of iron, this porphyrin, which is called protoporphyrin IX, forms the heme group (b).

the binding site from foreign competitor molecules that could render the heme site inactive, either through structural change, change in iron oxidation state, or through occupation of this site, thus preventing oxygen access to the active binding site.

The precise electronic environment of iron deserves special comment. In deoxyhemoglobin, the iron atom has four unpaired electrons, but in oxyhemoglobin it has no unpaired electrons. The iron in the oxygen-free deoxyhemoglobin is referred to as "high-spin" iron, whereas iron in oxyhemoglobin is called "low-spin" iron. Hund's rule of maximum multiplicity calls for the most energy-favored, lowest energy form to be the structure containing the highest number of unpaired electrons. The binding of oxygen, itself with two unpaired electrons, is probably the result of a favored energy of binding brought about through the coupling of the two sets of unpaired electrons—the favorable energy allowing the violation of Hund's rule.

There are two major protein–heme-binding macromolecules: myoglobin (Figure 16.2), which is used as an oxygen storage molecule in mammalian muscle, and hemoglobin which is used in oxygen transport. Myoglobin is single stranded with one heme site per chain, whereas hemoglobin is composed of four protein chains, each one containing a single heme site (Figure 16.4). In hemoglobin, there are two sets of equivalent chains composing its quaternary structure. These two chain types are referred to as α and β chains. The α chains contain 141 amino acid units and the β chains contain 146 units. The myoglobin contains 153 amino acid units. Each of these chains is similar and each forms the necessary environment to allow the heme site to bind oxygen in a reversible manner. The protein segments are described as being loosely helical with about 60%–80% of the structure as helical.

Although the chains are similar in overall structure, there exist somewhat subtle differences. For instance, the quaternary structure of hemoglobin permits interaction between the four chains. Structural movement brought about through binding of oxygen at one of the four heme sites acts to make it easier for subsequent oxygen addition at the other heme sites. Such cooperative binding of oxygen is not possible in the single-chained myoglobin. The consequence of this cooperative binding is clearly seen while comparing oxygen binding by both myoglobin and hemoglobin as a function of oxygen pressure (Figure 16.3). Oxygen binding occurs by myoglobin at even low oxygen pressures. This is referred to as hyperbolic behavior. By comparison, hemoglobin binding increases more slowly as the

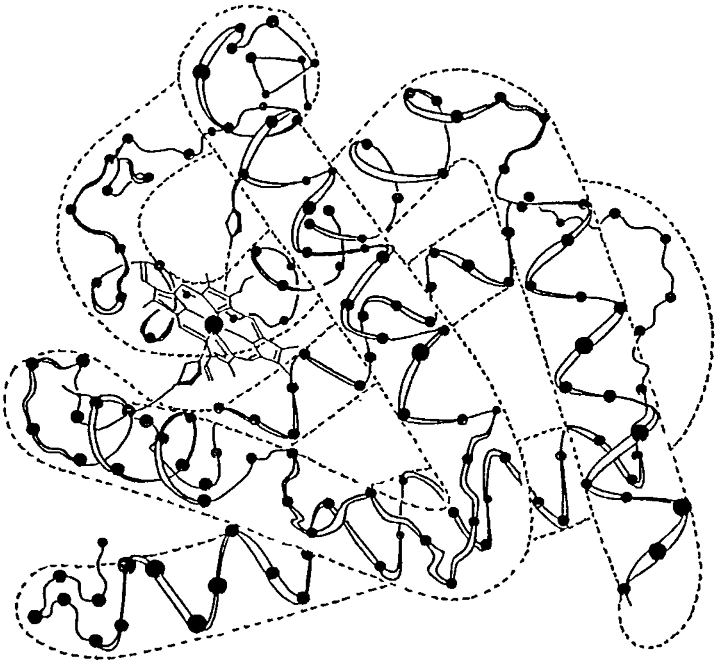


FIGURE 16.2 Generalized myoglobin structure showing some amino acid units as open circles to illustrate the “folded” tertiary structure.

oxygen pressure increases, occurring in a more sigmoidal fashion. Thus, initial binding of oxygen at a heme site is relatively difficult, becoming increasingly easier as the number of heme sites bonded increases.

The differences in oxygen-binding characteristics are related to the differing roles of hemoglobin and myoglobin. Thus, myoglobin is employed for the storage of oxygen in the muscle. Binding must occur even at low oxygen contents. Hemoglobin is used for

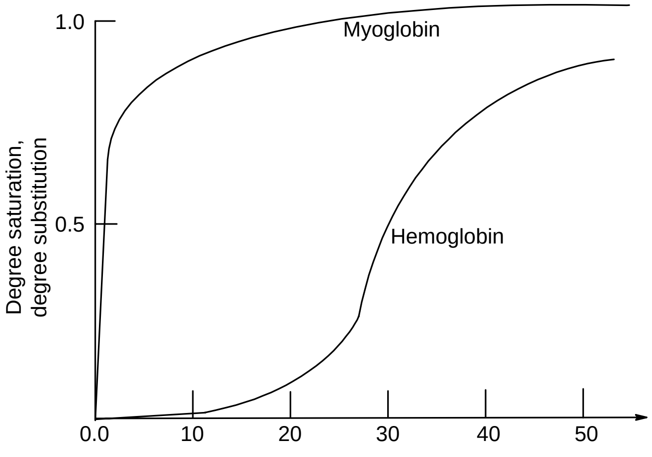


FIGURE 16.3 Degree of saturation as a function of oxygen pressure.

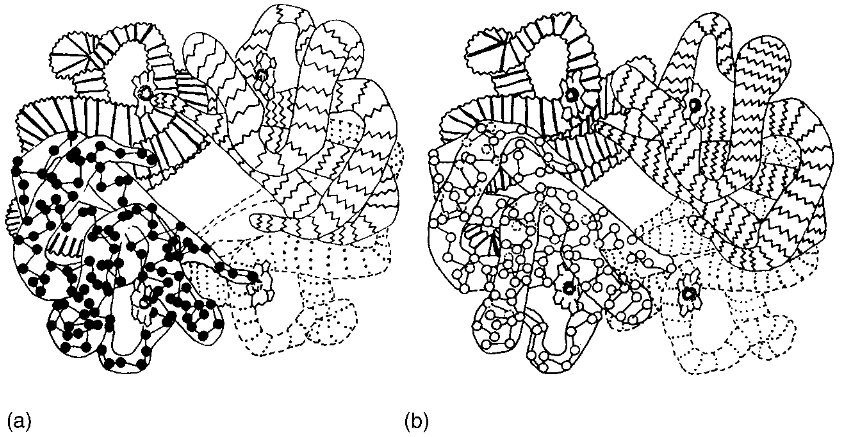
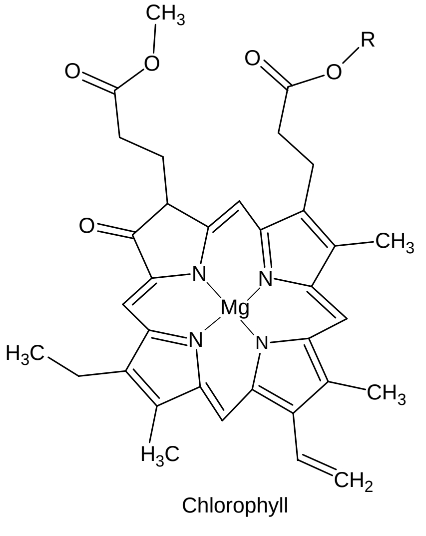


FIGURE 16.4 Space-filling models of deoxyhemoglobin (a) and oxyhemoglobin (b). Notice the small shifts in the overall geometry of the various protein chains and the decreased size of the inner core.

the transport of oxygen and becomes saturated only at higher oxygen concentrations. The oxygen content in the alveoli portion of our lungs is on the order of 100 torr (1 atm pressure = 760 torr). Here, almost total saturation of the heme-binding sites in hemoglobin occurs. By comparison, the oxygen level in the capillaries of active muscles is on the order of only 20 torr, allowing the hemoglobin to deliver about 75% of its oxygen and for myoglobin to almost reach saturation in oxygen binding.

Conformational changes accompany the binding and release of oxygen. These changes are clearly seen by superimposing the oxygen-containing form of hemoglobin–oxyhemoglobin, over the non-oxygen-containing form of hemoglobin–deoxyhemoglobin (Figure 16.4). It is interesting to note that most of the enzymes have their active sites on the surface but enzymes, such as myoglobin, that are dealing with "small molecules" such as oxygen, have their active sites "hidden away" in the internal portion so that other unwanted molecules cannot easily access them with the protein "tunnel" acting to restrain unwanted suitors.

Another important metal-containing enzyme, chlorophyll (structure 16.24), is structurally related to myoglobin and is responsible for photosynthesis, the conversion of water and carbon dioxide, with the aid of solar energy, to carbohydrates.



(16.24)

16.8 NATURE'S MACROMOLECULAR CATALYSTS

Probably, the most important reactions occurring on polymers involve the catalytic activity of a class of proteins called enzymes. The catalytic action is a result of the lowering of the activation energy for the rate-determining step in the reaction. In general terms, the catalytic action results from the formation of a complex between the enzyme and the molecule undergoing reaction. The decreased activation energy is a result of the reacting molecules being held by the enzyme in such a manner as to favor the occurrence of appropriate reaction. The two classical models employed to describe the formation of the complex between the reacting molecules(s) and the enzyme are the lock-and-key model and the induced-fit model. Briefly, the *lock-and-key model* calls for an exact or highly similar complementary fit between the enzyme and the reacting molecule(s) (Figure 16.5). Geometry plays an essential role in permitting the electronic (polar, electrostatic, etc.; attractions or repulsions) interactions to form the necessary complex with the correct geometry. Release is encouraged by the new geometry and electronic distribution of the resulting products of the reaction being sufficiently dissimilar. The *induced-fit model* is similar except that the enzyme originally does not fit the required shape (geometrical and electronic cavity). The required shape is achieved upon binding—the binding needs "assisting factors" or proximity and orientation to affect a decrease in the energy of the transition state. Figure 16.5 shows how the enzyme sucrase breaks sucrose into its basic units of glucose and fructose. The sucrose is held by the enzyme in such a fashion that water easily and efficiently breaks the ether bond forming two hydroxyl units that are released because they no longer have the required shape or size or electronic features of the enzyme cavity.

Enzyme reactions generally follow one of two kinetic behaviors. Briefly, the oxygen-binding curve for myoglobin is hyperbolic, whereas that for hemoglobin it is sigmoidal (Figure 16.6). In general, it is found that similar enzymes such as myoglobin follow a similar hyperbolic relationship between reaction extent and reaction time. More complex enzymes such as hemoglobin follow a sigmoidal relationship between reaction extent and reaction

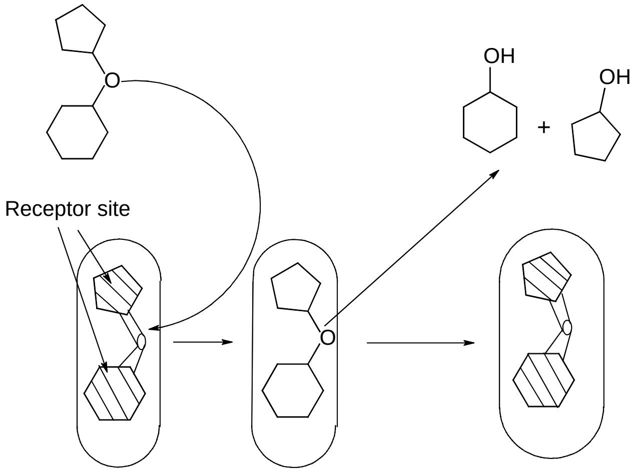


FIGURE 16.5 The two major models for the binding of reactant molecules to the active sites of nonallosteric enzymes. The sequence described the essential steps in the lock-and-key model, where the reactant(s) is attracted to the active site on the enzyme where the active site is a cavity of the same general size, shape, and (complementary) electronic features. Binding and the appropriate reactions occur resulting in a change in the geometry and electronic configuration of the product, causing its release. The second model (not shown) is the induced-fit model where the individual steps are similar to the lock-and-key except that the reactants "induce" a change in the conformation of the active site on the enzyme, allowing it to accept the reactant(s).

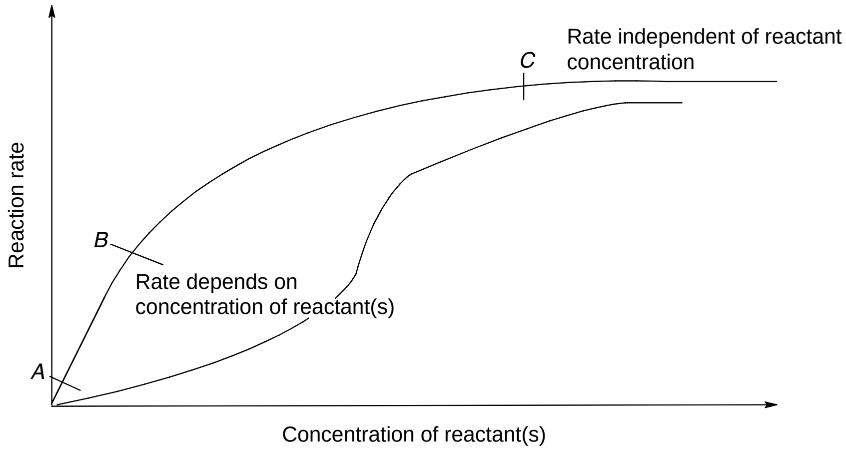


FIGURE 16.6 Dependence of reaction showing sigmoidal (bottom) and hyperbolic (top) behavior. The top plot also shows the initial rate of reaction as a function of reactant concentration when the concentration of enzyme remains constant.

time. The primary difference involves the ability of different portions of the overall hemoglobin structure, removed reaction sites, to affect the other. Molecules in which various removed sites affect the reactivity of other removed sites are called *allosteric enzymes*.

The Michaelis–Menten model is commonly employed in describing nonallosteric enzyme reactions. The overall model can be pictured as follows (Equation 16.25) where E represents the enzyme, M the reacting molecule(s), E + M → EM is associated with k_1 and the reverse reaction associated with k_{-1} and EM → E + P is associated with k_2.

$$\mathrm{E{+}M} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{EM} \overset{k_2}{\rightleftarrows} \mathrm{E{+}P} \tag{16.25}$$

Here, EM represents the enzyme complex and P the product(s). The rate of complex formation is described as

$$\text{Rate of complex formation} = -\mathrm{d[EM]/d}t = k_1[\mathrm{E}][\mathrm{M}] \tag{16.26}$$

The complex then either returns to form the initial reactants or forms the product(s) and the free enzyme, E. In kinetic terms, the change, or rate of breakdown of the complex is described as

$$\text{Rate of complex change} = -\mathrm{d[EM]/d}t = k_{-1}[\mathrm{EM}] + k_2[\mathrm{EM}] \tag{16.27}$$

The negative sign associated with the equation means that the terms are describing the rate of decrease in complex concentration. The rate of complex formation is rapid, and fairly soon the rate at which the complex is formed is equal to the rate at which it breaks down. This situation is called a steady state. Mathematically, this is described by

$$\mathrm{d[EM]/d}t = -\mathrm{d[EM]/d}t \tag{16.28}$$

and

$$k_1[\mathrm{E}][\mathrm{M}] = k_{-1}[\mathrm{EM}] + k_2[\mathrm{EM}] \tag{16.29}$$

The initial reaction rate, A to B, varies until the number of reactants clearly outnumbers the number of reaction sites on the enzyme, at which time, C, the rate becomes zero order, independent of the reactant concentration. Often it is difficult to directly measure the concentration of E as the reaction progresses. Thus, the concentration of E is generally substituted for using the relationship

$$[E] = [E_o] - [\mathrm{EM}] \tag{16.30}$$

where $[E_o]$ is the initial enzyme concentration.
Substitution of this description for $[E]$ into Equation 16.29 gives

$$k_1\,([E_o][\mathrm{M}] - [\mathrm{EM}][\mathrm{M}]) = k_{-1}[\mathrm{EM}] + k_2[\mathrm{EM}] \tag{16.31}$$

Separating out [EM] on the right-hand side gives

$$k_1\,([E_o][\mathrm{M}] - [\mathrm{EM}][\mathrm{M}]) = (k_{-1} + k_2)[\mathrm{EM}] \tag{16.32}$$

Bringing together all the rate constants from both sides of the equation gives

$$[E_o][\mathrm{M}] - [\mathrm{EM}][\mathrm{M}] = k'[\mathrm{EM}] \tag{16.33}$$

Moving the [EM]-containing terms to the right side gives

$$[E_o][\mathrm{M}] = k'[\mathrm{EM}] + [\mathrm{EM}][\mathrm{M}] \tag{16.34}$$

and separating out [EM] from the right side gives

$$[E_o][\mathrm{M}] = [\mathrm{EM}]\,(k' + [\mathrm{M}]) \tag{16.35}$$

Now division of both sides by $k' + [\mathrm{M}]$ gives

$$[\mathrm{EM}] = [E_o][\mathrm{M}]/k' + [\mathrm{M}] \tag{16.36}$$

The initial rate of product formation, R_i, for the Michaelis–Menten model depends only on the rate of complex breakdown, i.e.

$$R_i = k_2[\mathrm{EM}] \tag{16.37}$$

Substitution from Equation 16.36 into Equation 16.37 gives

$$R_i = k_2[E_o][\mathrm{M}]/k' + [\mathrm{M}] \tag{16.38}$$

This expression is dependent on the concentration of M and describes the initial part of the plot given in Figure 16.6.

Generally, the concentration of M far exceeds that of the enzyme sites such that essentially all the enzyme sites are complexed, i.e., $[\mathrm{EM}] = [E_o]$. (This is similar to a situation that occurs regularly in South Florida where four- and six-lane roads are funneled into a two-lane section of road because of a wreck or road construction.) Thus, the rate of product formation is maximized under these conditions. This maximum rate, R_m, allows us to substitute $[E_o]$ for [EM] in Equation 16.37 to give

$$R_m = k_2[E_o] \tag{16.39}$$

Since the enzyme concentration is constant, the rate of product formation under these conditions is independent of [M] and is said to be of zero order (Figure 16.6).

The maximum rate is directly related to the rate at which the enzyme "processes" or permits conversion of the reactant molecule(s). The number of moles of reactants processed per mole of enzyme per second is called the *turnover number*. Turnover numbers vary widely. Some are high, such as for the scavenging of harmful free radicals by catalase, with a turnover number of about 40 million. Others are small, such as the hydrolysis of bacterial cell walls by the enzyme lysozyme, with a turnover number of about one half.

The Michaelis–Menten approach does not describe the behavior of allosteric enzymes, such as hemoglobin, where rate curves are sigmoidal rather than hyperbolic. A more complex mode is called for to account for the biofeedback that occurs with allosteroid enzymes. Some affects may be positive such as those associated with hemoglobin, where binding by one site changes the geometry and electronic environment of the other remaining sites, allowing these additional sites to bind oxygen under more favorable conditions. The affects may also be negative, such as that of cytidine triphosphate, which inhibits ATCase and catalyzes the condensation of aspartate and carbamoyl phosphate-forming carbamoyl aspartate.

Two major models are typically used to describe these situations: the concerted model and the sequential model. In the *concerted model*, the enzyme has two major conformations: a relaxed form that can bind the appropriate reactant molecule(s) and a tight form that is unable to tightly bind the reactant molecule(s). In this model, all subunits containing reactive sites change at the same time (Figure 16.7). An equilibrium exists between the active and inactive structures. Binding at one of the sites shifts the equilibrium to favor the active relaxed form.

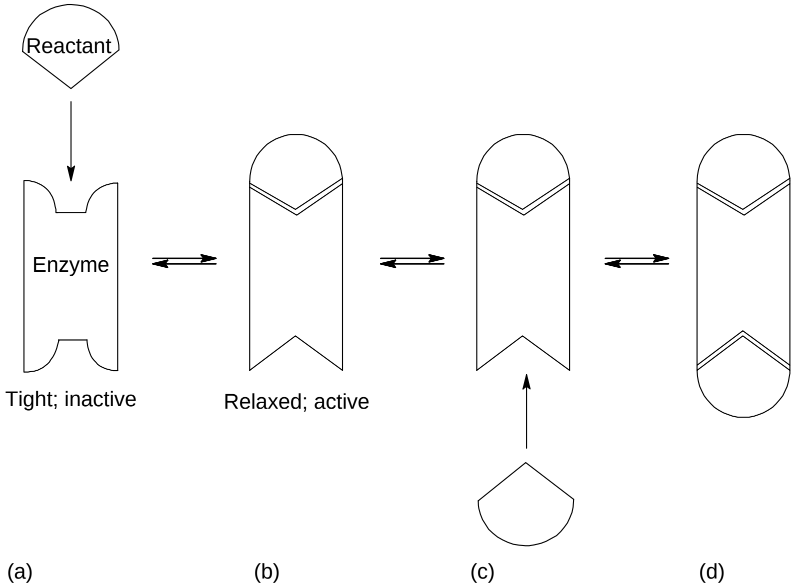


FIGURE 16.7 Concerted model for allosteric enzymes. The major steps are (a) and (b). An equilibrium exists between the tight (a) and relaxed (b) forms of the allosteric enzyme. The reactant molecule(s) approaches the reactive site of one of the enzyme sites present in the relaxed form (c). Binding occurs, shifting the equilibrium to the relaxed form(s). The second site is bound (d).

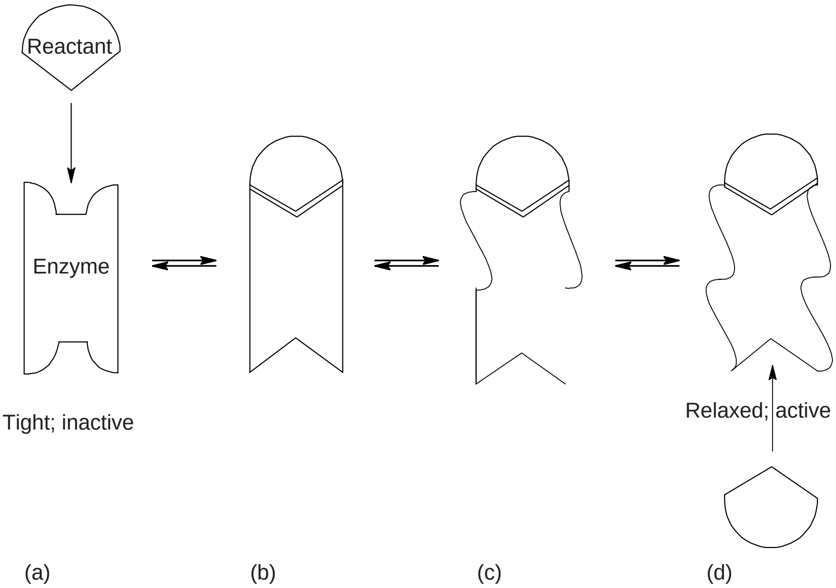


FIGURE 16.8 Sequential model for allosteric enzymes. The individual steps are as follows: the reactive molecule(s) approach the reactive site (a), which typically has a cavity similar to, but not the same as, the reactant molecule(s); a conformational change is effected so that the reactive molecule(s) can be bound (b), the bound portion of the enzyme changes shape; this shape change is transmitted to the other unit(s) containing active sites (c), the remaining enzyme portion containing active sites undergoes a conformational change that makes binding easier (d).

The major feature in the *sequential model* is the induction of a conformational change from the inactive tight form to the active relaxed form as the reacting molecule(s) is bound at one of the sites. This change from an unfavorable to a favorable structure is signaled to other potentially reactive sites bringing about a change to the more favored structural arrangement in these other sites (Figure 16.8).

Structural changes can be brought about through simple electrostatic and steric events caused by the presence of the reacting molecule(s). Structural changes also result as crosslinking and other primary bonding changes occur.

16.9 MECHANISMS OF ENERGY ABSORPTION

Let us consider a force, stress, acting on a material producing a deformation. The action of this force can be described in terms of modeling components: a Hookean spring and a Newtonian dashpot. In the Hookean spring, the energy of deformation is stored in the spring and may be recovered by allowing the spring to act on another load or through release of the stress; in either case, the site is returned to zero strain. A Newtonian dashpot is pictorially a frictionless piston and is used to describe chains flowing past one another. The energy of deformation is converted to heat. In actuality, the deformation of most plastics results in some combination of Hookean and Newtonian behavior. The Newtonian behavior results in net energy adsorption by the stressed material, some of this energy producing the work of moving chains in an irreversible manner while some of the energy is converted to heat.

There are three major mechanisms of energy absorption: shear yielding, crazing, and cracking. The latter two are often dealt with together and called *normal stress yielding*.

We can distinguish between a crack and a craze. When stresses are applied to polymeric materials, the initial deformation involves shear flow of the macromolecules past one another if it is above T_g, or bond bending, stretching, or breaking for glassy polymers. Eventually a crack will begin to form, presumably at a microscopic flaw, then propagate at high speed, often causing catastrophic failure. The applied stress results in a realigning of the polymer chains. This results in greater order, but decreased volume occupied by the polymer chains, i.e., an increase in free volume. This unoccupied volume often acts as the site for opportunistic smaller molecules to attack, leading to cracking and crazing and eventually property failure.

A *crack* is an open fissure, whereas a *craze* is spanned top to bottom by fibrils that act to resist entrance of opportunistic molecules such as water vapor. Even here, some smaller molecular interactions can occur within the void space, and eventually the specimen is weakened.

Crazing and cracking can be induced by stress or combined stress and solvent action. Most typical polymers show similar features. To the naked eye, crazing and cracking appear to be a fine, microscopic network of cracks generally advancing in a direction at right angles to the maximum principle stress. Such stress yielding can occur at low stress levels under long-term loading. Suppression of stress yielding has been observed for some polymers by imposition of high pressure.

In shear yielding, oriented regions are formed at 45° angles to the stress. No void space is produced in shear yielding. Crazing often occurs prior to and in front of a crack tip. As noted earlier, the craze portion contains both fibrils and small voids that can be exploited after the stress is released or if the stress is maintained. Since many materials are somewhat elastic, most plastics are not ideal elastomers and additional microscopic voids occur each time a material is stressed.

All three mechanisms result in a difference in the optical properties of the polymeric material because of the preferential reorientation, with realignment of the polymer chains resulting in a change in optical properties such as refractive index, allowing detection through various optical methods including visual examination, microscopy, and infrared spectroscopy of films and sheets. Crazed and cracked sites of optically clear materials appear opaque, whereas shear-yielded sites may appear to be "wavy" when properly viewed by the naked eye employing refracted light.

It is important to emphasize that the surface layers of most polymeric materials are different from those of the bulk material and are often more susceptible to environmental attack. Thus, special surface treatments are often employed in an attempt to protect the surface molecules.

Directly related to energy absorption is energy dissipation. Generally, the better a material can dissipate or share applied energy the more apt it is to retain its needed properties subsequent to the applied energy. Polymers dissipate applied energies through a variety of mechanisms including rotational, vibrational, electronic, and translational modes.

One area that illustrates aspects important to energy dissipation is the fabrication of protective armor. Such armor includes helmets, vests, vehicle exteriors and interiors, riot shields, bomb blankets, explosive containment boxes (aircraft cargo), and bus and taxi shields. In each case energy dissipation is a critical element in the desired behavior of the device. To illustrate this let us look at body armor.

Most of the so-called bulletproof vests were made of polycarbonates. More recently, layers of PE were found to have similar "stopping power" for a lesser weight of material.

Today, most body armor is a complex of polymeric materials. Rapid dissipation of energy is critical, allowing the impact energy to be spread into a wide area. Materials should be strong enough so as not to immediately break when impacted and they need to have enough contact with other parts of the body armor to allow ready transfer of some of the impact energy. If the material can adsorb some of the energy through bond breakage or heating, additional energy can be absorbed at the site of impact. Along with high strength, the material should have some ability to stretch, to move allowing the material to transfer some of the energy to surrounding material. If the connective forces between the components are too strong, total energy dissipation is reduced because a strong bond discourages another way of reducing the impact energy, i.e., allowing the various materials to slide past one another. Thus, a balance is needed between material strength, strength of bonding holding the components together, and the ability to readily dissipate the impact energy.

Recently, it was found that some sequences of layered materials are more effective at energy dissipation than others. One of the better combinations is obtained when aramid layers are adjacent to UHMWPE.

Another factor is breaking up the projectile. This is again done using polymeric materials—here composites such as boron carbide ceramics in combination with aramids, UHMWPE, or fibrous glass.

In the future, body armor may be flexible. Experimentation is underway with shear thickening material using polyethylene glycol (PEG) with nanoparticles that remain flexible until rapidly struck such as with a bullet whereupon it acts as a solid protecting the wearer from the major impact. Kevlar is also being employed to protect space craft and space men from discarded space junk and small meteors. Thus, experimentation in body armor is being applied to additional areas where impact protection is essential.

16.10 BREAKAGE OF POLYMERIC MATERIALS

When a plastic is broken by a sharp blow or cut, are polymer chains broken? The important factors include the nature of the polymer, chain length, and arrangement of the chains.

Sperling and coworkers looked at the question of how many chains are broken and the defining factors related to this breakage when a polymeric material is cut or broken. They used various chain lengths of PS, and employed a dental drill as the cutting implement.

Pictorially, the problem can be described as looking at a robin pulling a worm out of a hole. Does the robin get the entire worm or some fraction of the worm? The factors are similar and deal with the length of the worm and how far into the hole it is. If it is largely within the hole then it can grasp the dirt, roots, etc. around it to ‘‘hold on for dear life.’’ If not, the worm is a meal for the ‘‘early bird.’’

It turns out that the question dealt with here is related to determining the critical length of fibers that are to be used in a composite. When determining the optimum fiber length of a fiber in a matrix, measurements are made using fibers of differing lengths. If a fiber can be removed from the matrix unbroken, it is too short and if the fiber breaks before it can be removed, it is too long. Thus, fiber lengths should be such that the fiber just begins to break rather than allowing it to be removed intact. In a composite, the worm is the fiber and the soil is the matrix. For the plastic, the worm is the individual chain and the soil is the remainder of the plastic. For the composite, the fiber contains many individual polymer chains, while for the situation dealt with here, individual polymer chains will be examined.

The length of fiber or chain that can be removed without breaking is related to the frictional and attractive energies between the fiber and the matrix or other polymer chains holding onto the chain. Thus, if the strength holding together the polymer backbone is greater than the frictional energy holding the chain in place, the polymer chain will be removed unbroken. In general, what was found through calculations was that PS chains to 300 units in length are capable of being removed intact without breakage. This is in rough agreement with what Sperling found experimentally. Thus, individual PS chains up to about 300 units in length are removed from the plastic without chain breakage.

The relationship between chain length and chain breakage was found to be directly related to the typical length of chain necessary to produce physical cross-links, i.e., chain

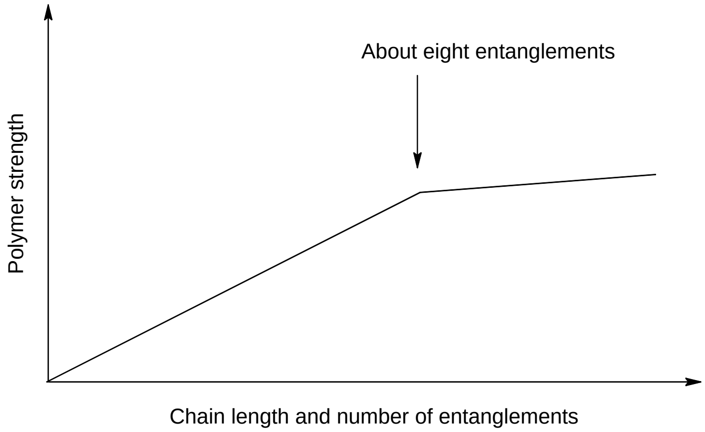


FIGURE 16.9 Idealized relationship between chain length and number of entanglements and polymer strength.

entanglements. (This is probably due to the fact that chain entanglements greatly increase the "apparent" chain length and frictional energy needed to be overcome to move a chain.) Typically, at least one chain entanglement is needed to guarantee some chain breakage. For many vinyl polymers, including PS, one chain entanglement occurs for every 300 units. Experimentally it was found that as the length of the PS chain increases so does the number of chain entanglements so that with a chain length of about 2000 (or an average of 7 chain entanglements), 50% of the chains are broken and when the chain length is about 4000 (or an average of 13 entanglements), approximately 100% of the chains break.

The production of chain entanglements is statically directly related to polymer length for linear chains, and almost independent of the nature of the vinyl unit for many polymers.

Chain length and entanglement are also related to the strength of the polymeric material. As chain length increases, the number of entanglements increases as does strength. At about 8 entanglements, the relationship between number of entanglements (and chain length) and polymer strength levels off with only small changes in polymer strength occurring as the chain length and number of entanglements further increases as shown in Figure 16.9.

Because the distance between each entanglement is about 300 units and to achieve nearly maximum strength 8 entanglements are needed, a chain of about 2400 (300 units/entanglement times 8 entanglements) units is needed. Calculations relating chain strength (related to the energy necessary to break a chain) and frictional force to hold a chain of varying length in place, i.e.,

$$\text{Chain strength} = \text{Frictional force as a function of chain length} \tag{16.39}$$

have been carried out with chain lengths of about 2000–3000 required before the frictional force necessary to break the chain occurs. This is in rough agreement with the chain length of 2400 calculated above using chain entanglement as the limiting factor.

As the polymer chain length increases, so does the viscosity of the melted polymer, requiring more energy to process the polymers using any technique that requires the polymer to flow. This includes most of the molding processing typically used to process vinyl polymers. For many applications, the maximum strength is not needed so that industry looks to a balance between chain length and necessary strength. This "balance" is often chosen such that the chain length is sufficient to give seven entanglements rather than the eight required to insure about 100% chain breakage and maximum polymer strength, as noted earlier.

There are exceptions to this. One exception is UHMWPE, which has few chain entanglements so it is easier to pull long chains from a PE matrix without chain breakage. The equivalent energy necessary to pull a UHMWPE chain from a PE matrix occurs at about a chain length of 100,000 (or a DP of about 3,300), much larger than that for PS.

For condensation polymers, the attractive forces between chains and chain units are greater so that physical chain entanglement is not necessarily the limiting factor, but rather other factors including localized crystallization become important.

16.11 SUMMARY

1. Polymers undergo reactions that are analogous to smaller molecules. Variation generally involves the need for reactants to have contact with the active site. This is more difficult for polymers.
2. Polymer degradation typically occurs via random chain scission, depolymerization, or both, resulting in a loss of chain length and properties associated with polymer length.
3. Among the most important reactions on polymers are those that occur with biomacromolecules such as involved in the transfer of oxygen and the activity of enzymes. Shape, size, electronic configuration are all essential factors in the transfer of oxygen and activity of enzymes. The transfer of oxygen can be mathematically described using the classical Michaelis–Menten approach. The two major models describing the activity of nonallosteric enzymes such as myoglobin are referred to as the lock-and-key model and the induced-fit model. Hemoglobin is an example of an allosteric enzyme where the two most popular models describing this behavior are the concerted and sequential models.

GLOSSARY

anchimeric assistance Reactions enhanced by the presence of a neighboring group.

chain scission Breaking of a polymer chain.

curing Cross-linking producing a polymer network.

cyclized rubber Isomerized rubber containing cyclohexane rings.

heme Iron-containing active site for hemoglobin and myoglobin.

hemoglobin Allosteric enzyme responsible for the transport of oxygen in our bodies; contains four myoglobin-like units.

hydrogenation Addition of hydrogen to an unsaturated compound.

induced-fit model One of two basic models employed to describe enzymatic behavior of nonallosteric molecules. Here, the steps are similar to the lock-and-key model except that the reactants "induce" a change in the conformation of the active site allowing the active site to bind with the reactant.

Kraton Trade name for ABA block copolymer of styrene (A) and butadiene (B).

Kuhn element Number of repeat units needed so that the most probable distance between the first and the growing end is back at the first unit again.

ladder polymer Double-stranded polymer for added stability.

lock-and-key model One of two basic models to describe the selectivity and catalytic nature of nonallosteric enzymes. In this model the reactant(s) is attracted to the active site on the enzyme, which is of the same general size, shape, and complementary electronic nature as the reactant.

macromolecular monomers (macromers) Polymers containing one reactive end group.

myoglobin Nonallosteric enzyme responsible for the storage of oxygen in our bodies. The activity follows the kinetic scheme described by Michaelis–Menten.

ozonolysis Reaction of an unsaturated organic compound with ozone.

telechelic polymers Polymers containing two active ends.

telomerization Abstraction of an atom by a macroradical.

topochemical reactions Reactions on the surface.

EXERCISES

1. In general, which metal ions are better chelated by polymers such as the salt of poly(acrylic acid)?
2. What is the general mechanism for the curing of step-reaction polymers?
3. Write the formula for perdeuterated PE.
4. What is the major difference between reactions occurring on benzene and on PS.
5. When would you expect a polymer to undergo degradation via random scission?
6. How might you cross-link a PE coating after it is applied to a wire?
7. How might you prepare a block copolymer of styrene and an alternation copolymer of ethylene and propylene?
8. What is the similarity between completely hydrogenated *Hevea brasiliensis* and completely hydrogenated gutta-percha?
9. What part does porphyrin play in the transmitting oxygen?
10. Would you expect PP chains with a DP of 200 to break when a PP plastic is broken into two pieces?
11. What are the most important structural factors involved in natural catalysis?
12. What product would be produced from the ozonolysis of polybutadiene?
13. Write the structural formula for the polymeric hydrolytic products from (a) PVAc and (b) poly(methyl methacrylate).
14. Why is commercial methylcellulose more soluble in water than native cellulose?
15. Why is CMC used in detergent formulations?
16. Would you expect the addition of chlorine or hydrogen to a double bond in a polymer to occur 100%?
17. What is the DS of cellulose nitrate when it is used as an explosive?
18. Why is the DS of cellulose triacetate only 2.8 and not 3.0?
19. Which is more polar: (a) cellulose triacetate or (b) cellulose diacetate?
20. Why is poly(vinyl butyral) not 100% vinyl butyral units?
21. If you have PVA and you want to make it less hydrophilic using a condensation reaction, what might you use?
22. What products would you expect from the combustion of most vinyl polymers?
23. What monomer would be obtained by the decomposition of PVA?
24. Which would be more resistant to nitric acid: (a) PS or (b) perfluoropolystyrene?
25. What ions would be removed from water by sulfonated PS: (a) cations or (b) anions?
26. What reaction occurs when tannic acid is added to proteins such as those present in cowhide?
27. Which of the following should be most susceptible to degradation by acids and bases: (a) PS; (b) PVC; (c) PET; (d) nylon-6,6; (e) proteins; (f) DNA.
28. Propose a procedure for recovering monomeric methyl methacrylate from scrap PMMA.
29. Why is PVC so thermally unstable?
30. Why are synthetic polymer scientists looking at results obtained from the biomolecular scientists?
31. Why is the active portion of myoglobin “hidden?”
32. What role does porphyrin structure play in the activity of hemoglobin?

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17 Synthesis of Reactants and Intermediates for Polymers

Many of the reactants used for the production of polymers are standard organic chemicals. However, because of the high-purity requirements and large amounts needed, special conditions have been developed that allow large amounts of high-purity reactants to be made in high yield. Section 17.1 deals with the availability of the general feedstocks. The remaining sections deal with the synthesis of particular polymer reactants.

17.1 MONOMER SYNTHESIS FROM BASIC FEEDSTOCKS

Most of the monomers widely employed for both vinyl and condensation polymers are derived indirectly from simple feedstock molecules. This synthesis of monomers is a lesson in inventiveness. The application of the saying that "necessity is the mother of invention" has led to the sequence of chemical reactions where little is wasted and by-products from one reaction are employed as integral materials in another. Following is a brief look at some of these pathways traced from basic feedstock materials. It must be remembered that often many years of effort are involved in discovering the conditions of pressure, temperature, catalysts, etc. that must be present as one goes from the starting materials to the products.

Fossil fuels refer to materials formed from the decomposition of once living matter. Because these once living materials contain sulfur and heavy metals such as iron and cobalt, they must be removed either prior or subsequent to use.

The major fossil fuels are coal and petroleum. Marine organisms were typically deposited in mud and under water, where anaerobic decay occurred. The major decomposition products are hydrocarbons, carbon dioxide, water, and ammonium. These deposits form much of the basis for our petroleum resources. Many of these deposits are situated so that the evaporation of the more volatile products such as water and ammonia occurred, giving petroleum resources with little nitrogen- or oxygen-containing products. By comparison, coal is formed from plant material that has decayed to graphite carbon and methane.

Only about 5% of the fossil fuels consumed today are used as feedstocks for the production of synthetic carbon-based products. This includes the products of the chemical and drug industries with a major portion acting as the feedstocks for plastics, elastomers, coatings, fibers, etc.

The major petroleum resources contain linear, saturated hydrocarbons (alkanes), cyclic alkanes, and aromatics. For the most part, this material is considered to have low free-energy content.

Raw or crude petroleum materials are separated into groups of compounds with similar boiling points by a process called fractionation. Table 17.1 contains a brief listing of typical fraction-separated materials. Accompanying or subsequent to this fractionation occurs a process called "cracking," whereby the hydrocarbon molecules are heated over catalysts

TABLE 17.1
Typical Straight Chain Hydrocarbon Fractions Obtained from Distillation of Petroleum Resources

Boiling Range (°C)	Average Number of Carbon Atoms	Name	Uses
<30	1–4	Gas	Heating
30–180	5–10	Gasoline	Automotive fuel
180–230	11,12	Kerosene	Jet fuel, heating
230–300	13–17	Light gas oil	Diesel fuel, heating
300–400	18–25	Heavy gas oil	Heating

that allow the hydrocarbon molecules to break up and then reform into structures that contain more branching, which allows for good combustion in our automobiles and trucks. Under other conditions, the cracking allows the formation of other desired feedstock molecules including methane, ethane, ethylene, propylene, benzene, etc. that eventually become our plastics, fibers, elastomers, sealants, coatings, composites, etc.

In 1925, Phillips Petroleum Company was only one of the dozens of small oil companies in Oklahoma. The only distinction was the large amount of natural gasoline (or naphtha), the lightest liquid fraction (Table 17.1), found in its crude oil. As was customary, Phillips, and most of the other oil companies of the time, employed a distillation process to isolate butane and propane. Even so, they were sued for the use of this distillation process probably because they were small, had no real research capacity of their own, and had no real legal defense team. Frank Phillips elected to fight supposedly including an argument that the ancient Egyptians had used a similar process to create an alcoholic equivalent to an Egyptian alcoholic drink. Phillips won the suit but became convinced that if the company was to remain successful it would need to have a research effort.

During the early dust bowl years (1935) they established the oil industry's first research team in Bartlesville, Oklahoma. George Oberfell, hired by Phillips to fight the lawsuit, planned the initial research efforts that involved three main initiatives: first, to develop technology to use light hydrocarbons in new ways as motor fuels; second, to develop markets for butane and propane; and third, to find new uses for the light hydrocarbons outside the fuel market. All three objectives were achieved.

Frederick Frey and Walter Shultze were instrumental early researchers. Frey was among the first to dehydrogenate paraffins catalytically to olefins and then the olefins to diolefins that serve as feedstocks to the production of many of today's polymers. In competition with Bakelite, he discovered the preparation of polysulfone polymers made from the reaction of sulfur dioxide and olefins creating a hard Bakelite-like material. Frey and Schultz also developed a process that allowed the production of 1,3-butadiene from butane that allowed the synthesis of SR.

Probably Frey's most important invention involved the use of hydrogen fluoride to convert light olefins, produced as by-products of a catalytic cracker, into high octane motor and aviation fuels. This process is still widely used. It came at a critical time for America's World War II efforts allowing fuel production for the Allied forces. This fuel allowed aircraft faster liftoffs, more power, and higher efficiency.

The major one-carbon feedstock is methane and it serves as the feedstock to a number of important monomers including hexamethylene tetramine and melamine, used in the synthesis of a number of cross-linked thermosets as well as vinyl acetate, ethylene, ethylene glycol, and methyl methacrylate (Table 17.1).

Formaldehyde, produced in the methane stream, serves as the basis for the formaldehyde-intensive resins, namely phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde resins. Formaldehyde is also involved in the synthesis of ethylene glycol, one of the two comonomers used in the production of PET. Formaldehyde also serves as the basic feedstock for the synthesis of polyacetals.

Another important use of methane is its conversion into synthesis gas (or syn-gas), a mixture of hydrogen gas and carbon monoxide as shown in Figure 17.1. Syn-gas can also be derived from coal. When this occurs, it is called water gas. Interestingly, the reaction of methane giving carbon monoxide and hydrogen can be reversed so that methane can be produced from coal through this route.

One major two-carbon feedstock is ethylene. From Figure 17.2, you can see that a number of the monomers are directly synthesized from ethylene. Again, while the "react" arrow goes directly from ethylene to the product, as noted earlier, it often takes years to develop an economical procedure to obtain the product in essentially 100% yield. Here, depending on the reaction conditions, a wide variety of intermediates and products are formed, which allow

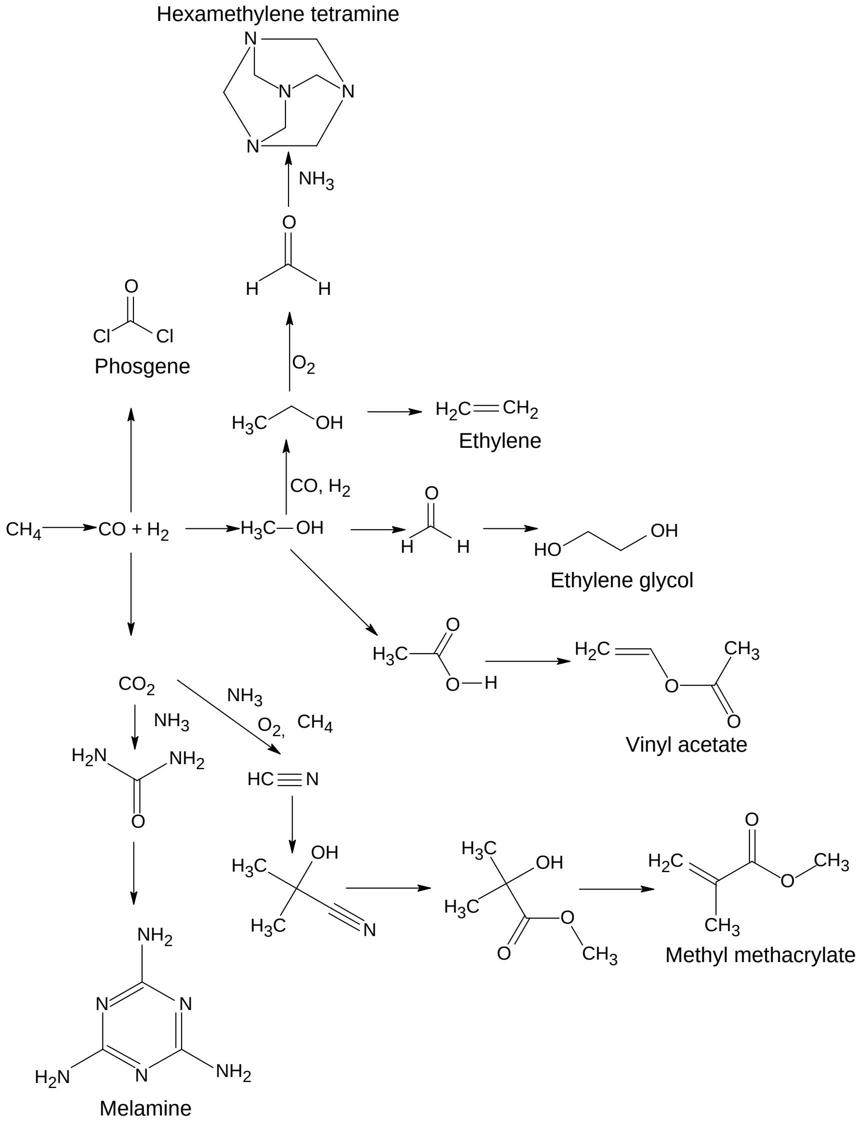


FIGURE 17.1 Monomer synthesis chemical flow diagram based on methane feedstock.

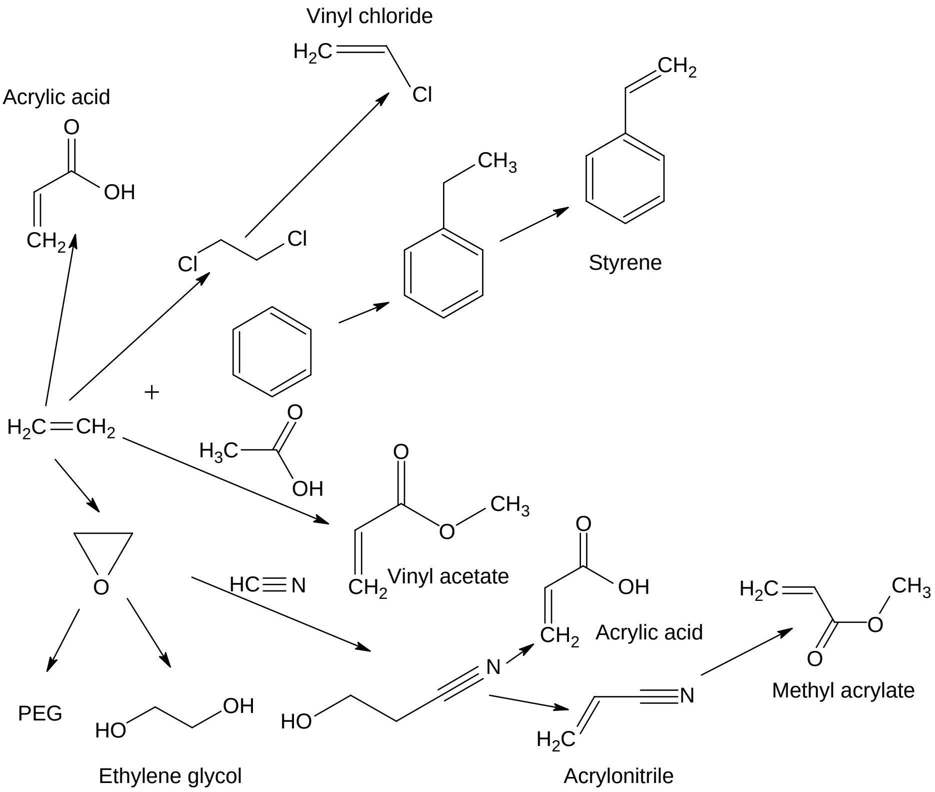


FIGURE 17.2 Monomer synthesis chemical flow diagram based on ethylene feedstock.

the synthesis of a number of polymers including poly(acrylic acid), PVC, PS, PVAc, polyesters (in particular PET), and poly(methyl acrylate). Of course, ethylene itself is part of the polymer feedstock pool being the feedstock for all of the PEs.

Another two-carbon feedstock is acetylene. Acetylene is typically obtained from coal by converting coke calcium carbide and then treating the calcium carbide with water. As shown in Figure 17.3, a number of important monomers can be made from acetylene. Even so, because of the abundance of other feedstocks from petroleum reserves, only some of the routes shown in Figure 17.3 are widely used.

Propylene is the basic three-carbon building block (Figure 17.4). Again, its polymerization gives PP. The ingeniousness of some of the synthetic routes is shown in the conversion of benzene, through reaction with propylene, to cumene and the consequent oxidation forming phenol and acetone that is subsequently converted to bisphenol A, a basic building block for certain polyesters. Phenol is involved in the synthesis of the phenol-formaldehyde resins, adipic acid, and 1,6-hexamethylenediamine. Acetone, in turn, is also involved in numerous important synthetic steps either as a reactant or solvent. It is involved in the synthesis of methyl methacrylate and isoprene.

The major four-carbon feedstock molecules are 1,3-butadiene and isobutylene, both involved in the synthesis of many monomers and intermediates. Butadiene is copolymerized with styrene to form SBR and with acrylonitrile to form ABS rubbers.

Benzene forms the basis for a number of monomers (Figure 17.5) including those that retain their aromatic character like styrene, and those that do not, like adipic acid.

In summary, monomer synthesis from basic, readily available inexpensive feedstocks based on fossil fuels is both an art and a science developed over the last half century or so.

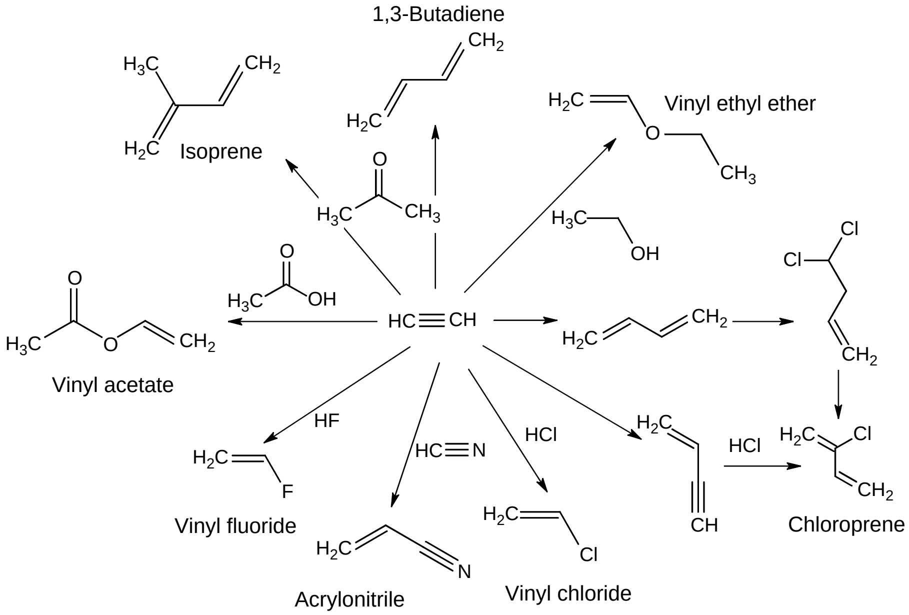


FIGURE 17.3 Monomer synthesis chemical flow diagram based on acetylene feedstock.

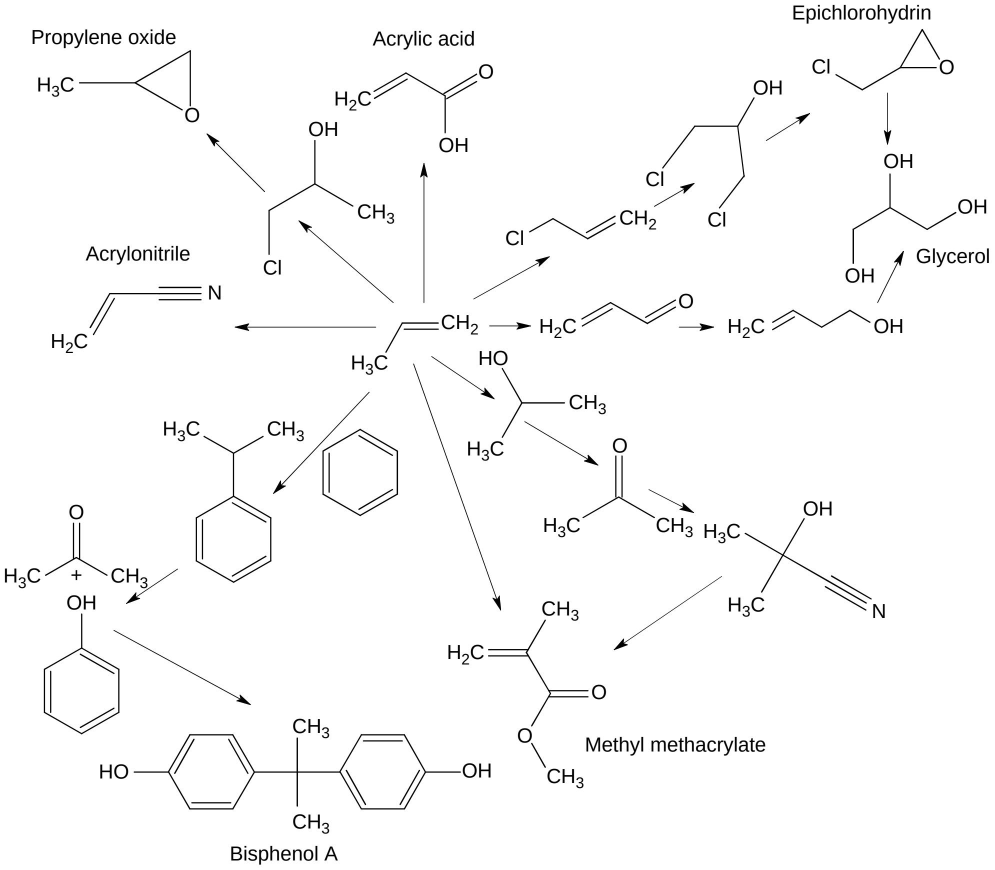


FIGURE 17.4 Monomer synthesis chemical flow diagram based on propylene feedstock.

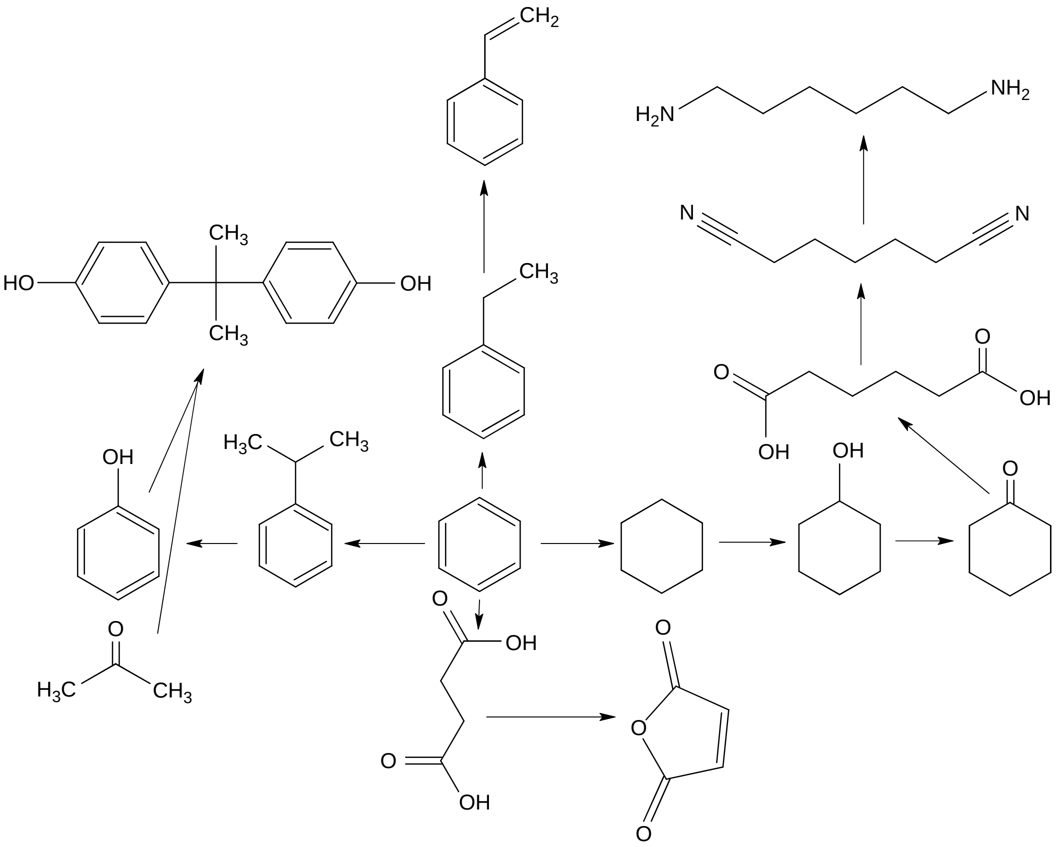
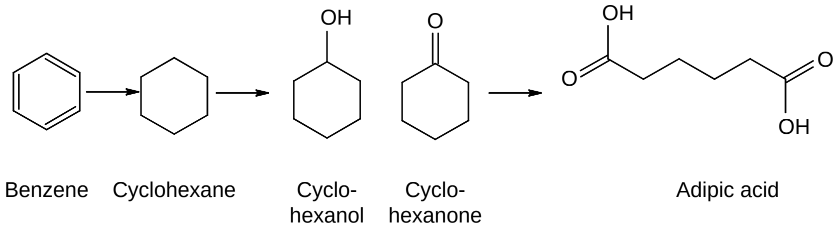


FIGURE 17.5 Monomer synthesis chemical flow diagram based on benzene feedstock.

It represents a delicate balance and interrelationship between feedstocks and so-called by-products from one reaction that become critical reactants in another reaction. Monomer and polymer synthesis continues to undergo change and improvement as the natural environment and societal and worker health continue to be dominant factors.

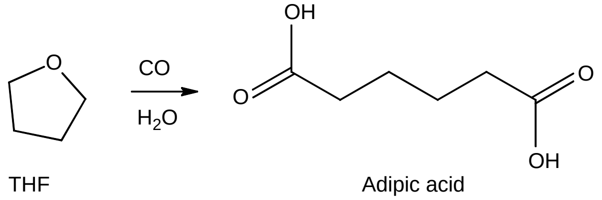
17.2 REACTANTS FOR STEP-REACTION POLYMERIZATION

Adipic acid (1,4-butanedicarboxylic acid) is used for the production of nylon-6,6 and may be produced from the oxidation of cyclohexane as shown in structure 17.1. Cyclohexane is obtained by the Raney nickel catalytic hydrogenation of benzene. Both the cyclohexanol and cyclohexanone are oxidized to adipic acid by heating with nitric acid.



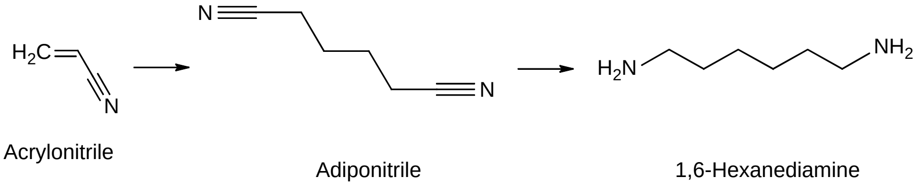
(17.1)

Adipic acid can also be made from THF, obtained from furfural. It is carbonylated in the presence of nickel carbonyl–nickel iodide catalyst. Furfural is a chemurgic product obtained by the steam-acid digestion of corn cobs, oat hulls, bagasse, or rice hulls.



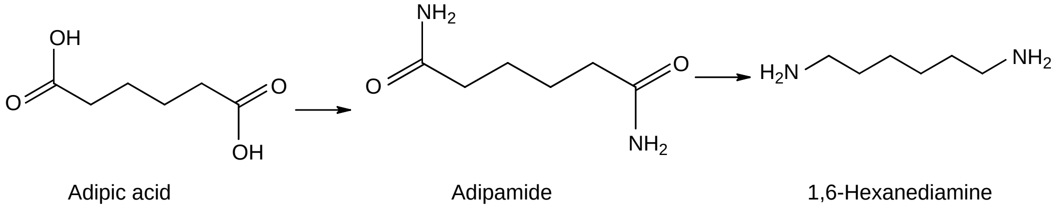
(17.2)

Adiponitrile may be produced from the hydrodimerization of acrylonitrile or from 1,3-butadiene via 1,4-dicyanobutene-2. Adiponitrile is then hydrogenated forming 1,6-hexanediamine.



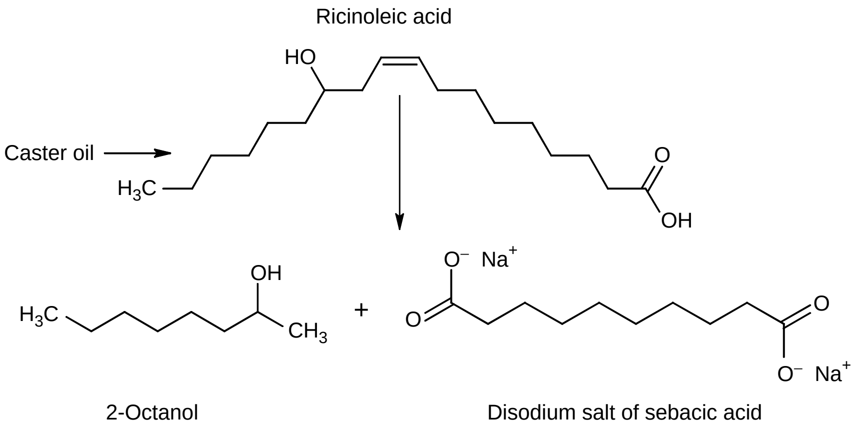
(17.3)

1,6-Hexanediamine can also be obtained by the liquid phase catalytic hydrogenation of adiponitrile or adipamide, which is made from adipic acid.



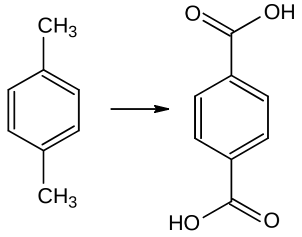
(17.4)

Sebacic acid (1,8-octane dicarboxylic acid), which is used to make nylon-610, has been produced from 1,3-butadiene and by the dry distillation of castor oil (ricinolein). The cleavage of ricinoleic acid gives 2-octanol and the salt of sebacic acid.

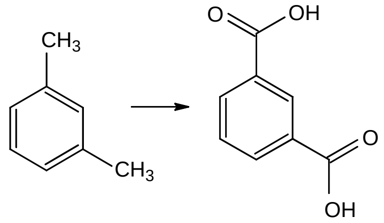


(17.5)

Phthalic acid (1,2-benzene dicarboxylic acid), isophthalic acid (1,3-benzene dicarboxylic acid), and terephthalic acid (1,4-benzene dicarboxylic acid) are made by the selective oxidation of the corresponding xylenes. Terephthalic acid may also be produced from the oxidation of naphthalene and by the hydrolysis of terephthalonitrile.

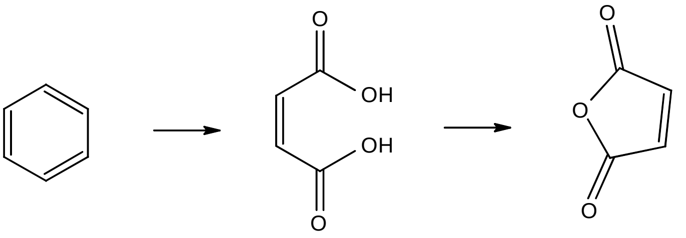


p-Xylene Terephthalic acid (17.6)



m-Xylene Isophthalic acid (17.7)

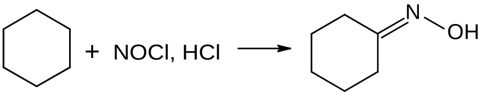
Maleic anhydride (2,5-furandione) is obtained as a by-product in the production of phthalic anhydride and by the vapor phase oxidation of butylene or crotonaldehyde. It is also obtained by the dehydration of maleic acid and by the oxidation of benzene. Maleic anhydride is used for the production of unsaturated polyester resin. This reactant, like most reactants, is fairly toxic and should be treated as such.



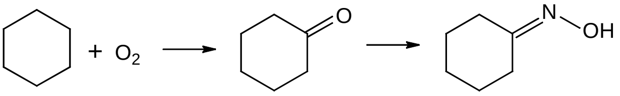
Benzene Maleic acid Maleic anhydride

(17.8)

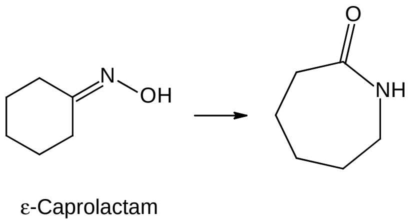
2-Pyrrolidone is a lactone used for the production of nylon-4. This reactant may be produced by the reduction ammoniation of maleic anhydride. ε-Caprolactam, used in the production of nylon-6, may be produced by the Beckman rearrangement of cyclohexanone oxime (structure 17.11). The oxime may be produced by the catalytic hydrogenation of nitrobenzene, the photolytic nitrosylation of cyclohexane (structure 17.9), or the reaction of cyclohexanone and hydroxylamine (structure 17.10). Nearly one-half of the production of caprolactam is derived from phenol.



(17.9)

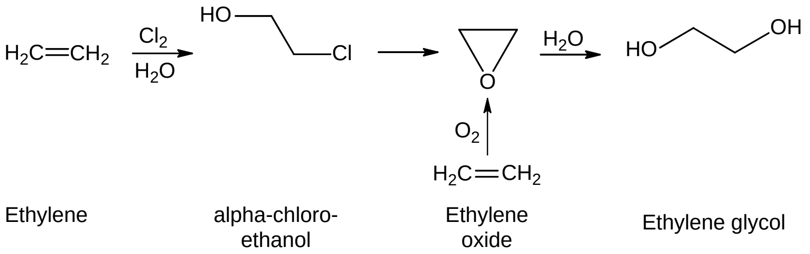


(17.10)



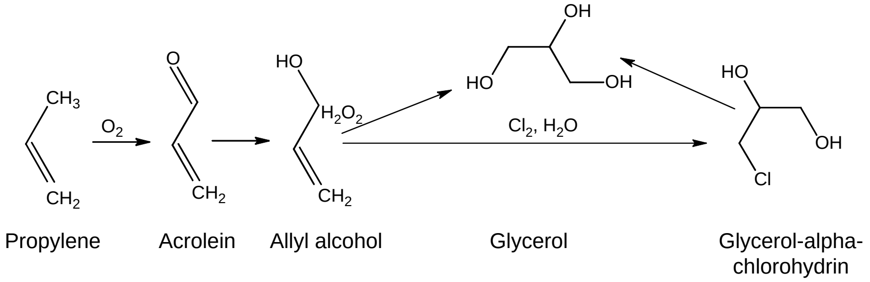
(17.11)

Ethylene oxide, used for the production of ethylene glycol and PEO, is obtained by the catalytic oxidation of ethylene. Ethylene glycol, used in the production of PET, is produced by the hydrolysis of ethylene oxide.



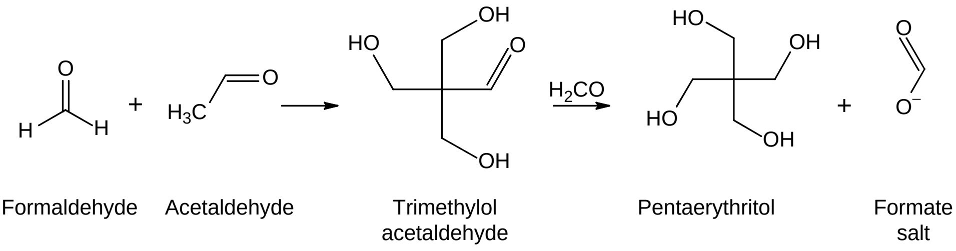
(17.12)

Glycerol, used for the production of alkyds, is produced by the catalytic hydroxylation or the hypochlorination of allyl alcohol. Allyl alcohol is produced by the reduction of acrolein, which is in turn obtained by the oxidation of propylene.



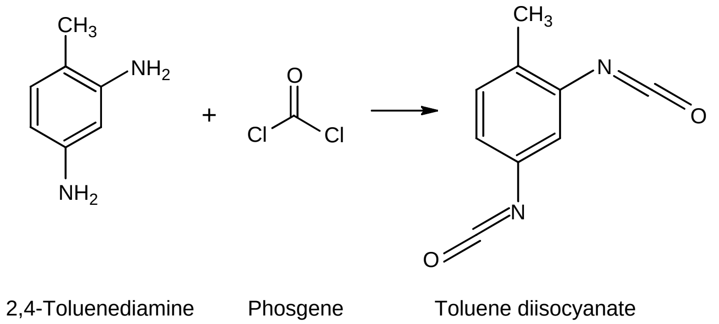
(17.13)

Pentaerythritol, used in the production of alkyds, is produced by a crossed Cannizzaro reaction of the aldol condensation product of formaldehyde and acetaldehyde. The by-product formate salt is a major source of formic acid.



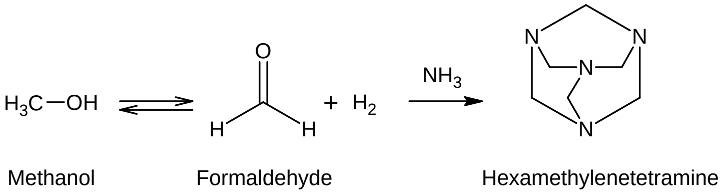
(17.14)

2,4-TDI, used for the production of PUs and polyureas, is obtained by the phosgenation of 2,4-toluenediamine. Phosgene is obtained by the reaction of chlorine and carbon monoxide.



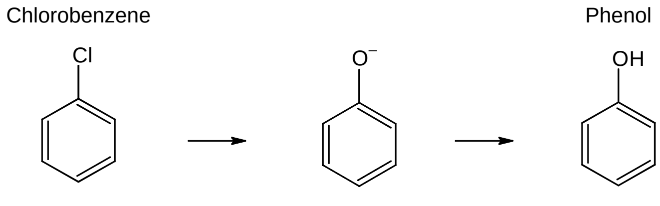
(17.15)

Formaldehyde, used in the production of phenolic and amino resins, is produced by the catalytic hot-air oxidation of methanol. In turn, hexamethylenetetramine is produced by the condensation of ammonia and 30% aqueous formaldehyde (formalin).

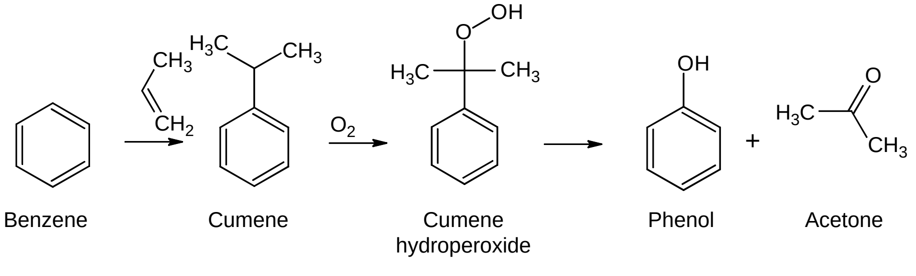


(17.16)

While some phenol is produced by the nucleophilic substitution of chlorine in chlorobenzene by the hydroxyl group (structure 17.17), most is produced by the acidic decomposition of cumene hydroperoxide (structure 17.18) that also gives acetone along with the phenol. Some of the new processes for synthesizing phenol are the dehydrogenation of cyclohexanol, the decarboxylation of benzoic acid, and the hydrogen peroxide hydroxylation of benzene.

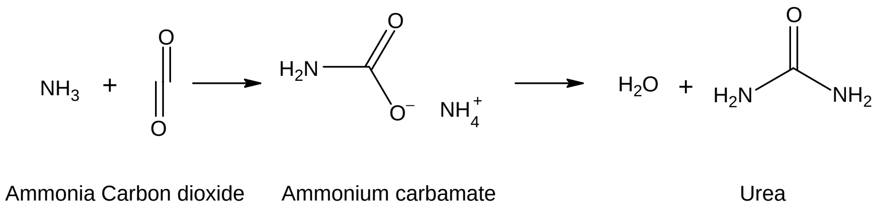


(17.17)



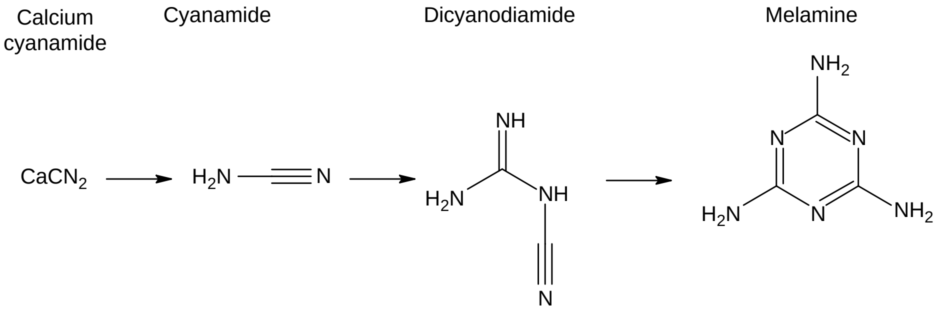
(17.18)

Urea, which is used for the production of urea-formaldehyde resins, is made by the *in situ* decomposition of ammonium carbamate, which is made by the condensation of ammonia and carbon dioxide at 200°C and 200 atm.

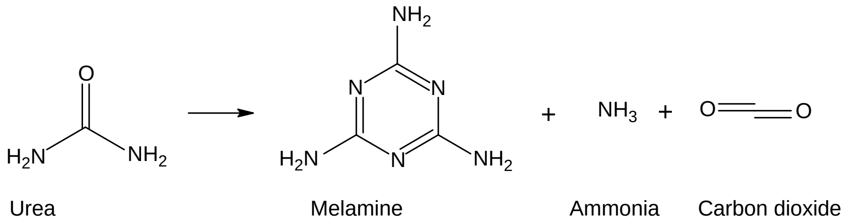


(17.19)

Melamine (cyanuramide) is obtained by heating dicyanodiamide (structure 17.20), which is obtained by heating cyanamide. Melamine, which is used for the production of melamine-formaldehyde resins, is also obtained by heating urea (structure 17.21)

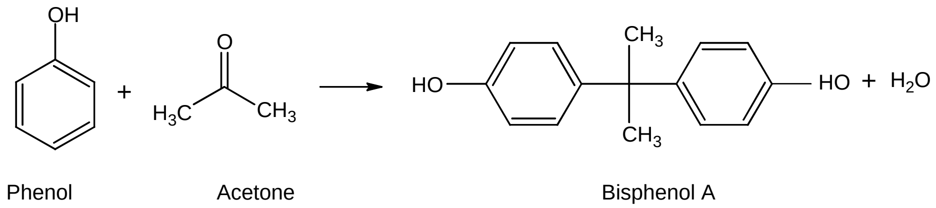


(17.20)



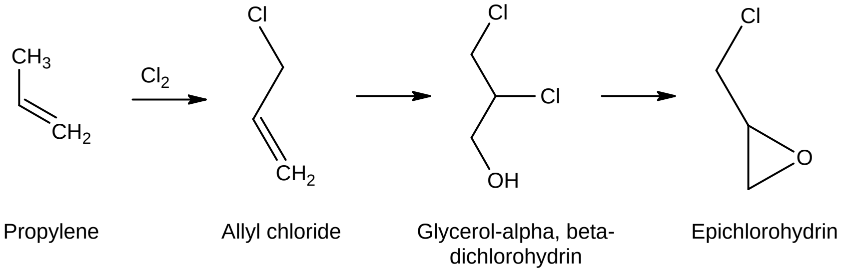
(17.21)

Bisphenol A [(bis-4-hydroxyphenol)dimethylmethane], used for the production of epoxy resins and polycarbonates, is obtained by the acidic condensation of phenol and acetone. Here, the carbonium ion produced by the protonation of acetone attacks the phenol molecule at the para position producing a quinoidal oxonium ion that loses water and rearranges to a *p*-isopropylphenol carbonium ion. The water attacks another phenol molecule, also in the para position, giving another quinoidal structure that rearranges to bisphenol A. It has been found that bisphenol A may be involved in one of the endocrine systems. The consequences of this are still being determined.



(17.22)

Epichlorohydrin (chloropropylene oxide) is used for the production of epoxy resins. It is produced by the dehydrochlorination of 2,3-dichloro-1-propanol (structure 17.23). The hydrin is produced by the chlorohydrination of allyl chloride.



(17.23)

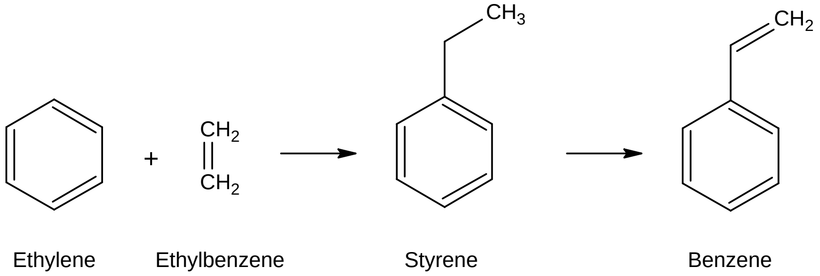
Methyltrichlorosilane is produced by the Grignard reaction of silicon tetrachloride and methylmagnesium chloride (structure 17.24). Dimethyldichlorosilane, used in the synthesis of polydimethylsiloxane, is obtained by the reaction of methylmagnesium chloride and methyltrichlorosilane (structure 17.25).

$$H_3CMgCl + SiCl_4 \rightarrow H_2CSiCl_3 + MgCl_2 \tag{17.24}$$

$$H_3CMgCl + H_3CSiCl_3 \rightarrow (H_3C)_2SiCl_2 + MgCl_2 \tag{17.25}$$

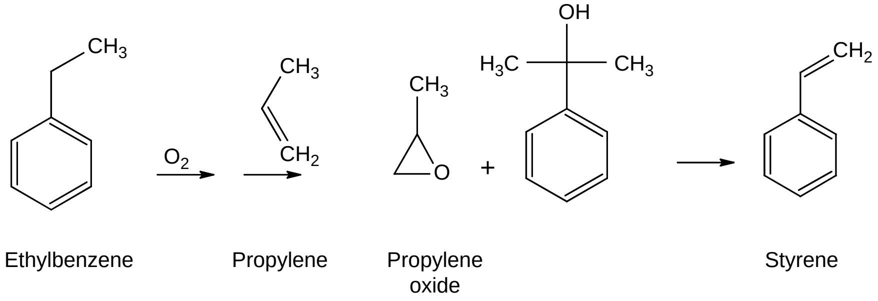
17.3 SYNTHESIS OF VINYL MONOMERS

Styrene is produced by the catalytic vapor phase dehydrogenation of ethylbenzene. Ethylbenzene is made by the Friedel–Crafts condensation of ethylene and benzene. Styrene is also produced by the palladium acetate-catalyzed condensation of ethylene and benzene and by the dehydration of methylphenylcarbinol obtained by the propylation of ethylbenzene. Because of the toxicity of styrene, its concentration in the atmosphere must be severely limited.



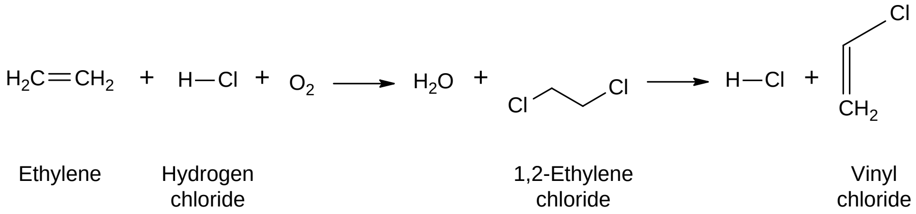
(17.26)

A process to produce styrene monomer and propylene oxide simultaneously was introduced in 1969.



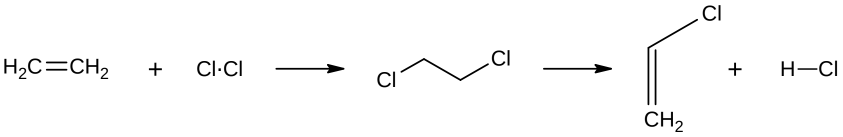
(17.27)

Vinyl chloride, formerly obtained from acetylene, is now produced by the transcatalytic process where chlorination of ethylene, oxychlorination of the by-product hydrogen chloride, and dehydrochlorination occur in a single reactor.

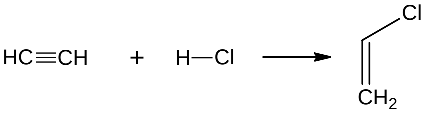


(17.28)

Vinyl chloride is also produced by the direct chlorination of ethylene and the reaction of acetylene and hydrogen chloride (structure 17.29). The hydrogen chloride generated in the chlorination of ethylene can be employed in reaction with acetylene allowing a useful coupling of these two reactions (equation 17.30).

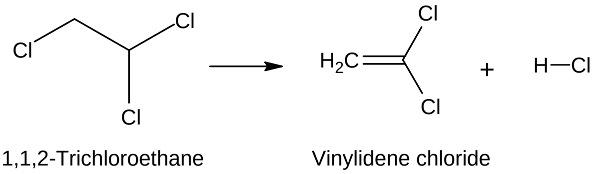


(17.29)



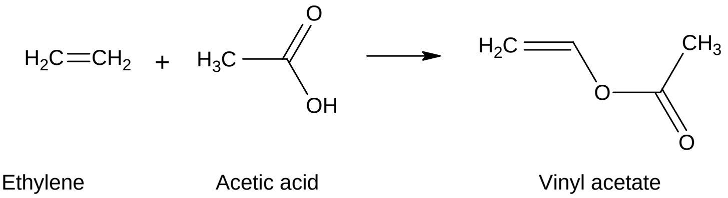
(17.30)

Vinylidene chloride is produced by the pyrolysis of 1,1,2-trichloroethane at 400°C in the presence of lime or base. Since both vinylidene chloride and vinyl chloride are carcinogenic, their concentrations must be kept low.



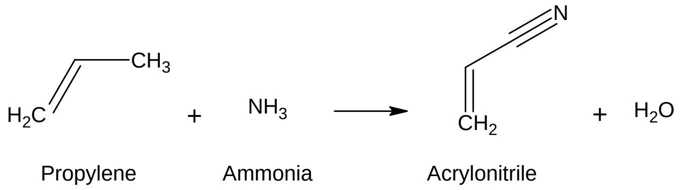
(17.31)

Vinyl acetate was produced by the catalytic acetylation of acetylene, but this monomer is now produced by the catalytic oxidative condensation of acetic acid and ethylene (structure 17.32). Other vinyl esters can be produced by the transesterification of vinyl acetate with higher boiling carboxylic acids.



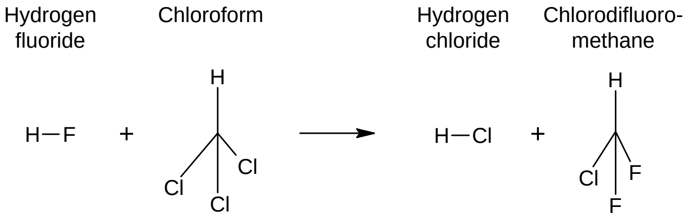
(17.32)

Acrylonitrile (vinyl cyanide) is produced by the ammoxidation of propylene. Again, since this monomer is carcinogenic, care must be taken to minimize exposure to it.

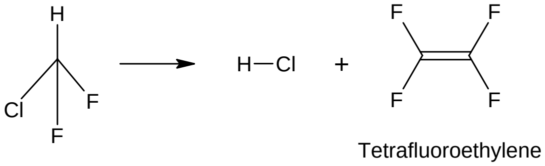


(17.33)

Tetrafluoroethylene is produced from the thermal dehydrochlorination of chlorodifluoromethane (equation 17.35) which in turn is produced from chloroform and HF (equation 17.34)

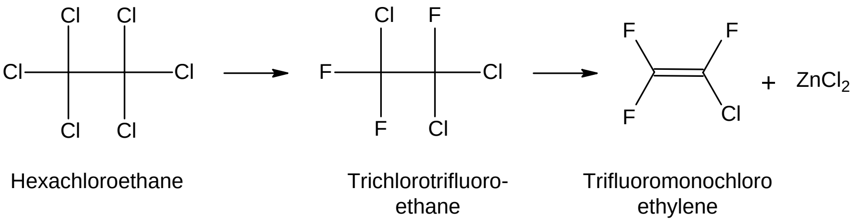


(17.34)



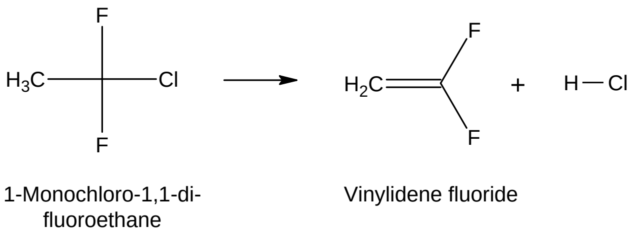
(17.35)

Trifluoromonochloroethylene is obtained from the zinc metal dechlorination of trichlorotrifluoroethane. The latter is produced by the fluorination of hexachloroethane.



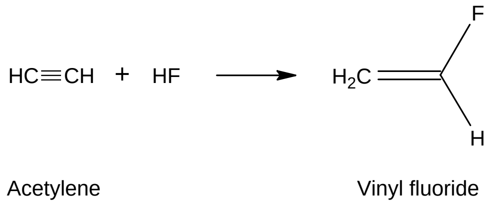
(17.36)

Vinylidene fluoride is produced by the thermal dehydrochlorination of 1-monochloro-1,1-difluoroethane.



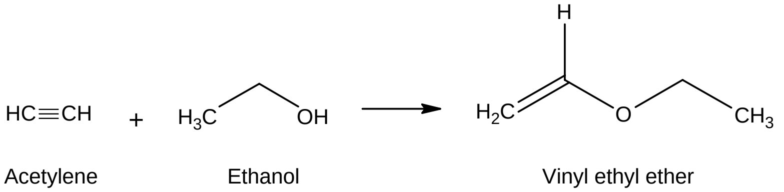
(17.37)

Vinyl fluoride may be obtained by the catalytic hydrofluorination of acetylene.



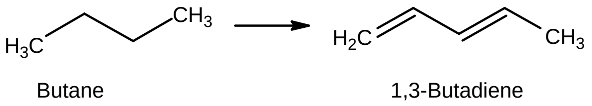
(17.38)

Vinyl ethyl ether is obtained by the ethanolysis of acetylene in the presence of potassium ethoxide.



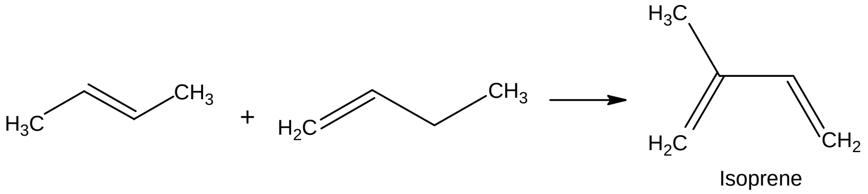
(17.39)

1,3-Butadiene, used for the production of elastomers, is produced by the catalytic thermal cracking of butane and as a by-product of other cracking reactions.



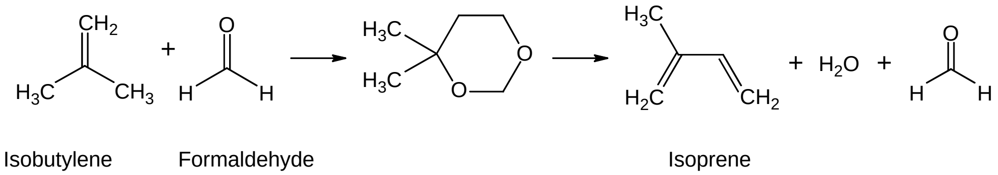
(17.40)

The isoprene monomer is not readily available from direct cracking processes. Several routes are employed for its synthesis. One route begins with the extraction of isoamylene fractions from catalytically cracked gasoline streams. Isoprene is produced by subsequent catalytic dehydrogenation.



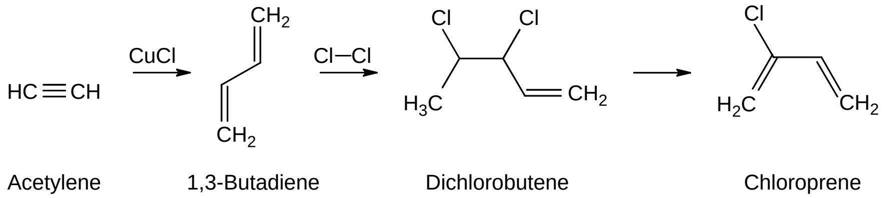
(17.41)

Dimerization of propylene is also used to produce isoprene. Several steps are involved. Initially, dimerization of propylene to 2-methyl-1-pentene occurs. Then isomerization to 2-methyl-2-pentene is effected. Finally, the 2-methyl-2-pentene is pyrolyzed to isoprene and methane. Another multistep synthesis starts with acetylene and acetone. Perhaps the most attractive route involves formaldehyde and isobutylene (equation 17.42).



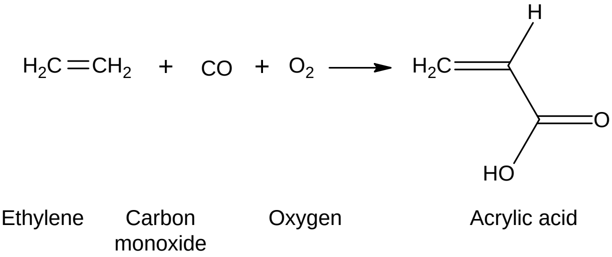
(17.42)

Chloroprene, used for the production of neoprene rubber, is obtained by the dehydrochlorination of dichlorobutene. The latter is produced by the chlorination of 1,3-butadiene, which in turn is synthesized from acetylene.



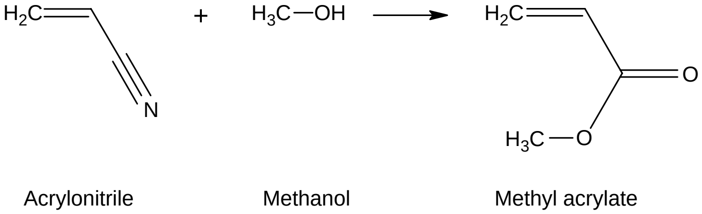
(17.43)

Acrylic acid can be prepared by the catalytic oxidative carbonylation of ethylene or by heating formaldehyde and acetic acid in the presence of KOH.



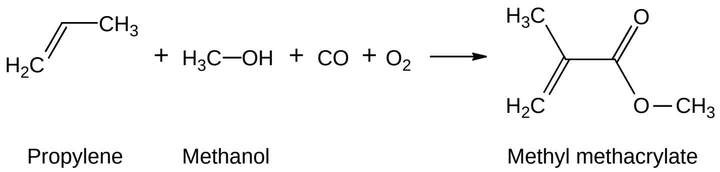
(17.44)

Methyl acrylate may be obtained by the addition of methanol to the reactants in the previous synthesis (equation 17.44) for acrylic acid or by the methanolysis of acrylonitrile (equation 17.45).



(17.45)

Methyl methacrylate may be prepared by the catalytic oxidative carbonylation of propylene in the presence of methanol.

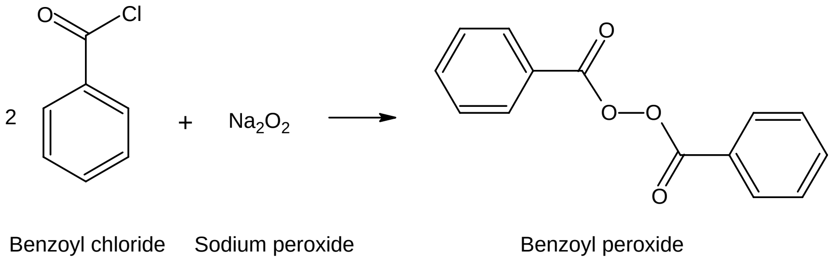


(17.46)

17.4 SYNTHESIS OF FREE RADICAL INITIATORS

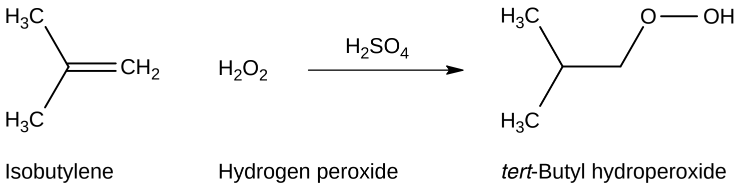
Free radical initiators are compounds containing covalent bonds that readily undergo hemolytic cleavage producing free radicals. The most widely used organic free radical initiators are peroxides and azo compounds. Here, we will briefly describe the synthesis of the more widely employed free radical initiators.

Benzoyl peroxide is produced when benzoyl chloride and sodium peroxide are stirred in water.



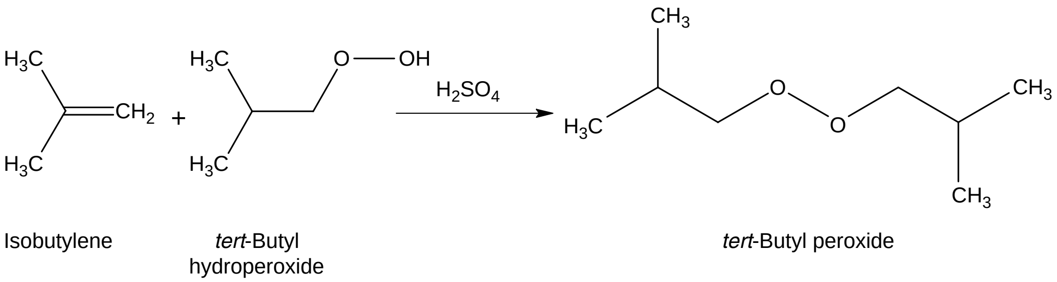
(17.47)

tert-Butyl hydroperoxide is produced by the acid-catalyzed addition of hydrogen peroxide to isobutylene.



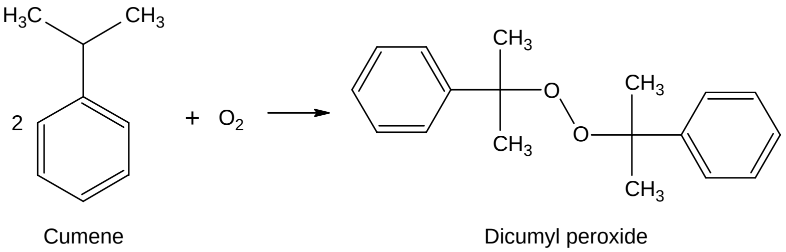
(17.48)

tert-Butyl peroxide is produced when *tert*-butyl hydroperoxide is added to isobutylene.



(17.49)

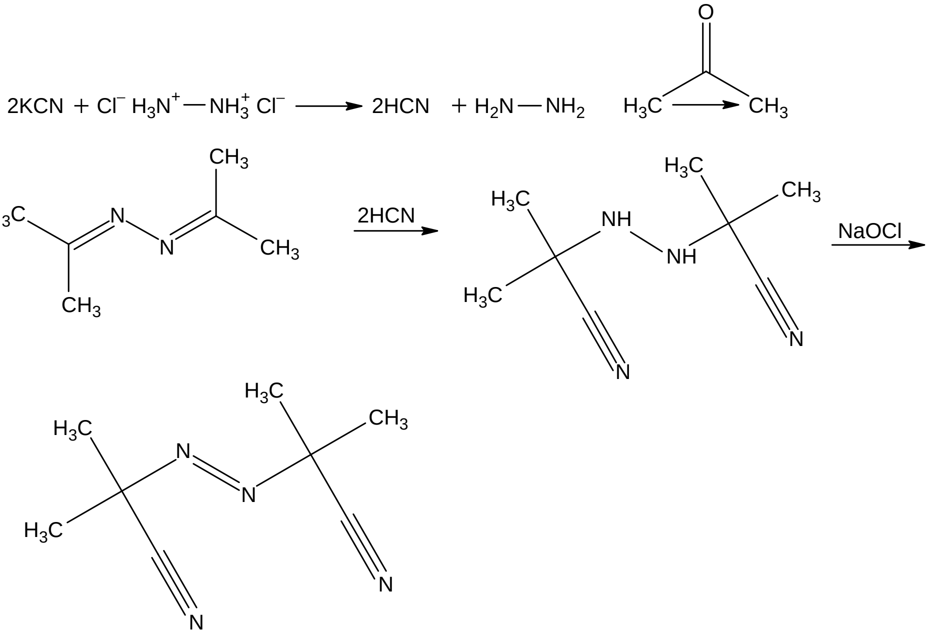
Dicumyl peroxide is produced by the air oxidation of cumene.



(17.50)

All initiators are potentially explosive compounds and must be stored and handled with care. 2,2′-AIBN is obtained from the reaction of acetone with potassium cyanide and hydrazine hydrochloride. As shown in equation 17.51, the reaction produces hydrogen cyanide and hydrazine. The latter reacts with acetone forming acetone dihydrazone, which reacts with

HCN producing a substituted hydrazone. This hydrazone is then oxidized to AIBN by the addition of sodium hypochlorite.



AIBN

(17.51)

When methyl ethyl ketone is used in place of acetone, 2,2′-azobis-2-butyronitrile is produced.

17.5 SUMMARY

1. Feedstocks for the synthesis of monomers of basic polymeric materials must be readily available and inexpensive because they are utilized in polymer synthesis in large quantities, allowing the polymeric materials to be inexpensive. Basic feedstocks are petrochemical and coal-based.
2. Monomer synthesis is both an art and science developed by great and ongoing research efforts allowing the inexpensive and safe availability of the starting materials upon which the polymer industry is based. Commercial monomer synthesis is based on both the availability of inexpensive materials and an "interconnectiveness" between products and synthetic by-products that are essential to the synthesis of other essential materials.
3. The precise conditions of synthesis are continually being refined. They are based on "high" science.

GLOSSARY

Cannizzaro reaction An internal oxidation–reduction reaction of aldehydes.

carbamide Urea.

carcinogenic Cancer causing.

chemurgic compound Compound made from a plant source.

Friedel–Crafts condensation Condensation that takes place in the presence of a Lewis acid such as aluminum chloride.

Grignard reagent RmgX.

Raney nickel A porous nickel catalyst produced from a nickel–aluminum alloy.

EXERCISES

1. Why are there so many methods for the preparation of adipic acid?
2. Write equations for the industrial synthesis of the following:
   (a) adipic acid; (b) hexamethylenediamine; (c) sebacic acid; (d) terephthalic acid; (e) maleic anhydride; (f) ε-caprolactam; (g) ethylene glycol; (h) glycerol; (i) pentaerythritol; (j) TDI; (k) hexamethylenetetramine; (l) phenol; (m) urea; (n) melamine; (o) bisphenol A; (p) epichlorohydrin; (q) methyltrichlorosilane; (r) styrene; (s) vinyl chloride; (t) vinyl acetate; (u) acrylonitrile; (v) vinyl ethyl ether; (w) methyl methacrylate
3. Name a reactant or monomer produced by the following:
   (a) Grignard reaction; (b) Friedel–Crafts reaction; (c) Beckman rearrangement; (d) a chemurgic process; (e) a crossed Cannizzaro reaction
4. Why are catalysts so important in the synthesis of monomers?
5. Name three monomers that are derived from methane.
6. Why is it important to be able to make many different monomers from the same starting feedstock?
7. What is one basic feedstock for the synthesis of bisphenol A?
8. Why are most of the major monomer producers oil companies?
9. In the synthesis of peroxides as initiators why is added care wise?
10. Why is it important to save at least some of our petroleum for future generations?

FURTHER READING

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18 Polymer Technology

Today, nearly 10,000 American companies are active in the general area of synthetic polymers. Following is a brief description of these companies divided according to their function.

- *Manufacturers*: There are over 200 major manufacturers of general-purpose polymers and numerous other manufacturers of specialty polymers.
- *Processors*: Some companies manufacture their own polymeric materials for subsequent processing, but the majority purchases the necessary polymeric materials from other companies. Processors may specialize in the use of selected polymers, such as nylons and polycarbonates, or focus on particular techniques of processing, such as coatings, films, sheets, laminates, and bulk molded and reinforced plastics.
- *Fabricators and finishers*: A majority of companies are involved in the fabrication and finishing of polymers, i.e., production of the end products for industrial and public consumption. Fabrication can be divided into three broad areas: machining, forming, and fashioning. Machining includes grinding, sawing, screwing, and other techniques. Forming includes molding and other methods of shaping and joining by welding, gluing, screwing, and other techniques. Fashioning includes cutting, sewing, sheeting, and sealing. Fabrication sequences vary with the polymeric material and desired end product.

While much classic polymer technology was developed without the benefit of science, modern polymer technology and polymer science are closely associated. The technology of fibers, elastomers, coatings, composites, drug delivery, and plastics is discussed in this chapter.

Chemistry is moving center stage in many areas of medicine, biology, engineering, environmental science, and physics. While solid state physics is traditionally based on silicon, polymers offer a much wider vista of opportunities for application and fine-tuning those applications. Some areas are based on single crystals that may be small in our sight, but are large when compared to individual molecules. Even single silicon wafers with a minimum pattern dimension of 200 nm are on the order of ten times the size of individual molecules. Eventually, electronic, photonic, and stress–strain behavior individuality can be placed into single giant chains creating chains that behave as entire assemblies behave today.

Polymer processing can be defined as the process whereby raw materials are converted into products of desired shape and properties. Thermoplastic resins are generally supplied as pellets, marbles, or chips of varying sizes and they may contain some or all of the desired additives. When heated above their T_g, thermoplastic materials soften and flow as viscous liquids that can be shaped using a variety of techniques and then cooled to “lock” in the micro- and gross structure.

Thermosetting feedstocks are normally supplied as meltable and/or flowable prepolymer, oligomers, or lightly or non-cross-linked polymers, which are subsequently cross-linked forming the thermoset article.

The processing operation can be divided into three general steps—preshaping, shaping, and postshaping. In preshaping, the intent is to produce a material that can be shaped by application of heat and/or pressure. Important considerations include:

- Handling of solids and liquids including mixing, low, compaction, and packing
- Softening through application of heat and/or pressure
- Addition and mixing or dispersion of added materials
- Movement of the resin to the shaping apparatus through application of heat and/or pressure and other flow aiding processes
- Removal and recycling of unwanted solvent, unreacted monomer(s), by-products, and waste (flash)

The shaping step may include any or combination of the following:

- Die forming (including sheet and film formation, tube and pipe formation, fiber formation, coating, and extrusion)
- Molding and casting
- Secondary shaping (such as film and blow molding, thermoforming)
- Surface treatments (coating and calendering)

Postshaping processes include welding, bonding, fastening, decorating, cutting, milling, drilling, dying, and gluing.

Polymer processing operations can be divided into five broad categories:

- Spinning (generally for fibers)
- Calendering
- Coating
- Molding
- Injection

Table 18.1 lists some of the major forms of each of these processing groups.

Essentially all of the various processing types utilize computer-assisted design (CAD) and computer-assisted manufacture (CAM). CAD allows the design of a part and incorporates operating conditions to predict behavior of the pieces before the real operation. CAD also transfers particular designs and design specifications to other computer-operated systems, e.g., CAMs, which allow the actual construction of the part or total apparatus. CAM systems operate most modern processing systems, many allowing feedback to influence machine operation.

Processing and performance are interrelated to one another and to additional factors. Jaffe relates these major groups of factors in an interactive diamond shown in Figure 18.1. Understanding these factors and their interrelationships becomes increasingly important as the specific performance requirements become more specific. Performance is related to the chemical and physical structure and to the particular processing performed on the material during its lifetime. The physical structure is a reflection of both the chemical structure and the total history of the synthesis and subsequent exposure of the material to additional forces. These “additional” forces are included under the broad idea of processing and include any influence that contributes to the secondary (and greater) structure—stress–strain, light, chemical, etc. The portion of the diamond relating processing to physical structure encompasses the study of structure–property relationships. A single material may be processed using only a single process somewhat unique to that material (such as liquid crystals) or by a variety of processes (such as PE) where the particular technique is dictated by such factors as end use and cost.

TABLE 18.1
Major Forms of Polymer Processing Groupings

Process	**Typical Form of Product**
Calendering	Films, sheets
Coating	Film
Injection	Solid
Reaction injected	
Reciprocating screw	
Two-stage	
Molding	
Blow	Hollow
Displacement	
Extrusion	
Injection/transfer	
Stretch	
Cold solid	
Compression	Solid, hollow
Rotational	Solid, hollow
Thermoforming	Hollow
Transfer	Solid
Spinning	Fibers
Dry	
Gel	
Melt	
Reaction	
Wet	

The primary and secondary structures greatly influence possible processing scenarios. Here, the secondary structure is generally the same as the physical structure and the primary structure is generally the same as the chemical structure. The end properties and uses are governed by intrinsic properties that in turn are related to the primary and secondary structures—the chemical and physical structures.

The term "meso" will be used to describe local chain organizations that occur within the nano- and microscale regions (Figure 18.2). While the terms mesophase and mesoregions have been employed in describing order within liquid crystals, the definition will be

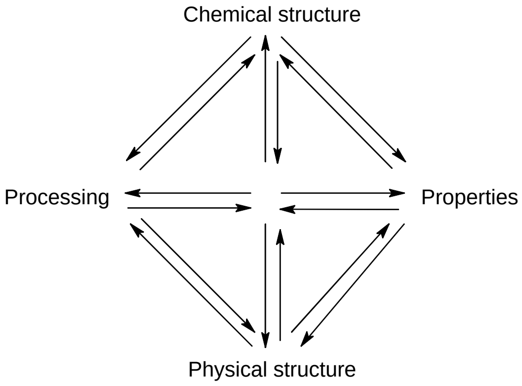


FIGURE 18.1 Relationships, which influence the important interrelationships that exist for polymeric materials with respect to processing and end-product properties.

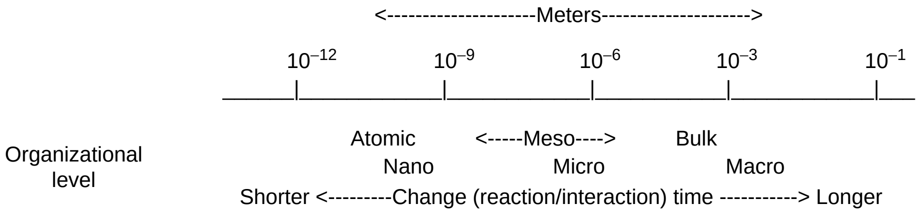


FIGURE 18.2 Relationship between organizational level and size.

broadened to include other ordered regions within a material's physical or secondary structure. We generally describe polymer secondary structure in simple terms of ordered or disordered and crystalline or amorphous. The ordered regions can be further described in terms of mesoregions or mesophases according to their permanency and ability to influence changes within and about these regions.

Jaffe describes four mesophase classifications. Permanent mesogens are materials whose microstructures are highly fixed such as in LCs, which are characterized by highly ordered structures in the quiescent state. They exhibit relatively low viscosities in uniaxial flows and can be easily realigned through application of processing forces such as extrusion. To be processed, such polymers must be in the mesogenic state below their decomposition temperature. This can be achieved through the use of a specific solvent or the introduction of special comonomer units that allow them to melt (or soften), but that are introduced in such a manner as to preserve their LC character. As solids, such materials exhibit high molecular orientation, high tensile moduli (near to theoretical), poor compression (i.e., little unoccupied volume), poor shear behavior, and high tensile strengths (on the order of 4 GPa). Such materials are anisotropic conductors and generally offer good liquid and gas barrier properties. Properties are controlled by the inherent chemical structure, molecular orientation, defect occurrences, and stress-transfer mechanisms. Defects often act as the "weak-links" in a chain, limiting mechanical properties so that defect detection, and elimination or curtailment is important and can be dependent on the processing conditions. Only certain processing techniques are suitable.

Accessible mesogens are formed from polymers that are thermotropic (i.e., polymers that have a phase organization that is temperature dependent) but have an accessible isotropic phase below their decomposition temperature. Such polymers can be processed either when the material is in its mesogenic phase or ordered state using LC-type processing forming strong well-ordered products, or at temperatures where the ordered mesogenic structure is absent. In temperature-assisted systems, the material is rapidly cooled, quenched, preventing the mesogenic structure formation and producing a metastable isotropic glass or rubber. The metastable material can be processed employing less energy and force followed by simple annealing and slower cooling, which allows the formation of the ordered mesogenic structures along with the appearance of associated properties. Examples of assembled mesogens include groups of polymer coils and polymers with side chains that can form such mesogens. In the former case, tertiary mesophase structures can be formed when the bundles of coiled chains come together.

Transient mesogens are regions present in flexible, random coil polymers often caused by application of external forces including simple flowing or shearing. These regions occur through local segmental chain movements within the chain network at points of minimum chain entropy such as sites of entanglements. They are fibrillar-like and appear to be the nucleating phase and key to the row and shish-kebab-like structures in oriented polymer crystals.

These latter groups include many of the so-called crystallites and crystalline regions of common polymers.

TABLE 18.2
Generic Names for Synthetic Fibers According to the ISO and FTC

ISO	FTC
Acetate	Acetate
Acrylic	Acrylic
Aramid	Aramid
Chlorofiber	Vinyon/saran
Cupro/viscose/modal/deacetylated acetate	Cupra/rayon
Elastane	Spandex
Glass	Glass
Modacrylic	Modacrylic
Nylon/polyamide	Nylon/polyamide
Polyester	Polyester
Polyethylene/polypropylene–polyolefin olefin	Vinylal vinal

Understanding the factors that govern the formation of mesogens will assist in determining the processing conditions for the production of materials with specified amounts, sizes, and distribution of such crystalline microstructures. Mesophases can be local or permeate the entire structure. They can be large or small, and present in a random or more ordered arrangement.

18.1 FIBERS

18.1.1 Polymer Processing—Spinning and Fiber Production

Most polymeric materials are controlled by the Federal Trade Commission (FTC) with respect to the relationship between the name and content including fibers. While the FTC controls industry in the United States, the international standards are generally determined by the International Organization for Standardization (ISO). Table 18.2 contains a brief listing of some of the ISO and FTC names for some of the most utilized fibers.

Fiber production continues to increase for most general groupings. Table 18.3 contains approximate fiber production by fiber type.

The dimensions of a filament or yarn are expressed in terms of a unit called the "tex," which is a measure of the fineness or linear density. One tex is 1 g/1000 m or 10^{-6} kg/m. The tex has replaced denier as a measure of the density of the fiber. One denier is 1 g/9000 m, so 1 denier = 0.1111 tex.

TABLE 18.3
Global Production of Fibers by Fiber Type (2005)

Fiber Type	Global Production Million Tons	Global Production Percentage
Cellulosic	2.0	6
Acrylic	2.7	8
Nylon	3.9	11
Olefin	5.9	17
Polyester	21	58

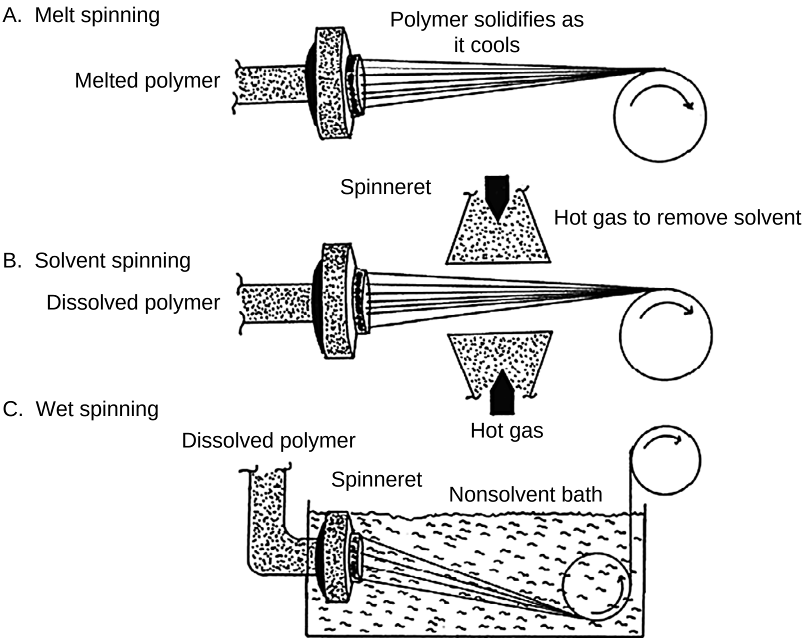


FIGURE 18.3 Fiber production using the three major spinning techniques.

Although some natural polymers produced "natural" fibers, those from synthetic and regenerated natural polymers are generally produced using one of the spinning processing techniques. Three spinning processes are generally employed in the large-scale commercial production of fibers. The first produces fiber from the melted polymer—melt spinning. The other two techniques form fibers from concentrated polymer solutions—dry and wet spinning. Figure 18.3 illustrates the essentials of these three spinning techniques. Table 18.4 is a listing of the most common polymers made into fibers by these three processes.

18.1.1.1 Melt Spinning

Melt spinning was developed in the 1930s. In melt spinning the polymer is melted or extruded, clarified by filtration, and pumped through a die having one or more small holes. The die is called a spinneret. The number, shape, and size of the hole can vary considerably. The number of holes ranges from several to several thousand. For continuous filament formation, the

TABLE 18.4
(Preferred) Spinning Processes

	Dry Spinning	Wet Spinning	
Melt Spinning	Regeneration	Coagulation	
Nylon	Acetate	Acrylic	Viscose
Polyester	Triacetate	Aramid	Cupro
Polyethylene	Acrylic	Elastane/Spandex	
Polypropylene	Elastine/Spandex	Poly(vinyl chloride)	
Poly(vinylene chloride)	Poly(vinyl chloride)		
	Aramid		
	Modacrylic		
	Vinyal		

TABLE 18.5
Typical Spinning Temperatures for Selected Polymers

(Typical) Polymer	Melting Point (°C)	Spinning Temperature (°C)
Nylon-6	220	280
Nylon-6,6	260	290
Poly(ethylene terephthalate)	260	290
Poly(vinylidene chloride), copolymers	120–140	180
Poly(*p*-phenylene sulfide)	290	300
Polyethylene	~130	220–300
Polypropylene	170	250–300

number of holes is on the order of 10–100. The exit hole is usually circular, giving round fibers. Other shaped holes are also employed that produce fibers with varying shapes.

The extruded fiber is then often uniaxially stretched by take-up rollers rotating at different speeds. The fiber stretching encourages the polymer chains to align on a molecular level producing increased strength in the direction of the pull.

To produce the melted polymer, the polymer chips, rods, marbles, or sheets are heated forming a melted pool of material. In order to minimize oxidation, the melted polymer is blanketed by an inert gas such as nitrogen or argon. The fluidity (inverse of viscosity) of the melt increases with increased temperature as does the cost to provide the necessary energy and tendency for unwanted reactions to occur. Thus, the polymer melt is generally assisted to and through the spinneret by means of an extruder, which may also be used to supply some or all of the heating.

Typical melt spinning temperatures are given in Table 18.5.

Many nylon and polyester assemblies are configured so that there is a continuous progression from the melt formation of the polymer, and without hardening, the melted polymer is melt-spun into fibers.

Monofilament is produced at a lower spinning speed, in comparison with chopped filament, because of the problem of heat buildup within the monofilament. The monofilament is generally cooled by passing it through cold water or by winding it on to a cold quench roll.

18.1.1.2 Dry Spinning

Polymer concentrations on the order of 20%–40% are employed in dry and wet spinning. In this process the solution is filtered and then forced through a spinneret into a spinning cabinet through which heated air is passed to dry the filament. For economical reasons, the gas is usually air, but inert gasses such as nitrogen and superheated water are sometimes used.

Volatile solvents are used to assist in the drying. Water has been used for some systems, such as PVA, where the polymer is water soluble. Solvent removal and recycling is important. Spinning is usually carried out using either low (about 1%–2%) or high (10%–50%) solvent in the filament. The amount of solvent influences the drawing process. In high solvent cases the filaments are plasticized allowing greater extension of the filament and greater alignment of the polymer chains to occur at lower temperatures and lower stresses. The extra solvent is removed just before, during, or after stretching. Before extrusion, the polymer solution is heated to just above its boiling point, increasing the likelihood for ready removal of the solvent.

Fibers produced by dry spinning have lower void concentrations in comparison to melt-spun fibers because the presence of solvent molecules causes voids that are often “remembered” by the polymer. This is reflected by greater densities and lower dyeability for the dry spun fibers.

Fibrous glass is the most important inorganic fiber. It is produced by melt spinning in both a continuous filament and staple form. The molten glass is fed directly from the furnace, or melted from rods or marbles, to the spinneret. As the fibrous glass emerges it is attenuated, quenched, lubricated, and wound forming a yarn or continuous filament. The temperature for spinning is on the order of 1200°C–1500°C. This temperature is important since it controls the output, and in conjunction with the removal speed, helps control the properties of the resultant fiber including thickness and density.

18.1.1.3 Wet Spinning

Wet spinning is similar to dry spinning except that fiber formation results from the coagulation of the polymer solution as it is immersed into a nonsolvent bath. Since the coagulation process is relatively long, the linear velocity of wet spinning is less than for either melt or dry spinning. Wet spinning allows the placement of holes in the spinneret face to be close together, allowing productivity to be increased. Even so, it remains the slowest of the traditional spinning processes. The equipment used for wet spinning is similar to that used in dry spinning though it is not necessary to heat the polymer solution to a high temperature. The spinnerets are immersed in tanks containing the nonsolvent. Wet spinning is the most complex of the three spinning processes, typically including washing, stretching, drying, crimping, finish application, and controlled relaxation to form tow material. Spinning of naturally derived materials generally includes additional steps such as aging and ripening to achieve the desired viscosity and chain length.

Fibers made from wet spinning generally have high void contents compared with all the other processes, giving them increased dyeability. The surface is rougher with longitudinal serrations, and from passing through a round die hole, which has a circular or bean-shaped circumference.

Hollow fibers for gas and liquid separation are prepared by passing the air through the material just before it is immersed into the nonsolvent bath.

18.1.1.4 Other Spinning Processes

There are a number of lesser used, but still important, spinning processes. Following is a summary of some of these. In *reaction spinning* a prepolymer is generally used, which is further reacted upon by a material that may be in solution in a bath. Further treatments may include cross-linking of the fiber. The most important example is the production of selected segmented PU elastomeric fibers. Here the prepolymer is the soft segment, generally a low molecular weight polyether or polyester. Reaction with an aromatic diisocyanate converts the end groups, generally hydroxyls, into isocyanate groups. The bath contains a diamine such as 1,2-diaminoethane. The reaction between the amine and isocyanate forms the hard urea linkages. Some segmented PUs, such as Lycra™, are formed using conventional dry spinning.

Fibers can be formed from intractable materials such as ceramics and polytetrafluoroethylene through extrusion of a suspension of fine particles in a solution of a matrix polymer. The matrix polymer-intractable material is coagulated embedding, aligning the intractable material in the matrix polymer. The filament is then heated decomposing the matrix polymer. During this process, the material is sintered and drawn giving small, often with little flexibility—fibrils.

Gel spinning is used to produce high-strength and modulus fibers. High molecular weight (such as 10^6 Da for PE) polymer is dissolved in a high-temperature solvent at low concentrations (~1%). The hot solution is extruded into a cooling zone such as a liquid nonsolvent. The resulting gel-like filament contains polymer with lots of entrapped liquid. This gel-like filament can be easily drawn. The drawing can be carried out even though the liquid is removed before drawing. During this process, the low density of polymer chains in the gel allows a decreased chain entanglement allowing greater linear chain conformations to occur as the fiber is drawn.

Some low orientation polymers exhibit what is referred to as necking. In necking, a filament extends preferentially at only selected sites known as necks or necking sites. This behavior occurs with many thermoplastic materials near their T_g. At lower temperatures brittle fracture may occur at high tensions instead of necking. At higher temperatures filament extension occurs uniformly without preferred necking sites. Commercially, filament extension is carried out at sufficient temperatures to avoid necking. For multifilament yarns, filament elongation is generally carried out by first heating the filament with subsequent application of the stress necessary to stretch it. For monofilaments and tows, the heating and application of the stress occur together.

In addition to centrifugal spinning, several fiber forming techniques are employed in fiber formation, which do not employ a spinneret. In electrostatic spinning a high voltage, generally >5000 V, is applied to a viscous solution of the polymer dissolved in a volatile solvent with a high dielectric constant but low conductivity contained in a fine capillary tube. A stream of filaments emerge from the capillary. These filaments are collected on a suitable surface.

18.1.2 NONSPINNING FIBER PRODUCTION

Fibers can also be made using specific conditions employing blow molding of a melt. They can also be mechanically made by machining. Thus, polytetrafluoroethylene fibers are made by machining a thin film from a block of the polymer and then drawing the film at 300°C.

Fibers can be made by directly pulling some of the polymer from the melt. Similarly, fibers can be made using the interfacial process with fibers formed as a reaction of the two coreactants, which occurs at or near the interface. Neither instance has been used in industrial-scale fiber formation.

Fibers are commercially made from uniaxially drawn film. The film is extruded, slit into tapelike strips, drawn, fibrillated, and wound. As in the case of spinning, the drawing produces preferred alignment of the polymer chains along the axis of pull. If the drawing precedes slitting, the fiber gives some cross orientation and is less apt to split.

Fibrillation can be achieved mechanically by drawing and pulling thin sheets of polymer. This is compounded if twisting is also involved. A rough idea of this process can be demonstrated by cutting several ribbons of film from a trash bag. Take one and pull. It will elongate and eventually form a somewhat thick filament-like material. Do the same to another strip but also twist it.

Film can be heated and/or stretched and cut eventually giving filament-like materials. Unfibrillated slit-film materials are used in weaving sacks and other packaging. Randomly fibrillated slit-film material is used to make twines and ropes, while controlled fibrillated material is used to make yarns for use in carpet backings and furnishing fabrics.

Whiskers can be made of some metals from simple scraping of the metal to form filament-like whiskers of high strength. Carraher and coworkers produced a number of metal-containing polymers, generally rigid and rodlike, which spontaneously form fiber-like structures from the reaction solution or when mechanically agitated, form fiber-like organizations.

18.1.2.1 Natural Fibers

Most plant and animal materials contain natural fibers that have been concerted into useful fibers for thousands of years including ropes, building materials, brushes, textiles, and brushes (Table 18.6). Animal protein fibers such as wool and silk are no longer competitive with synthetic fibers with respect to cost but are still often utilized in the production of high-end rugs. Some of these rugs are hundreds of years old yet retaining their color and physical properties.

Plant fibers such as cotton, abaca, agave, flax, hemp, kapok, jute, kenaf, and ramie are still in use but even cotton is no longer "king."

TABLE 18.6
Common Natural Sources of Fibers

Animal	Vegetable
Alpaca	Cotton
Angora	Hemp
Camel	Jute
Cashmere	Linen
Mohair	Ramie
Silk	Sisal
Vicuna	
Wool	
Mineral	**Derived from Plants**
Asbestos	Paper
Fiber glass	Rayon (and related materials)
Metal-intense whiskers, fibers	Modal

Regenerated proteins from casein (lanital), peanuts (ardil), soybeans (aralac), and zine (vicara) are used as specialty fibers. Regenerated and modified cellulose products, including acetate, are still widely used today and the production of fibers is similar to that described above for synthetic fiber production. Most regenerated cellulose (rayon) is produced by the viscose process where an aqueous solution of the sodium salt of cellulose xanthate is precipitated in an acid bath. The relatively weak fibers produced by this wet spinning process are stretched to produce strong rayon.

18.2 ELASTOMERS

Before World War II, hevea rubber accounted for over 99% of all elastomers used, but synthetic elastomers account for more than 70% of all rubber used today. NR and many synthetic elastomers are available in latex form. The latex may be used, as such, for adhering carpet fibers or for dipped articles, such as gloves, but most of the latex is coagulated and the dried coagulant used for the production of tires and mechanical goods.

Over 5.5 billion pounds of synthetic rubber is produced annually in the United States. The principle elastomer is the copolymer of butadiene (75%) and styrene (25) (SBR) produced at an annual rate of over 1 million tons by the emulsion polymerization of butadiene and styrene. The copolymer of butadiene and acrylonitrile (Buna-H, NBR) is also produced by the emulsion process at an annual rate of about 200 million pounds. Likewise, neoprene is produced by the emulsion polymerization of chloroprene at an annual rate of over 125,000 t. Butyl rubber is produced by the low-temperature cationic copolymerization of isobutylene (90%) and isoprene (10%) at an annual rate of about 150,000 t. Polybutadiene, polyisoprene, and EPDM are produced by the anionic polymerization of about 600,000, 100,000, and 350,000 t, respectively. Many other elastomers are also produced.

18.2.1 ELASTOMER PROCESSING

The processing of elastomeric (rubbery) material is quite varied and dependent on the end use, form of the material (dry or in solution) and material processed. Latex forms of rubber can be properly mixed with additives using simple (or more complex) stirring and agitation. The mixing or agitation should be such as to not cause a separation or breakdown of the latex or foam formation. Straight, coagulant, and heat-assisted dipping processes are commonly used to produce a variety of tubes, gloves, etc. Latexes are also used to make thread for the garment industry, and adhesives for shoes, carpets, and tape formation.

We will look at the processing involving bulk rubber. The manufacture of rubber products from this material can be divided into four steps:

1. Mastication
2. Incorporation or compounding
3. Shaping
4. Vulcanization

The shaping and vulcanization steps are combined in a number of processes such as transfer or injection molding or may be separated as in the extrusion and subsequent vulcanization sequence. An outline of these steps is given in Figure 18.4.

We will look at the processing of natural dry rubber first since its processing is similar to other elastomers and because of its historical importance. NR is a dispersion of rubber particles in water. Unvulcanized raw rubber obtained by coagulation and drying has large chains with chain lengths on the order of 10^5 carbons.

Mastication is intended to bring the material to the necessary consistency to accept the compounding ingredients. Mastication results in a lowering of chain size to an average chain length on the order of 10^4 carbons. Two basic types of internal mixers are used. The Banbury has rotors rotating at different speeds creating a “kneading” action such as that employed in handling bread dough. A shearing action between the rotors and the walls of the mixer is also achieved. The Shaw Intermix employs rotors that turn at the same speed and closely intermesh causing an intracompound friction for mixing, thus closely resembling a mill’s mixing action.

The next step is the incorporation of various additives—compounding. Typical additives include fillers, processing aids, activators, age resistors, sulfur, antioxidants, and antiozone compounds, extenders, plasticizers, blowing agents, pigments, and accelerators.

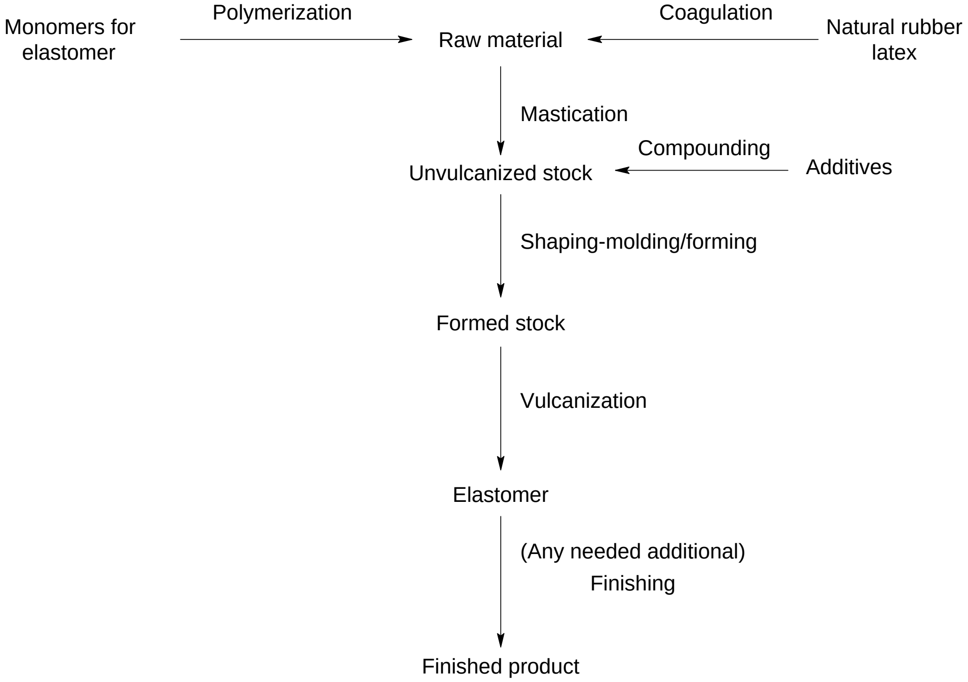


FIGURE 18.4 Outline of steps involved in the processing to form elastomeric materials.

An important aspect in the compounding is the amount of crystallization of the rubber. If the rubber is in a highly crystalline state, it will mix poorly if at all. Thus, partially crystallized rubber must be heated before it will yield to mixing.

Stabilizers are materials that help the rubber withstand oxidative aging and ozone attack. They act by intercepting the active free radicals breaking the free radical-associated degradation process. Amines and phenols are generally employed. Reinforcing fillers, of which carbon black is the most important, are added to improve the mechanical properties such as hardness, abrasion resistance, modulus, and tear resistance. It is believed that the rubber adheres to the carbon surface. Carbon black also helps in retarding UV degradation and increases the electrical conductivity, reducing triboelectric charging and acting as an antistatic material.

NR can be compounded without fillers to give a vulcanized material with high elongation (about 800%) and high tensile strength (about 28 MPa)

The internal mixers fragment the large rubber molecules by high shear forces. Depending on the particular assembly and ingredients the created free radicals can combine to give larger molecules or may form smaller chains. Breakdown is often assisted by the use of chemical peptizers such as thiophenols, mixtures of salts of saturated fatty acids, and aromatic disulfides. The fatty acids mainly generally act as dispersing agents and processing aids.

The viscous prerubber is now shaped by addition to a mold of the desired shape. Addition can be achieved by simply pouring the material into the mold but usually the material is added to the mold employing the usual molding addition (extrusion, compression, and transfer) techniques. The material can also be treated using most of the other "thermoplastic" processing techniques such as calendering, coating, and extrusion.

The material is now heated to cure, set, or vulcanize (all terms are appropriate) the material into the (typically) finished shape. Between 1% and 5% of sulfur (by weight) is added in typical black rubber mixes giving a vulcanized material with an average of about 500 carbon atoms between cross-links. Larger amounts of sulfur will give a tougher material eventually giving a somewhat brittle, but quite strong, ebonite as the amount of sulfur is increased to about 40%. Sometimes additional finishing may be desirable including painting, machining, grinding, and cutting.

These steps are typical for most of the synthetic elastomers. The use of sulfur for vulcanization is common for the production of most elastomers. Magnesium and zinc oxides are often used for the cross-linking of polychloroprene (CR). Saturated materials such as EPM and fluoroelastomers are cross-linked using typical organic cross-linking agents such as peroxides.

Carbon black is widely used as a reinforcing agent for most synthetic elastomers. It is especially important for synthetic elastomers such as SBR, nitrile rubber (NBR), and BR that do not crystallize at high strains. Thus, non-carbon-filled SBR has a tensile strength of about 2 MPa and with addition of carbon black this increases to about 20 MPa.

The above processing applies to the processing of typical bulk carbon backbone-intensive elastomers. Other important classes of elastomers are also available. PUs represent a broad range of elastomeric materials. Most PUs are either hydroxyl- or isocyanate-terminated. Three groups of urethane elastomers are commercially produced. Millabile elastomers are produced from the curing of the isocyanate group using trifunctional glycols. These elastomers are made from high polymers made by the chain extension of the PU through reaction of the terminal isocyanate groups with a polyether or polyester. Low molecular weight isocyanate terminated PUs are cured through a combination of chain extension by reaction with a hydroxyl-terminated polyether or polyester and trifunctional glycols giving cast elastomers. Thermoplastic elastomers are block copolymers formed from the reaction of isocyanate-terminated PUs with hydroxyl-terminated polyethers or polyesters. These are generally processed as thermoplastic materials as are the thermoplastic elastomers. Many of these materials have little or no chemical cross-linking. The elastomeric behavior is due to the presence of physical hard domains that act as cross-links. Thus, SBR consists of soft butadiene blocks sandwiched between PS hard blocks. These hard blocks also act as a well-dispersed fine-particle reinforcing material increasing the tensile strength and modulus. The effectiveness of these hard blocks greatly decreases above the T_g (about 100°C) of PS.

Polysiloxanes (silicons) form another group of important elastomers. Again, processing typically does not involve either carbon black or sulfur.

18.3 FILMS AND SHEETS

Films, such as regenerated cellulose (cellophane), are produced by precipitating a polymeric solution after it has passed through a slit die. Other films, such as cellulose acetate, are cast from a solution of the polymers, but most films are produced by the extrusion process. Some relatively thick films and coextruded films are extruded through a flat slit die, but most thermoplastic films, such as PE film, are produced by air-blowing a warm extruded tube as it emerges from a circular die (Figure 18.5). Films and sheets are also produced employing calendering. Calendering is also used to apply coatings to textiles or other supporting material.

The most widely used films are LDPE, cellophane, PET, PVC, cellulose acetate, polyfluorocarbons, nylons, PP, PS, and Saran. The strength of many films is improved by biaxial orientation, stretching. Most of the thermoplastics used as films may also be extruded as

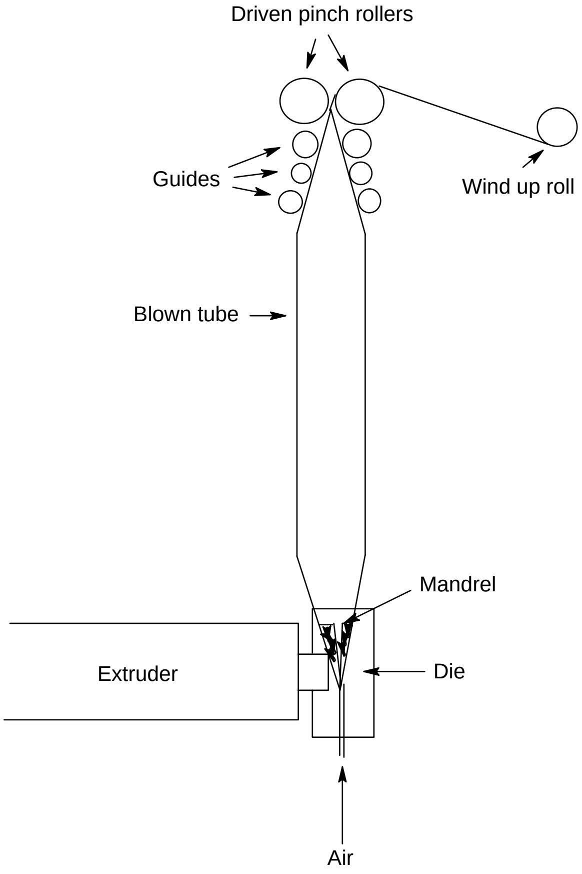


FIGURE 18.5 Film formation employing extrusion.

relatively thick sheets. These sheets may also be produced by pressing a stack of film at elevated temperature (laminating) or by the calendering process.

Wire is coated by being passed through a plastic extruder, but most materials are coated with solutions, emulsions, or hot powders. The classic brushing process has been replaced by roll coating, spraying, and hot powder coating. The application of polymers from water dispersions to large objects, such as automobile frames, has been improved by electrodepositon of the polymer onto the metal surface.

Printing inks are highly filled solutions of resins. The classic printing inks were drying oil-based systems but the trend in this almost billion-dollar business is towards solvent-free inks.

18.3.1 Calendering

Calendering is simply the squeezing or extruding of a material between pairs of corotating, parallel rollers to form film and sheets. It can also be used to mix and impregnate such as in the case of embedding fiber into slightly melted matrix material to form impregnated composite tapes. It can also be used to combine sheets of material such as sheets of impregnated paper and fiber woven and nonwoven mats to form laminar composite materials. It is also used in processing certain rubber material and textiles. Calendering is also employed in conjunction with other processing techniques such as extrusion in the formation of films from extruded material. It is also used to coat, seal, laminate, sandwich, finish, and emboss.

The major bulk processed thermoplastic using calendering is PVC sheets and films including blends and copolymers. A sample recipe to produce PVC sheet might include a plasticizer such as a dialkyl phthalate, pigment, filler, lubricant, and stabilizer.

Because of the variation in flexibility, the terms film and sheet vary with materials. For PVC, films have a thickness of 6 mil (0.15 mm) and less while sheets are thicker than this. While PVC is relatively rigid with a tensile modulus greater than about 690 MPa (105 psi), thin films are easily folded. Films are generally shipped as rolls with the PVC rolled around a central rigid core. Sheets are generally shipped as flat layered sheets.

A partial flow chart illustrates the particular features of the production of a PVC sheet as follows:

Raw materials → Mixing of raw materials in the specified amounts (with heating) → Cooling → Milling–powdering chipping of mixed material → Feeding of stock into first calender nip → Calendering → Stripping and drawdown (if needed) → Embossing (if needed) → Relaxing and tempering → Cooling → Trimming (if needed) → Stacking (or continued processing) → Quality control → Sales → Fabrication into final product

In addition to controlling the recipe materials and PVC properties including molecular weight and molecular weight distribution, the major processing considerations are:

- Calender speed
- Temperature
- Thickness or gauge
- Orientation
- Finish
- Embossing

Films and thin sheets are typically drawn to impart additional unidimensional strength. For films, both unidirectional and bidirectional drawing is used.

18.4 POLYMERIC FOAMS

Until 1920, the only flexible foam available was the natural sponge, but chemically foamed rubber and mechanically foamed rubber latex were introduced before World War II. These foams may consist of discrete unit cells (unicellular, closed cell), or they may be composed of interconnecting cells (multicellular, open cells) depending on the viscosity of the system at the time the blowing agent is introduced. Over 1.5 million tons of foamed plastic is produced annually in the United States.

Unicellular foams are used for insulation, buoyancy, and flotation applications, while multicellular foams are used for upholstery, carpet backing, and laminated textiles. Expanded PS (Styrofoam), which is produced by the extrusion of PS beads containing a volatile liquid, is used to produce low-density moldings such as foamed drinking cups and insulation boards. Foamed products are also produced from PVC, LDPE, urea resins, ABS, and PU. PU foams are versatile materials, which range from hard (rigid) to soft (flexible). These are produced by the reaction of a polyol and a diisocyanate.

18.5 REINFORCED PLASTICS (COMPOSITES) AND LAMINATES

18.5.1 Composites

Theoretical and material considerations for composites are dealt with in Chapter 8. Here we will focus more on processing considerations.

Composites are generally composed of two phases, one called the *continuous* or *matrix phase*, which surrounds the *discontinuous* or *dispersed phase*. There are a variety of polymer-intense composites that can be classified as shown in Figure 18.6.

Many of these composite groups are used in combination with other materials including different types of composites and like types of composites except differing in orientation.

Many naturally occurring materials such as wood are reinforced composites consisting of a resinous continuous phase and a fibrous discontinuous reinforcing phase (Table 18.7).

Composites are also used extensively where light but very strong materials are needed such as in the construction of the new Boeing 767 where composites play a critical role in the construction of the exterior. They are also used where excessive high heat stability is needed such as in the reusable space vehicle (Figure 18.7).

Here we will briefly look at each of the main groupings of composites.

18.5.2 Particle-Reinforced Composites—Large-Particle Composites

Some materials to which fillers have been added can be considered composites. These include a number of the so-called cements including concrete (Section 12.2). As long as the added particles are relatively small, of roughly the same size, and evenly distributed throughout the mixture, there can be a reinforcing effect. The major materials in Portland cement concrete

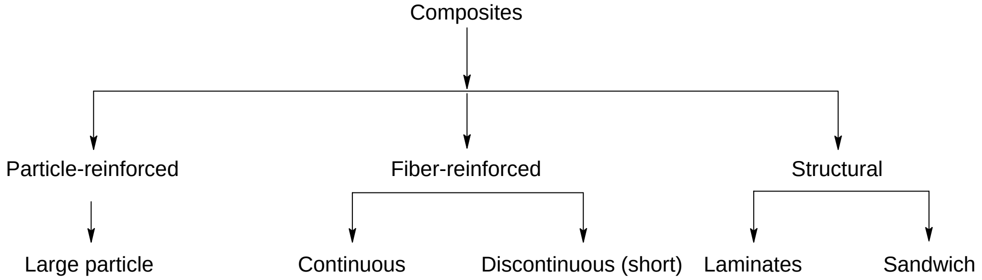


FIGURE 18.6 Classification of polymer-intense composites.

TABLE 18.7
Materials Used for Heat Protection in the Space Shuttle Orbiter. The Locations Are Given in Figure 18.7

Identifier	Maximum Operating Temperature (°C)	Description of Material
Advanced flexible reusable surface insulation	810	Quartz batting sandwiched between AFRSI quartz and fibrous glass fabric
Felt reusable surface insulation	400	Nylon felt with a silicone rubber FRSI coating
High-temperature reusable surface insulation	1250	Silica tiles, borosilicate glass coating insulation HRSI with silicon boride added
Low-temperature reusable surface	650	Silica tiles with a borosilicate coating insulation–LRSI
Reinforced carbon–carbon–RCC	1650	Pyrolized carbon–carbon coated with silicon carbide (SiC)

are the Portland cement, a fine aggregate (sand), course aggregate (gravel and small rocks), and water. The aggregate particles act as inexpensive fillers. The water is also inexpensive. The relatively expensive material is the Portland cement. Good strength is gained by having a mixture of these such that there is a dense packing of the aggregates and good interfacial contact, both achieved by having a mixture of aggregate sizes—thus the use of large gravel and small sand. The sand helps fill the voids between the various larger gravel particles. Mixing and contact is achieved with the correct amount of water. Enough water must be present to allow a wetting of the surfaces to occur along with providing some of the reactants for the setting up of the cement. Too much water creates large voids and weakens the concrete.

18.5.3 FIBER-REINFORCED COMPOSITES

Mathematically the critical fiber length necessary for effective strengthening and stiffening can be described as follows:

$$\begin{aligned}\text{Critical fiber length} &= [\text{Ultimate or tensile strength} \times \text{fiber diameter}/2]\\ &\quad \times \text{the fiber-matrix bond strength or the shear yield strength}\\ &\quad \text{of the matrix — whichever is smaller}\end{aligned}$$

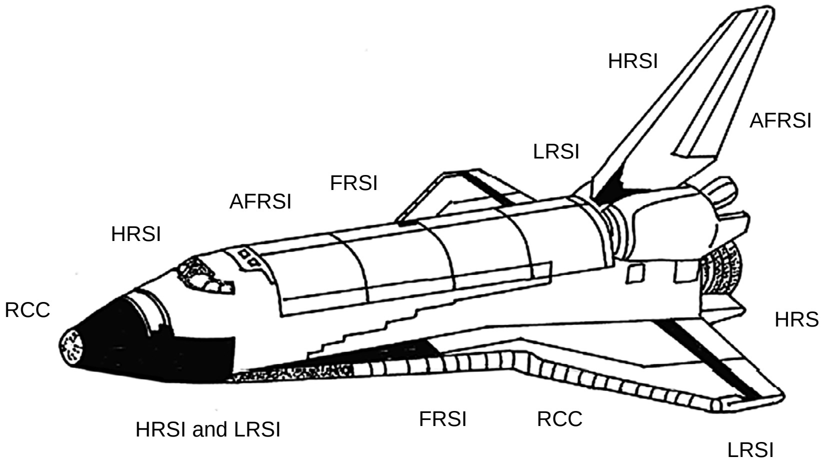


FIGURE 18.7 Location of various advanced materials, including composites, employed for heat protection in the Space Shuttle Orbiter. The descriptions of the materials are given in Table 18.7.

Fibers whose length is greater than this critical fiber length are called continuous fibers, while those that are less than this critical length are called discontinuous or short fibers. Little transference of stress and thus little reinforcement is achieved for short fibers. So, fibers whose lengths exceed the critical fiber length are used.

Fibers can be divided according to their diameters. Whiskers are very thin single crystals that have large length/diameter ratios. They have a high degree of crystalline perfection and are essentially flawless. They are one of the strongest materials known. Whisker materials include graphite, silicon carbide, aluminum oxide, and silicon nitride. Fine wires of tungsten, steel, and molybdenum are also used but here, even though they are fine relative to other metal wires, they have large diameters. The most used fibers are those that are either crystalline or amorphous or semicrystalline with small diameters.

18.5.3.1 Processing of Fiber-Reinforced Composites

There exists a wide variety of particular operations but briefly they can be described in terms of filament winding, preimpregnation of the fiber with the partially cured resin, and pultrusion, which is used to produce rods, tubes, beams, etc. with continuous fibers that have a constant cross-sectional shape. The fiber (as a continuous fiber bundle, weave or tow) is impregnated with a thermosetting resin and pulled through a die that shapes and establishes the fiber/resin ratio. This stock is then pulled though a curing die that can machine or cut producing the final shape such as filled, and hollow tubes and sheets.

The term used for continuous fiber reinforcement *preimpregnation* with a polymer resin that is only partially cured is "prepreg." Prepreg material is generally delivered to the customer in the form of a tape. The customer then molds and forms the tape material into the desired shape finally curing the material without having to use any additional resin. Preparation of the prepreg can be carried out using a calendering process. Briefly, fiber from many spools are sandwiched and pressed between sheets of heated resin with the resin heated to allow impregnation but not so high as to be very fluid.

Thus, the fiber is impregnated in the partially cured resin. Depending upon the assembly the fiber is usually unidirectional, but can be made so that the fibers are bidirectional or some other combination. The process of fitting the prepreg into, generally onto, the mold is called "lay-up." Generally a number of layers of prepreg are used. The lay-up may be done by hand, called hand lay-up, or done automatically, or some combination of automatic and hand lay-up. As expected, hand lay-up is more costly but is needed where one-of-a-kind products are produced.

In filament winding the fiber is wound to form a desired pattern, usually but not necessarily hollow and cylindrical. The fiber is passed through the resin and then spun onto a mandrel. After the desired number of layers of fiber is added, it is cured. Prepregs can be filament-wound. With the advent of new machinery, complex shapes, and designs of the filament can be readily wound.

18.5.4 STRUCTURAL COMPOSITES

Structural composites can be combinations of homogeneous and composite materials. Laminar composites are composed of two-dimensional sheets that generally have a preferred high-strength direction. The layers are stacked so that the preferred high-strength directions are different, generally at right angles to one another. The composition is held together by a resin. This resin can be applied as simply an adhesive to the various surfaces of the individual sheets or the sheet can be soaked in the resin before laying them together. In either case, the bonding is usually of a physical type. Plywood is an example of a laminar composite. Laminar fibrous glass sheets are included as part of the modern ski construction. These fibrous glass sheets are fiber-reinforced composites used together as laminar composites.

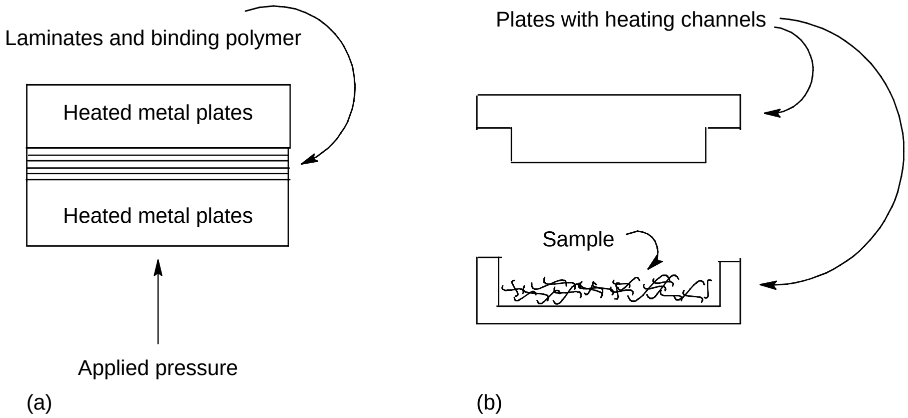


FIGURE 18.8 Assembly employed for the fabrication of laminates (a) and reinforced plastics (b).

Laminar materials are produced by a variety of techniques. Coextrusion blow molding produces a number of common food containers that consist of multilayers such as layers consisting of PP/adhesive/PVA/adhesive/adhesive/PP.

Sandwich composites are combinations where a central core(s) is surrounded generally by stronger outer layers. Sandwich composites are present in the modern ski and as high-temperature stable materials used in the space program. Some cores are very, light acting somewhat like a filler with respect to high strength, with the strength provided by the outer panels. Simple corrugated cardboard is an example of a honeycomb core sandwich structure except that the outer paper-intense layers are not particularly strong. Even in the case of similar PE and PP corrugated structures, the outer layers are not appreciatively stronger than the inner layer. In these cases the combination acts to give a lightweight but strong combination, although they are not truly composites but simply exploit a common construction.

18.5.4.1 Laminating

Laminating is a simple binding together of different layers of materials. The binding materials are often thermosetting plastics and resins. The materials to be bound together can be paper, cloth, wood, or fibrous glass. These are often referred to as the reinforcing materials. Typically sheets, impregnated by a binding material, are stacked between highly polished metal plates, subjected to high pressure and heat in a hydraulic press producing a bonded product, which may be subsequently treated, depending on its final use (Figure 18.8a). The end product may be flat, rod-shaped, tubular, rounded, or some other formed shape.

Reinforced plastics differ from high-pressure laminates in that little or no pressure is employed. For instance, in making formed shapes, impregnated reinforcing material is cut to a desired shape, the various layers are added to a mold, and the molding is completed by heating the mold (Figure 18.8b). This process is favored over the high-pressure process because of the use of a simpler, lower-cost mold and production of strain-free products.

18.6 MOLDING

Molding is a general technique that can be used with plastics and thermosetting materials when employing mobile prepolymer. Molding is used to produce sheetlike, foamed, hollow, or solid materials from very small to very large objects. Here we will look at various molding processes.

18.6.1 Injection Molding

The most widely employed processing techniques for thermoplastics are extrusion and injection molding. Injection molding is also used to produce some thermoset products utilizing fluid prepolymer.

Injection molding involves forcing, injecting, a molten polymer into a mold where it cools becoming solid. The mold separates allowing the molded material to be released. The mold parts are again joined and the process restarts.

Injection molding allows the rapid, economical production of small to large parts. It provides close tolerances and the same machine can be used to mold many different articles. Parts can be molded combining the polymer with other polymers and with any number of additives. Further, it can be run so that various parts can be easily married as part of an entire or combined-parts production assembly of an article. The ability to easily modify the operating conditions of the injection-molding machine is important because of the variety of articles that may be needed, variety of material employed to produce the same (general) article, variety of materials to produce different injection-molded articles, and the variability of supposedly the same polymer material from batch to batch.

Injection molding is not new. A patent was issued in 1872 for an injection-molding machine for camphor-plasticized CN, celluloid. Almost all of the machines used today are reciprocating or two-stage screw types. Both types employ a reciprocating Archimedean-like screw similar to that of a screw extruder. A few are of the plunger type.

A traditional injection apparatus consists of a hopper, which feeds the molding powder to a heated cylinder where the polymer is melted and forced forward by a reciprocating plunger or screw. The cooled part is ejected when the mold opens and then the cycle is repeated. The molten material passes from the nozzle through a tapered sprue, a channel or runner, and a small gate into the cooled mold cavity. The polymer in the mold is easily broken off at the gate site and the materials in the sprue, runner, and gate are ground and remolded. An illustration of such an injection-molding press is given in Figure 18.9. The hopper (a) feeds the molding powder to a heated cylinder (b) where the polymer is melted and forced forward by a reciprocating plunger (c) (or screw). The molten material advances towards a spreader or torpedo into a cool, closed, (here) two-piece mold (d). The cooled part is ejected when the mold opens and then the cycle is repeated. The molten plastic is passed from the nozzle through a tapered sprue, runner, and a small gate into the cooled mold cavity. The plastic in

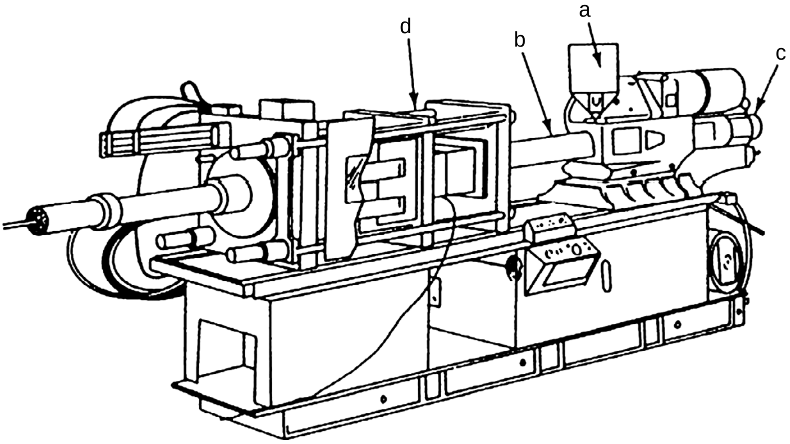


FIGURE 18.9 Cross section of an injection-molding press. (From Seymour, R., *Modern Plastics Technology*, Reston Publishing, Reston, VA, 1975. With permission.)

the narrow gate section is easily broken off and excess material remaining within the sprue, runner, and gate are ground and remolded.

In a reciprocating screw machine, the material is collected in front of the screw, which continues to move backwards as additional material is melted. The area where the melted material is collected corresponds to the heating chamber or pot in a two-stage system. The material is melted by the internally generated heat caused by the friction of the polymer segments and chains rubbing against one another. The screw is also good at mixing so that additive introduction and mixing of different polymers can be achieved in the same step with overall polymer melting.

As the size of the molded product becomes larger it is more difficult to control uniformity and to maintain a sufficient clamping force to keep the mold closed during filling. RIM overcomes these problems by largely carrying out the polymerization reaction in the mold. The most widely used RIM materials are PU and PU-reinforced elastomeric materials. Most of the automotive interior panels (such as dashboards) are produced using RIM.

On a molecular level, partially crystalline to amorphous polymers are normally used. As the material is heated, Brownian motion occurs resulting in a more random chain arrangement. When a unidirectional force is applied to a resting polymer melt, the chains tend to move away from the applied force. If the applied force is slow enough to allow the Brownian movement to continue to keep the polymers in a somewhat random conformation, the movement of the polymer melt is proportional to the applied stress, i.e., the flow is Newtonian.

As the rate of movement increases, chain alignment occurs along the direction of flow with movement too fast for the Brownian factors to return the system to a somewhat random state and flow is then non-Newtonian. Most systems are operated, at least at the injection stage, under non-Newtonian conditions so that some polymer alignment occurs. If the polymer melt flow rate continues to increase, polymer chains align parallel to the flow plane and eventually reach a point where it again becomes Newtonian. Even so, the polymer chains have been aligned as the flow processes move through the non-Newtonian flow range.

As the molten polymer is injected into the cold mold, it rapidly solidifies locking in at least some of the ‘‘orientated’’ chain conformations. As the material enters the cold mold, the flow turbulence occurring with the outermost layers is generally sufficient to result in a more randomized, more amorphous outer structure. As the outermost chains cool, they ‘‘drag’’ the next chains effectively aligning them, giving a more ordered structure. Finally, the cooling of the inner material is slowed because of the heat uptake of the outer layers, allowing Brownian movement to again somewhat randomize these chains. Thus, the structure of the molded part is varied and can be further varied by controlling the flow rate, cooling rate, and flow and cooling temperatures for a specific injection-produced material. Figure 18.10 contains an

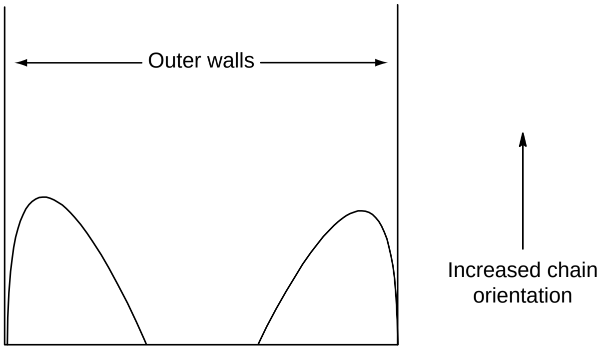


FIGURE 18.10 Idealized relationships between the distance from the outer wall and chain alignment.

idealized relationship between the distance from the outer wall of a tube and the amount of chain aligning.

18.6.2 BLOW MOLDING

Most molded material, as well as most processed material, will have a different surface or skin composition compared with the bulk or core material. Take a look at a common disposable PS foam plate. The surface or skin is smooth. Break it and look at the core and it is different being more cellular. This difference is greater than having simply a difference in appearance. There also exist different fine molecular-level differences. Molecular structure, and associated bulk properties, is controlled in part by the particular processing and processing particulars.

Blow molding has been used for many years in the creation of glass bottles. In about 1872, the blow molding of thermoplastic objects began by the clamping of two sheets of cellulose nitrate between two mold cavities. Steam was injected between the two sheets, softening the sheets and pushing the material against the mold cavities. But, it was not until the late 1950s that large-scale use of blow molding began with the introduction of blow-molded HDPE articles.

Figure 18.11 contains a sketch of an extrusion blow-molding scheme. Here a heat-softened hollow plastic tube, or parison, is forced against the walls of the mold by air pressure. The sequence of material introduction into the mold and subsequent rejection of the material from the mold is generally rapid and automated. Approximately 1 million tons of thermoplastics are produced by this technique annually.

While there are a wide variety of blow-molding techniques, there are three main blow-molding procedures:

- Injection blow molding that employs injection molded "test-tube" shaped preforms or parisons
- Extrusion blow molding that uses an extruded tube preform or parison
- Stretch blow molding that employs an injection molded, extrusion blow-molded preform, or extruded tube preform

The major difference between injection and extrusion blow molding is the way the soft hollow tube (called a preform or parison) is made. In injection blow molding, two different molds are used. One mold forms the preform and the other mold is used in the actual blow-molding operation to give the final shaped article. In the molding process, the softened material preform, from the preform mold, is introduced into the blowing mold and blow-molded to

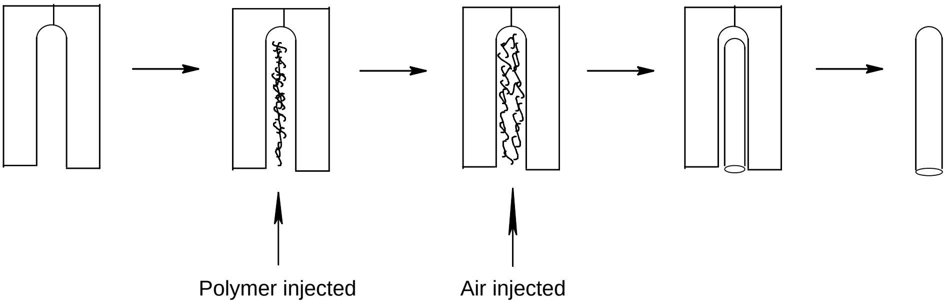


FIGURE 18.11 Steps employed in simple extrusion blow molding of a test tube. From left to right: mold closed; softened material introduced; air or other gas injected forcing the softened thermoplastic against the walls of the mold; and, after suitable cooling, the mold is opened giving the molded plastic test tube.

fit the cavity of the second “finished” blow mold. This process is sometimes also called transfer blow molding because the injected preform is transferred from the preform mold to the final blow mold. This allows better control of the product wall thickness and the thickness of the various curved locations.

Injection blow molding is typically used to produce smaller articles, generally with a total volume of 500 mL or less. Because two molds are used, there is little waste material that must be recycled and there is no bottom weld joint. It allows the production of small articles that at times are very difficult to manufacture in any other way.

Extrusion blow molding is the most common process used to produce hollow articles larger than 250 mL up to about 10,000 L. In extrusion blow molding the softened material is extruded continuously or intermittently. The preform is introduced, the mold halves closed, and air or other gas introduced forcing the preform material against the mold surfaces. After cooling, the mold is opened and the formed article rejected. Articles with handles and off-set necks can be manufactured using extrusion blow molding. Unlike injection blow molding, waste that must be cut away and recycled is produced as the two halves of the mold are pressed together.

In continuous extrusion blow molding, the preform is continuously produced at the same rate as the article is molded, cooled, and released. To avoid interference with the preform formation, the mold-clamping step must be rapid to capture the preform and move it to the blow mold station. There are various modifications of this that allow essentially continuous operation.

The stretching is best done just above the material’s T_g allowing a balance between good alignment because of ease in chain movement, and a decreased tendency to form crystalline areas in the melt allowing ready flow of material. A diagram illustrating this is found in Figure 18.12 for a typical polymer.

In the one-step process, preform production, stretching, and blowing all occur in the same machine. In the two-step sequence, the preform is produced in a separate step. The preform can be stretched before blowing in either the one-step or two-step process. In the one-step process, the preform is simply stretched just before, during, or just after the air is blown into the preform forcing it against the cavity walls.

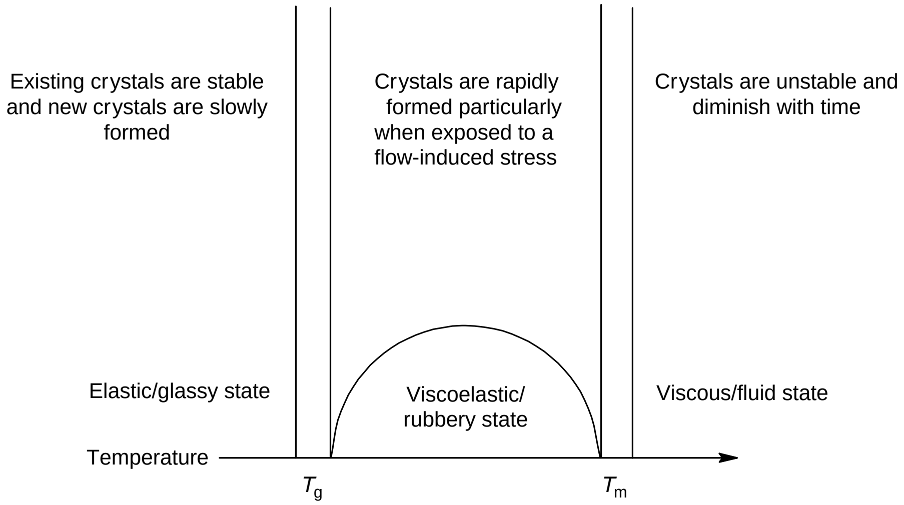


FIGURE 18.12 Idealized formation of order, crystals, as a function of temperature. The raised curve between the T_g and T_m ranges illustrate an idealized rate of crystal formation. This figure is sometimes referred to as the “Molders’ Diagram of Crystallization.”

Multilayered articles can be made by coinjection blow-molding or coextrusion methods. A three-layer system generally contains a barrier layer sandwiched between two “exterior” layers. These are actually laminar products. In the coextrusion sequence, several extruders can be used to place the material into the mold. The multilayer container is then produced from blowing air into the preform.

18.6.3 ROTATIONAL MOLDING

In rotational molding, also known as rotomolding, the mold (or cavity) is filled with material, either as a solid powder or liquid. The mold is closed, placed in a heated oven, and then rotated biaxially. The mold is then cooled, opened, and the article recovered. Powders of about 35 mesh (500 μm) are typical though different sizes are also employed. The distribution of particles and additives is determined by the mixing/rotation ratio.

Almost any mold design can be incorporated into rotational molding. Tanks used for agricultural, chemical, and recreational vehicle industries are made using rotational molding as are containers used for packaging and material handling, battery cases, portable toilets, vacuum cleaner housings, light globes, and garbage containers. Rotational molding produces little waste as well as a material with uniform wall thickness and strong corner sections.

18.6.4 COMPRESSION AND TRANSFER MOLDING

Although there are a number of molding processes, compression and transfer molding are the main techniques for molding articles from thermosetting materials. In compression or transfer molding, the material, thermoplastic or thermoset material, is heated sufficiently to soften or plasticize the material to allow it to enter the mold cavity. The softened material is held against the mold by pressure. For thermoplastics it is then cooled below the T_g thus locking in the shape. For thermosets it is held until the cross-linking occurs thereby locking in the article shape.

The most widely employed molding process is compression molding where the material is placed in the bottom half of an open heated mold. The second half of the mold is closed and brings heat and pressure against the material softening, further and eventually allowing it to cross-link, if it is a thermoset. When completed, the pressure is released and the article removed from the mold. Generally excess material, or flash, is produced. Figure 18.13 contains a representation of a simple compression molding assembly.

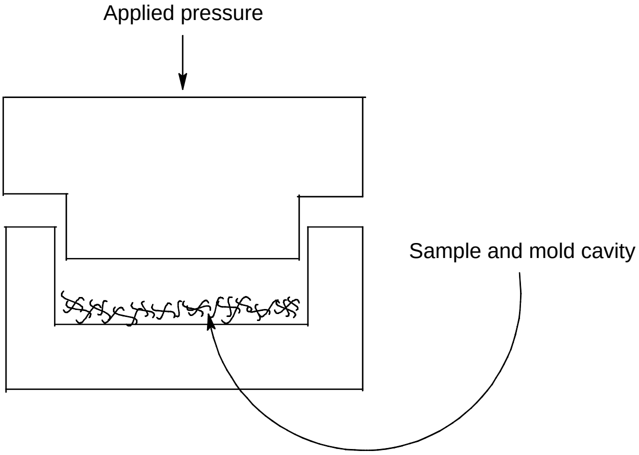


FIGURE 18.13 Representation of a compression molding assembly.

Compression molding is one of the oldest materials handling processes. Ancient Chinese employed compression molding to form articles from paper Mache. Rubber articles were made in the early 19th century from composites of woody fibers and gum shellac. Baekeland used compression molding to make many of his early PF products.

Transfer (or plunger) molding introduces the material to be molded through a small opening or gate after the mold is closed. This process can be used when additional materials, such as a glass globe or other designed object, are placed in the mold before closing the mold.

In true transfer or pot-type molding, the mold is closed and placed in a press. The softened material is introduced into an open port at the top of the mold. The plunger is placed into the pot and the press closed. As the press closes, it pushes against the plunger, forcing the molding material into the mold cavity. Excess molding compound is used to ensure that there is sufficient material to fill the mold. After the material is cured and/or cooled the plunger is removed and the part removed from the mold. In plunger molding, the plunger is part of the press rather than part of the mold. Because of this it can be smaller than the pot-type plunger. The clamping action of the press keeps the mold closed. Here there is less material waste compared with the pot-type molding.

In cold molding, the compound is compacted in a mold at around room temperature. The compressing operation is similar to that employed in the production of KBr pellets from powdered KBr. The compound generally contains a lot of filler and binder. The compacted material is removed from the mold and placed in an oven where it becomes cross-linked. Ceramic materials are often produced using cold molding.

While most molding involves thermosetting materials such as phenol, urea, and melamine–formaldehyde prepolymers, many elastomeric and thermoplastic materials are molded. These include unsaturated polyesters, alkyd resins, epoxies, PVC, silicones, synthetic and natural elastomers, and diallyl phthalate polymers where the molded end products are also generally thermosets. Because all of these materials are good heat-insulating materials, the charge is generally preheated before it is introduced into the mold. With thermosets, slow heating may give cross-linking prior to the desired time, so that rapid heating is preferred followed by fast introduction into the mold. In compression molding, the rapid closing of the mold causes some frictional heating and in transfer molding, frictional heating is produced from the rapid and forced flow of the material, through small gates, into the mold cavity.

Some thermosets are postheated to finish curing allowing better control of the final amount of cross-linking and thus properties. Without postcuring, the product may continue to undergo cross-linking over the next few months giving a material with varying properties over this period of time. Some of the thermosets, particularly the formaldehyde resins, give off some gas during polymerization. These gasses can be retained within the mold increasing the pressure, or released during the process. If the gasses are retained during the process the part can be recovered without noticeable effects, but if it is removed too soon blisters and ruptures may occur as a result of these gasses. However, often the gas is released periodically during the molding process. The time of opening is called the dwell. The step is referred to as breathe and dwell. Timing and duration of the breath and dwell steps are important.

While curing reactions occur at room pressures, it is important for good mold contact to employ high pressures, generally on the order of 20–70 MPa though some molding processes can get by with low pressure (0.7–7 MPa). Under pressure, the molecules behave as non-Newtonian fluids and some ordering occurs. Further, forced flow of polymers and prepolymers into the mold causes some aligning of the molecules. Thus, the fine structure, and associated properties, can be somewhat controlled by flow rates, heating or cooling, curing rate and extent, and pressure with speed associated with many of these factors. For instance, if a homogeneous, isotropic-behaving material is wanted, the flow rate into the mold should be slow and flow pathway short. Further, for thermosetting materials, the time that the material is preheated should be low and the rate rapid. Thus, there exist many balances where the end result is reached, not surprisingly, through a mix of science and practice (trial and error). Each machine, mold, and material will present a new opportunity for determining the optimum set of conditions.

In solvent molding, a mold is immersed in a solution and withdrawn, or a mold is filled with a polymer and evaporation or cooling occurs producing an article such as a bathing cap. Solvent molding and casting are closely related.

18.6.5 THERMOFORMING

Thermoforming involves heating a sheet or thick film just above its T_g or T_m, stretching it against a rigid mold, cooling, and trimming the formed part. Inexpensive aluminum, wood, epoxy, and steel molds are often employed. This allows the construction of inexpensive molds that allow the production of low-volume articles. All thermoplastic materials that can be formed into sheets can be thermoformed provided the heating does not exceed the ability of the sheet to support itself.

Thermoforming is employed to convert extruded sheets into smaller items such as packaging containers, plates, trays, bath tubs, pick-up truck liners, freezer liners, cabinetry, and cups. The skin packaging that involves a flexible plastic skin drawn tightly over an article on a card backing is made by thermoforming. Thermoforming permits the production of small to large articles including those with thin walls such as drinking cups. Thus, thermoforming is employed to produce articles with a relatively high surface/thickness ratio. Figure 18.14 illustrates the operation of a simple plug-assisted vacuum thermoforming assembly.

Multilayered materials can be readily formed using thermoforming including food packaging that may involve inclusion of layers of ethylene–vinyl alcohol copolymers, PS, polyolefins, and/or copolymers of vinylene dichloride and vinyl chloride. Microwavable food trays from (crystallized) PET are manufactured using thermoforming.

PS is the most widely used resin material for thermoforming. HIPS is employed largely in the packaging areas including disposables (foam drinking cups, lids, lunch trays, and food service containers), packaging for medical devices, and food packaging (meat and poultry trays, egg cartons, dairy and delicatessen containers, and barrier packages). ABS is thermoformed to produce more durable articles such as refrigerator inner door liners, recreational vehicle and boat parts, automotive panels, picnic coolers, and luggage exteriors. High-density PE is used in the manufacture of pick-up trucks, golf cart tops, and sleds. Crystallized PET is used in the thermoforming of food trays that can be heated in a microwave or regular oven. Also used to make frozen-food oven-friendly trays is coextruded polycarbonate–polyetherimide. Polycarbonates and PMMA are thermoformed to produce skylights, windows, tub and shower stalls, and outdoor display signs. PVC is used in the production of blister packaging of pharmaceuticals, foods, cosmetics, and hardware.

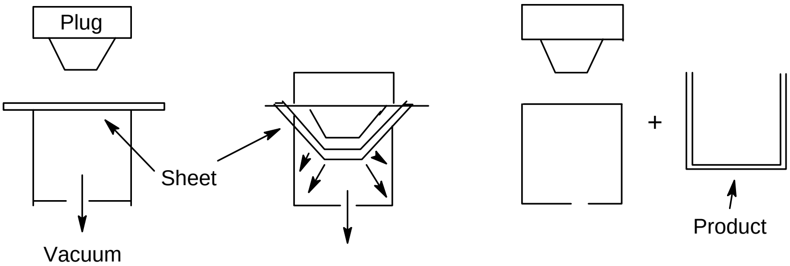


FIGURE 18.14 Steps in plug-assisted vacuum thermoforming. Initially vacuum is applied and the plug is pulled into the sheet pushing it into the mold. Further vacuum pulls the sheet against the walls of the mold. Finally, vacuum is turned off and the plum and formed product removed.

Thermoforming is easily carried out for materials where the "sag" temperature is broad. Amorphous resins such as foamed, oriented, and HIPS, acrylics, and PVC are primary resins employed in thermoforming. Semicrystalline thermoformable resins include both high-density and low-density PE. Control of conditions is more important where the sag temperature range is narrower such as for semicrystalline resins like PP, some polyesters, and fluoropolymers. The range for effective sag can be increased through the introduction of appropriate branching, copolymerization, and addition of selected additives including crystallization modifiers.

Although some molding techniques are adaptable to the production of thermoset materials, thermoforming is carried out using thermoplastic materials.

There are a wide variety of thermoforming techniques in use today.

Vacuum can be used in a process called basic vacuum forming. The sheet is fixed to a frame, heated, and vacuum applied, which implodes the sheet to conform to the mold contour. The vacuum site is generally at the base of the male mold. It cools as it comes into contact with the cold mold. For thick sheets, extra cooling is supplied by means of forced air or mist-sprayed water. Articles formed using vacuum forming typically have thinner walls, the further the sheet must travel to the mold location. The excess plastic material is trimmed and reused. At times vacuum forming is run in-line with a sheeting extruder. It is similar to the plug-assisted system described in Figure 18.14 except no plug is used.

In drape forming, the thermoplastic sheet is clamped and heated and the assembly then sealed over a male mold. The mold may be forced into the sheet or the sheet may be pulled into the mold by introduction of a vacuum between the sealed sheet and mold. By draping the sheet over the mold, the part of the sheet touching the mold remains close to the original thickness. Foamed PS and polyolefins are generally used in this procedure.

In pressure forming, positive pressure is employed to assist the sheet-contents into the mold. The major advantage is a decreased cooling time for pressure forming. Crystalline PS, high-density PE, and oriented PP are used in this procedure.

After the heated sheet is sealed across the mold, a shaped plug is pushed into the sheet, stretching it as it enters into the mold cavity in plug-assisted forming. The plug is generally of such a size and shape as to assist in the formation of the final mold shape and generally occupies about 90% of the mold volume. As it gets near the bottom of the mold, full vacuum is applied.

A variety of the plug-assisted processes are the prestretching-bubble techniques. In pressure-bubble plug-assisted forming, a heated sheet is sealed across a female cavity and pressure is blown through the cavity forcing the sheet from the mold. An "assist-plug" is then forced against the blown bubble with the heated sheet beginning to form about the plug as it forces the sheet against the female mold. As the top part of the mold approaches the female mold bottom, vacuum is applied through the mold causing the material to collapse onto the mold. Alternately, positive pressure can be applied on the "plug" side forcing the sheet against the mold walls. In the reverse of the pressure-bubble technique, called vacuum snapback forming, the heated sheet is sealed against a vacuum female cavity and controlled vacuum draws the concave shaped sheet away from the entering male mold. The male mold is then pressed against the sheet and vacuum applied through the male mold and/or pressure applied from the female cavity side forcing the material against the male mold. Luggage and automotive parts are made using this technique.

In pressure-bubble vacuum snapback, the heated sheet is clamped and sealed against a pressure box. Air is forced through the female pressure box forcing the sheet to push outward from the pressure box. A male mold is then pressed against the bubble and as it pushes into the pressure box, excess air is forced from the pressure box forcing the heated sheet to take the shape of the male mold. The major difference between the vacuum snapback and pressure-bubble vacuum snapback is that in the vacuum snapback process vacuum from a female pressure box distorts the sheet away from the male mold and into the female pressure box, while in the pressure-bubble vacuum snapback excess pressure from the female pressure box forces the heated sheet towards the male mold and away from the female pressure box.

Similar to pressure-bubble vacuum snapback forming, air slip forming seals a heated sheet to the surface of a pressure chamber employing a male mold. It differs in the way the bubble is produced. Here, the heated sheet is clamped above a male mold. Pressure against the mold is created by the upward motion of the male mold towards the sheet causing it to bubble away from the oncoming mold. At the right time, a vacuum is applied through the male mold that causes the sheet material bubble to collapse and form about the male mold.

Trapped-sheet contact heat pressure forming utilizes a heating plate that contains many small vacuum and air pressure holes. A sheet is placed between the heating plate and female mold. Initially, excess air pressure from the mold pushes the sheet into contact with the heating plate. The heating plate then heats the sheet and after desired heating, vacuum is applied from the female and/or pressure applied through the heating plate pulls/pushes the heated sheet material into the female mold. Additional pressure can be used for trimming the article. Candy and cookie box liners and some medical packaging are made using this process.

These bubble-associated processes are aimed at prestretching the heated sheet to allow more even walls and bottoms to be formed.

In matched-mold forming, a heated sheet is placed between a matched female and male mold parts. As the two mold halves close, they distort the sheet to their shape. The air between the mold halves is removed. The article walls are more uniform than for many of the thermoforming techniques. This technique is used for the production of foamed PS and foamed polyolefins food containers.

A number of other techniques have been developed either to handle special materials or to create specific articles.

18.7 CASTING

Casting is employed in making special shapes, sheets, films, tubes, and rods from both thermoplastic and thermoset materials. The essential difference between most molding processes and casting is that no added pressure is employed in casting. In casting, the polymer or prepolymer is heated to a fluid, poured into a mold, cured at a specific temperature, and removed for the mold. Casting of films and sheets can be done on a wheel or belt or by precipitation. In the case of a wheel or belt, the polymer is spread to the desired thickness onto a moving belt as the temperature is increased. The film is dried and then stripped off. “Drying” may occur through solvent evaporation, polymerization, or cross-linking.

18.8 EXTRUSION

Extrusion involves a number of processing operations and is widely used. We will look at extrusion as it is involved in several of these processes. These processing operations are used together or separately. A representative extruder is shown in Figure 18.15. The extruder accepts granulated thermoplastic in a hopper (c), and forces it from the feed throat (d) through a die (f). The die may be circular for the production of a rod or pipe, or flat for the production of a sheet, or it may have any desired profile for the continuous production of almost any uniformly shaped product. The screw (a) advances the polymer through a heated cylinder (barrel) (b) to a breaker plate and protective screen pack (e) before it enters the die (f). The extrusion process may be divided into a feed or transport zone, a compression or transition zone, and a metering zone. Over 1 million tons of extruded pipes are produced annually in the United States.

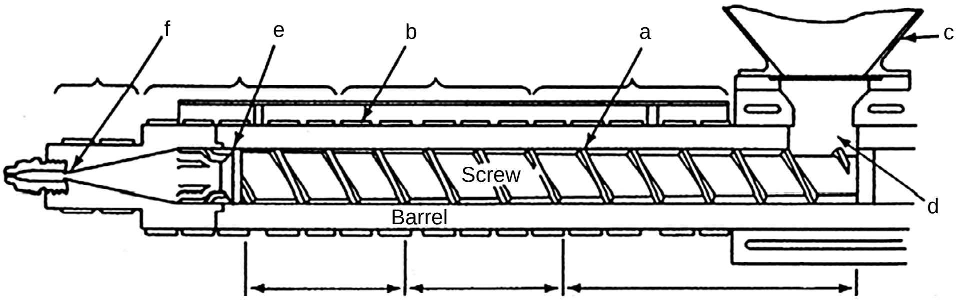


FIGURE 18.15 Sketch details of screw and extruded zones. (From Seymour, R., *Modern Plastics Technology*, Reston Publishing, Reston, VA, 1975. With permission.)

In extrusion, a fluid material, generally rendered fluid through heating, is forced through a shaping device. Since there is a need for quickness and because the preshaped material is quite viscous, extrusion requires high pressure to drive or force the melt through a die. The melts can be extruded as pipes, sheets, films, or poured into molds.

Along with moving and shaping the molten material, extruders also act to disperse additives and are often the agent for creating heat, thus enabling the material to become molten.

18.9 COATINGS

The fundamental purpose of painting is decoration, whereas the purpose of coating is for protection. In truth, we often do not differentiate between the two terms. Government edicts concerning air, water, solid particulates, and worker conditions are having real effects on the coatings industry with the generation of new coating techniques. Paint solvents, in particular, are being looked at in view of increased environmental standards. The volatile organic compound (VOC) regulations under Titles I and VI of the Clean Air Act specify the phasing out of ozone-depleting chemicals—namely chlorinated solvents. Baseline solvent emissions are to be decreased. These, and related regulations, affect the emission of all organic volatiles, whether in coatings or other volatile-containing materials.

A major driving force in coatings continues to be a move towards water-based coatings. Another is to eliminate the "odor" of the coating. Most waterborne coatings actually contain about 8%–10% nonaqueous solvent. The odor we get as the coating is drying is mainly due to this solvent evaporating. Work continues to develop the right balance of properties and materials that will allow the latex particles to flow together and coalesce into suitable films without the need of nonaqueous liquids.

Another area of active research is the development of paints that dry under extreme or unusual conditions including under water and on cool substrates. The latter allows the painting season for exterior coating to be extended, particularly in the northern states.

Work continues in making more durable exterior paints. Remember that there is a difference in requirements of exterior and interior paints. For instance, interior paints are generally required to be faster drying and more durable against scraps and punctures since it is the inside of the house that generally experiences such traumatic events. By comparison, exterior paints need to remain flexible and adhered under a wide variety of humidity and temperature. A more durable exterior coating should allow it a longer lifetime because it can better withstand stress caused by the pounding of the rain, sticks, and human afflicted dings and dents. Binders or coating resins are critical to the performance of coatings. They bind the components together. Since the primary cost of most commercial application of coatings is labor, the market will allow price increases for products that give added positive properties. Table 1.7 contains a listing of the production of paints for the year 2005.

Paint manufacturers in the United States sell about 1450 million gallons of coating material annually or about 5 gal for every man, woman, and child. Paint is typically a mixture of a liquid and one or more colorants (pigments). The liquid is called a vehicle or binder (adhesive) and may include a solvent or thinner along with the coating agent. The colored powders are called pigments, which may be prime or inert. Prime pigments give the paint its color. These may be inorganic, such as titanium dioxide (titanium (IV) oxide—the most widely used pigment by far) for white (but contained in many colored paints as well), iron oxides for browns, yellows, and reds, or organic compounds such as phthalocyanine for greens and blues. Inert pigments such as clay, talc, calcium carbonate, and magnesium silicate make the paint last longer and may contribute to the protective coating as do mica chips in some latex paints that actually form a clad on drying. The paint may also contain special additives and catalysts. Thus, many paints in wet areas contain an agent to fight fungus, rot, and mold.

Vehicles include liquids such as oils (both natural and modified natural) and resins and water. A latex vehicle is made by suspending synthetic resins, such as PMMA, in water. This suspension is called an emulsion, and paints using such vehicles are called latex, waterborne, or emulsion paints. When the vehicle comes in contact with air, it dries or evaporates, leaving behind a solid coating. For latexes, the water evaporates, leaving behind a film of the resin.

Paints are specially formulated for specific purposes and locations. Following is a brief description of the most popular paint types:

- *Oil paints*: Oil paints consist of a suspension of pigments in a drying oil, such as linseed oil. The film is formed by a reaction involving atmospheric oxygen, which polymerizes and cross-links the drying oil. Catalysts may be added to promote the cross-linking reaction. Oil paints, once dried, are no longer soluble, although they can be removed through polymer degradation using the appropriate paint stripper.
- *Oil varnishes*: Varnish coatings consist of a polymer, either natural or synthetic, dissolved in a drying oil together with appropriate additives such as catalysts to promote cross-linking with oxygen. When dried, they produce a clear, tough film. The drying oil is generally incorporated, along with the dissolved polymer, into the coating.
- *Enamels*: Classical enamel is an oil varnish with a pigment added. The added polymer is typically selected to provide a harder, glossier coating than the oil varnish mixture. Today, there are latex enamels that are similar to the oil enamels except that no natural oil is present.
- *Lacquers*: Lacquers consist of polymer solutions to which pigments have been added. The film is formed through simple evaporation of the solvent leaving the polymer film as the coating. These coatings are formed without subsequent cross-linking; thus the surface exhibits poor resistance to some organic solvents.
- *Latex paints*: Latex paints today account for more than one-half of the commercial paint sold. They are characterized by quick drying (generally several minutes to several hours), little order, and easy cleanup (with water). Latex paints are polymer latexes to which pigments have been added. The film is formed by coalescence of the polymer particles on evaporation of the water. The polymer itself is not water soluble, though these paints are called waterborne coatings.

18.9.1 PROCESSING

Many different processes are used to apply a thin layer of liquid-melted polymer, polymer solution or dispersion including rollers, spraying, calendering, and brushing. Here we will look at the industrial application of coatings onto film and sheetlike materials. Figure 18.16

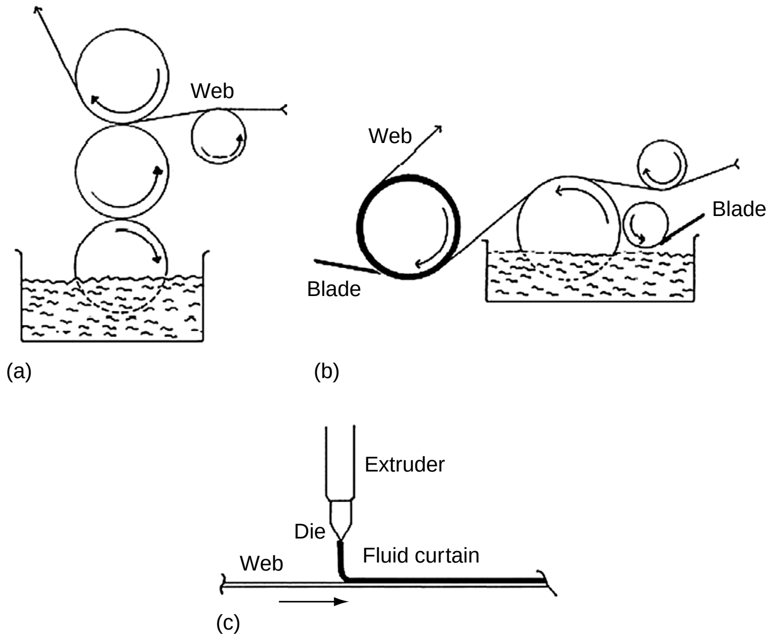


FIGURE 18.16 Three principal industrial coatings processes for films and thin sheets: (a) roll coating; (b) blade coating; and (c) curtain coating.

contains examples of general coating processes employed to achieve this. The moving sheet is called a web. In roll coating (Figure 18.16a) the lower roller picks up the coating material, transfers it to the second roller, and finally to one surface of the mat. Spacing of the rollers, viscosity of the polymer solution in the dip tank, and roller speed and size control the thickness of the applied coating.

In blade coating (Figure 18.16b), a flexible blade helps control the coating thickness. The blade may be located after the bath or within the bath as part of the roller system. The blade is flexible and adjustable so that the amount of coating material can be controlled by application of force on the blade and/or by the distance at which the blade is from the web or roller. Both these processes are forms of calendering. The third main coating process involves direct application of the coating material, forming a so-called fluid curtain (Figure 18.16c). This process, curtain coating, is usually used in conjunction with a curing process. The coating thickness is controlled by web speed, polymer concentration, and rate of application from the extruder.

Coatings can be divided according to formulation, drying mechanism or other system of categorizing. Table 18.8 contains a summary of coatings according to drying mechanism.

A coating is normally a mixture of various components. For instance, the label on a latex emulsion-type paint might have as major components PMMA, titanium dioxide as the white pigment, and water. It could also have china clay and calcium carbonate as extenders, carboxymethylcellulose as a colloid thickener, a defoaming agent, a plasticizer, a surfactant-dispersing aid, additional coloring agents, and an added fungicide.

The hiding power is a measure of the ability of the coating to achieve a specified degree of "hiding" or obliteration. Industrially, it is often tested by comparing the reflectance of the coated surface overpainting a black surface (i.e., the tested paint applied over a black surface) with white panels. The ability to cover or hide is related to the scattering of incident light hitting the surface and returning to the observer or light meter. As the film surface increases, the ability of light to penetrate the surface coating and be scattered from the (black for tests)

TABLE 18.8
Major Coatings Systems as a Function of Drying Mechanism

A. Film formation through chemical reaction
  (a) Through reaction of unsaturated double-bond sites with oxygen
    Alkyds
    Drying oils–fatty acid and related
  (b) Cold curing and thermosetting by reaction with vehicle components
    Epoxies
    Polyurethanes
    Unsaturated polyesters
    Urea and melamine–formaldehyde
B. Film formation through evaporation
  (a) Solution types
    Bituminous coatings
    Cellulose derived-acetate, acetate butyrate, ethyl, nitrate
    Chlorinated rubbers
    Poly(acrylic esters) such as poly(methyl methacrylate)
    Poly(vinyl chloride) copolymers
  (b) Dispersion types
    Poly(acrylic esters) such as poly(methyl methacrylate)
    Poly(vinyl acetate) and copolymers
    Poly(vinyl chloride) organosols
    Poly(styrene-co-butadiene)

undercoating lessens. For a simple white latex paint, no absorption occurs and we can consider the scattering occurring at the interfaces of the transparent polymer matrix and the dispersed pigment particles. The scattering coefficient of polymers can be obtained from reflectance measurements. While the refractive indices for most polymers do not widely vary (generally about 1.5), the scattering coefficients can vary widely. For good scattering, the refractive index of the polymer should differ from that of the pigment. For instance, while calcium carbonate, with a refractive index of about 1.6, is often used as a pigment in paints, it has a much lower hiding power than titanium dioxide (rutile titanium (IV) oxide), with a refractive index of about 2.8.

Scattering efficiency increases as the pigment surface area becomes larger, thus smaller particles aid in increasing the scattering to a lower limit determined by the wavelength of light, and thereafter reduced size produces a rapid loss in scattering efficiency. For good scattering, and good hiding power, the particles should be dispersed in a homogeneous manner so that dispersing agents are commonly used.

18.10 ADHESIVES

In contrast to coatings, which must adhere to one surface only, adhesives are used to join two surfaces together. Resinous adhesives were used by the Egyptians at least 6000 years ago for bonding ceramic vessels. Other adhesives, such as casein from milk, starch, sugar, and glues from animals and fish, were first used at least 3500 years ago.

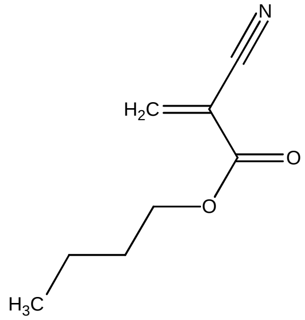
Adhesion occurs generally through one or more of the following mechanisms. Mechanical adhesion with interlocking occurs when the adhesive mixture flows around and into two rough substrate faces. This can be likened to a hook and eye, where the stiff plastic hooks get caught in the fuzz-like maze of more flexible fibers. Chemical adhesion is the bonding of primary chemical groups. Specific or secondary adhesion occurs when hydrogen bonding or polar (dipolar) bonding occurs. Viscosity adhesion occurs when movement is restricted simply due to the viscous nature of the adhesive material.

Adhesives can be divided according to the type of delivery of the adhesive or by type of polymer employed in the adhesive. Following are short summaries of adhesives divided according to these two factors:

- *Solvent-based adhesives*: Solvent-based adhesion occurs through action of the adhesive on the substrate. Solidification occurs on evaporation of the solvent. Bonding is assisted if the solvent partially interacts or, in the case of model airplane glues and PVC piping glues, actually dissolves some of the plastic (the adherent). Thus, model airplane glues and PVC glues often contain volatile solvents that dissolve the plastic, forming what is called a solvent weld. Some of the PVC glues actually contain dissolved PVC to assist in forming a good weld. A major difference between home-use PVC adhesive and industrial PVC adhesive is added color for the commercial adhesive, so building inspectors can rapidly identify that appropriate solvent welding has been accomplished.
- *Latex adhesives*: Latex adhesives are based on polymer latexes and require that the polymers be near their T_g so that they can flow and provide good surface contact when the water evaporates. It is not surprising that the same polymers that are useful as latex paints are also useful as latex adhesives (such as PMMA). Latex adhesives are widely employed for bonding pile to carpet backings.
- *Pressure-sensitive adhesives*: Pressure-sensitive adhesions are actually viscous polymer melts at room temperature. The polymers must be applied at temperatures above their T_g to permit rapid flow. The adhesive is made to flow by application of pressure. When the pressure is removed, the viscosity of the polymer is sufficient to hold and adhere to the surface. Many tapes are of this type where the back is smooth and coated with a nonpolar coating so as not to bond with the sticky surface. The two adhering surfaces can be separated, but only with some difficulty.
- *Hot-melt adhesives*: Hot-melt adhesives are thermoplastics that form good adhesives simply by melting, followed by subsequent cooling after the plastic has filled surface voids. Nylons are frequently employed in this manner. Electric glue guns typically operate on this principle.
- *Reactive adhesives*: Reactive adhesives are either low molecular weight polymers or monomers that solidify by polymerization and/or cross-linking reactions after application. Cyanoacrylates, phenolics, silicon rubbers, and epoxies are examples of this type of adhesive. Plywood is formed from impregnation of thin sheets of wood with resin, with the impregnation occurring after the resin is placed between the wooden sheets.
- *Thermosets*: A number of thermosets have been used as adhesives. Phenolic resins were used as adhesives by Leo Baekeland in the early 1900s. Phenolic resins are still used to bind together thin sheets of wood to make plywood. Urea resins have been used since 1930 as binders for wood chips in the manufacture of particle board. Unsaturated polyester resins are used for body repair and PUs are used to bond polyester cord to rubber in tires, and vinyl film to particle board, and to function as industrial sealants. Epoxy resins are used in the construction of automobiles and aircraft and as a component of plastic cement.
- *Elastomers*: Solutions of NR have been used for laminating textiles for over a century. The Macintosh raincoat, invented in 1825, consisted of two sheets of cotton adhered by an inner layer of natural rubber. SBR is used as an adhesive in carpet backing and packaging. Neoprene (polychloroprene) may be blended with a terpene or phenolic resin and used as a contact adhesive for shoes and furniture.
- *Pressure-sensitive tape*: Pressure-sensitive tape, consisting of a coating of a blend of NR and an ester of glycerol and abietic acid (rosin) on cellophane, was developed over

half a century ago. More recently, NR latex and SR have been used in place of the NR solution. The requirement for pressure-sensitive adhesives is that the elastomers have a T_g below room temperature. Today, there are many other formulations used in the production of pressure-sensitive tapes.

- *Contact adhesives*: Contact adhesives are usually applied to both surfaces, which are then pressed together. Liquid copolymers of butadiene and acrylonitrile with carboxyl end groups are used as contact adhesives in the automotive industry.
- *Thermoplastics*: A number of thermoplastics have been used as adhesives. Polyamides and copolymers of ethylene and vinyl acetate (EVA) are used as melt adhesives. Copolymers of methyl methacrylate and other monomers are used as adhesives in the textile industry. PVAc is often used in school glues.
- *Anaerobic adhesives*: Anaerobic adhesives consist of mixtures of dimethacrylates and hydroperoxides (initiators) that polymerize in the absence of oxygen. They are used for anchoring bolts.
- *Cyanoacrylates*: One of the most interesting and strongly bonded adhesives are cyanoacrylates (Super Glue; Krazy Glue). These monomers, such as butyl-alpha-cyanoacrylate (structure 18.1), polymerize spontaneously in the presence of moist air, producing excellent adhesives. These adhesives, which have both the cyano and ester polar groups, are used for household adhesive problems as well as in surgery, mechanical assemblies, and as a "fast fix" for athletic cuts such as in boxing.



(18.1)

Many seemingly simple adhesive applications are actually complex. The labels on commercial dry cell batteries can contain over a dozen layers each present for a specific purpose. Although price is a major consideration, ease of application is another. Thus, while many naturally derived adhesives are less expensive, synthetic materials may be chosen because of ready application and consistency of the end product.

Important factors involved with pressure-sensitive adhesion are a balance between allowing molecular interaction between the adhesive and adherent (often referred to as "wetting") and the dynamic modulus of the adhesive mixture. This also involves a balance between "pull-off-rate" and "wetting rate." Mechanical adhesion with interlocking and diffusion factors is less important than for permanent adhesion. Pressure-sensitive adhesives present in "pull-off" tabs such as Post-it notes contain components similar to those in more permanent Scotch tape, except that particles of emulsified glass polymer are added to reduce the contact area between the adhesive and the substrate. Some polymers, such as PE, might appear to be decent adhesive materials, but even in its melt, it is not exceptionally tacky. This is believed to be the result of the high degree of chain entanglement. Since the dynamic modulus increases with increasing chain entanglement, PE is not "tacky" (does not easily contact and wet a substrate), and is not a useful pressure-sensitive adhesive.

18.11 SUMMARY

1. The processing of polymeric materials is well advanced in science, engineering, and technology, and continues to advance. The properties of the end product are dependent on the chemical structure, processing, and physical structure. The properties depend on the mesostructure of the particular polymer.
2. Fibers are processed using mainly one of three processes—melt spinning, where the polymer is melted and forced through spinnerets; dry spinning, where the dissolved polymer is forced through a spinneret and the solvent removed; and wet spinning, where the dissolved polymer is forced through a spinneret into a nonsolvent bath. Fibers are usually stretched as they are formed allowing the chains to further align giving added strength in the direction of the pull.
3. Elastomers are processed using four basic steps—mastication, incorporation or compounding, shaping, and vulcanization.
4. Films and sheets are made from precipitation and/or regeneration of a polymer solution or melt. Calendering is also used where the polymer is passed between a series of counterrotating rollers.
5. Unicellular (closed cell, discrete unit cells) and multicellular (open cells, interconnecting cells) foams are made through the chemical and physical introduction of gasses.
6. A wide variety of composites are made. Composites have two phases—the continuous or matrix phase, which surrounds the discontinuous or dispersed phase, usually a fiber material. Composites are strong and have many uses.
7. Molding employs a mobile prepolymer that may be thermoset or using a thermoplastic polymer. The polymer can be injection-molded (often for solid objects), blow-molded (for hollow objects such as bottles), rotation-molded, compression-molded, transfer-molded, or thermoformed. Casting is closely related to molding, except that the pressure is typically not used.
8. In extrusion, a fluid material is forced through a shaping device. The melts are extruded as pipes, sheets, films, or into molds.
9. Coatings and paints are used for decoration and protection. There are many different kinds of coatings with the majority being latex-based where the polymer is present in a suspension that forms a film when the water evaporates. Industrially, coatings are applied using roll coating, blade coating, and curtain coating processes.
10. The difference between coatings and adhesives is that coatings must adhere on only a single surface, but adhesives must bind together two surfaces. There is a wide variety of adhesives that make use of the various polymer properties. Adhesion can occur through physical locking together, through chemical (primary and secondary bond formation) joining, or through simply highly viscous material holding together materials.
11. Polymers are major materials in the nanotechnology revolution, including as conductive (photo and electronic) materials. Delocalization of electrons throughout a polymer chain or matrix is important for electronic conductance. This is often accomplished through doping, which encourages flow of electrons.
12. Polymers are also major materials in the biomedical areas and in the delivery of drugs.
13. For new polymeric materials to enter the marketplace, many things must be in place including a "flagship" property that meets a particular market need, ready availability, and money. It takes about $1 billion to introduce and establish a new polymer into the marketplace.

GLOSSARY

abaca Hemp-like fiber.
acrilan Polyacrylonitrile-based fibers.

acrylic fibers Polyacrylonitrile-based fibers.

adhesive Material that binds, holding together two surfaces.

biaxial orientation Process where a material, normally a film, is stretched in two directions at right angles to each other.

Buna-N Acrylonitrile-butadiene copolymer.

calender Machine for making polymeric sheets using counterrotating rolls.

casting Production of film by evaporation of a polymeric solution.

cellophane Regenerated cellulosic film.

charge Amount of polymer used in each molding or processing cycle.

coextruded film Film produced by the simultaneous extrusion of two or more polymers.

Dacron Trade name for PET fiber.

draw Depth of mold cavity.

drying oils Liquids employed in coatings that will be cured, cross-linked.

dry spinning Process for obtaining fiber by forcing a solution of a polymer through holes in a spinneret and evaporating the solvent from the extruded material (extrudate).

elastomer Rubber.

electrodeposition Use of an electric charge to deposit polymer film or aqueous dispersions onto a metal substrate.

engineering material Material that can be machined, cut, drilled, sawed, etc.; must have sufficient dimensional stability to allow these actions to occur.

extrusion Fabrication process in which a heat-softened polymer is continually forced by a screw through a die.

fibrillation Process for producing fiber by heating and pulling twisted film strips.

filament Continuous thread.

filament winding Process in which filament are dipped in a prepolymer, wound on a mandrel, and cured.

gate Thin sections of runner at the entrance of a mold cavity.

hemp Fiber from plants of the nettle family.

hevea rubber Natural rubber; *Hevea brasiliensis*.

Hycar Trade name for Buna-N elastomer.

jute Plant fiber used for making burlap.

Kodel Trade name for PET fiber.

lacquers Polymer solutions to which pigments have been added.

lamination Plying up of sheets.

latex Stable dispersion of a polymer in water.

mechanical goods Generally industrial rubber products like belts.

melt spinning Process of obtaining fibers by forcing molten polymer through holes in a spinneret and cooling the filaments.

molding powder or compound Premix of resin and other additives used as a molding resin.

multicellular Open celled.

Neoprene Trade name for polychloroprene.

nonwoven textiles Sheet produced by binding fibers with a heated thermoplastic.

oil paints Suspension of pigments in a drying oil.

oil varnish Polymer dissolved in a drying oil.

parison Short plastic tube which is heated and expanded by air in the blow-molding process.

Perlon Trade name for some PU fibers.

photoconductive Material that is conductive when exposed to light.

photoresponsive Material whose properties change when exposed to light.

pigment Coloring material; colorant.

polyacetylene Polymer whose conductivity increases when doped to be a conductor.

printing ink Highly pigmented coatings used in printing.

pultrusion Process in which filaments are dipped in a prepolymer, passed through a die, and cured.

rotational molding Polymer added to a warm, rotating mold; centrifugal force distributes the polymer evenly.

rovings Multiple untwisted strands of filaments.

runner Channel between the spruce and the mold cavity.

screen pack Metal screen that prevents foreign material form reaching the die in an extruder.
specific strength Strength based on mass rather than area.
spinneret Metal plate between the nozzle and runner.
sprue Tapered orifice between nozzle and runner. Term also used to apply to plastic material in the sprue.
structural foams Polymeric foamed article with a dense surface.
Styrofoam Trade name for foamed PS.
technology Applied science.
tenacity Fiber strength.
thermoforming Shaping of a hot thermoplastic sheet.
transfer molding Process in which a preheated briquette or preform is forced through an orifice into a heated mold cavity.
vehicle Liquid in a coating.
wet spinning Obtaining fibers by precipitation of polymeric solutions.

EXERCISES

1. Which is more important: (a) polymer science or (b) polymer technology?
2. Name three important natural fibers.
3. Name an important regenerated fiber.
4. Why is secondary cellulose acetate more widely used than the tertiary cellulose acetate?
5. What is the difference between rayon and cellophane?
6. Name three important synthetic fibers.
7. Name an elastomer produced by (a) cationic, (b) anionic, (c) free-radical, and (d) step-reaction polymerization techniques.
8. How is LDPE film produced?
9. Why is there a trend towards the use of less solvent in polymeric coatings?
10. What is meant by trade sales?
11. What are general steps needed before a new drug comes to market?
12. How would you produce a unicellular foam?
13. Which foam is preferable for upholstery: (a) unicellular or (b) multicellular?
14. Why do non-flame-retardant foams burn readily?
15. Why has reinforced plastic been used as an automobile body?
16. Why is graphite-reinforced epoxy resin a good candidate for parts in future automobiles?
17. Why are molded thermoplastics used more than molded thermosets?
18. Which of the following might you expect would increase their conductivity when doped: (a) PS, (b) PPO, (c) nylon-6,6, or (d) aramids?
19. Why are structural foams used for complex furniture?
20. What are some of the advantages of a blow-molded PET bottle?
21. Why would an article be thermoformed instead of being molded?
22. What is the limit to the length of an extrudate such as PVC pipe?
23. Name three popular laminates.
24. Why are the terms painting and coating often used interchangeably?
25. Why have latex waterborne coatings been popular with the general public?
26. Differentiate between oil paints, oil varnishes, latexes, enamels, and lacquers.
27. Briefly discuss the popular mechanisms related to adhesion and the general types of adhesives.
28. How might the mesophase structure be changed?
29. What is a disadvantage of employing spinning of polymers to form fibers using a nonsolvent bath assembly?
30. Are PU foams closed or opened celled?
31. Name a common laminate found in many kitchens.
32. Why are there so many different kinds of adhesives?
33. What is an advantage to using cyanoacrylates at a crash site?
34. There is a black room that you wish to lighten up by painting it a lighter color. What should you do?

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19 Selected Topics

The previous chapters allowed the weaving of polymer science fundamentals and applications into a carpet necessary for those involved in the sciences, engineering, biology, and biomedicines to understand as they ply their trade. This chapter enhances the areas where an understanding of basic polymer principles is important as polymers are employed in many areas in today's society that is becoming increasingly dependent on polymeric materials.

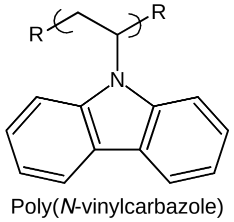
19.1 CONDUCTIVE POLYMERIC MATERIALS

Conductance behavior is dependent on the material and what is conducted. For instance, polymeric materials are considered poor conductors of sound, heat, electricity, and applied forces in comparison with metals. Typical polymers have the ability to transfer and "mute" these factors. For instance, as a force is applied, a polymer network transfers the forces between neighboring parts of the polymer chain and between neighboring chains. Because the polymer matrix is seldom as closely packed as a metal, the various polymer units are able to absorb (mute; absorption through simple translation or movement of polymer atoms, vibrational, and rotational changes) as well as transfer (share) this energy. Similar explanations can be given for the relatively poor conductance of other physical forces.

Even so, polymers can be designed that compete with metals and other nonpolymer materials in the area of conductance. Some of these are described in the following sections. Other materials that act similar to metals in the conductance of specific factors, which are covered elsewhere, are also described. For instance, force transference of ceramics is similar in some ways to that of metals because of a number of factors including the inability of the tightly packed ceramics to mute applied forces and their ability to directly "pass along" the results of such applied forces or stresses.

19.1.1 PHOTOCONDUCTIVE AND PHOTONIC POLYMERS

Some polymeric materials become conductive when illuminated with light. For instance, poly(*N*-vinylcarbazole) is an insulator in the dark, but when exposed to UV radiation it becomes conductive. Addition of electron acceptors and sensitizing dyes allows the photoconductive response to be extended into the visible and near-IR (NIR) regions. In general, such photoconductivity is dependent on the material's ability to create free-charge carriers, electron holes, through absorption of light, and to "move" these carriers when a current is applied.



(19.1)

Poly(*N*-vinylcarbazole)

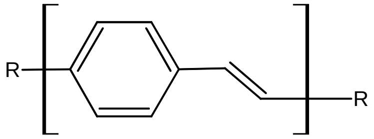
Related to this are materials whose response to applied light varies according to the intensity of the applied light. This kind of behavior is referred to as nonlinear behavior. In general, polymers with whole-chain delocalization or large-area delocalization where electrons are optically excited may exhibit such nonlinear optical behavior.

A photoresponsive sunglass whose color or tint varies with the intensity of the sunlight is an example of nonlinear optical material. Some of the "smart" windows are also composed of polymeric materials whose tint varies according to the incident light. Currently, much material is stored using electronic means but optical storage is becoming a common practice with the use of CD-ROM and WORM devices. Such storage has the advantages of rapid retrieval and increased knowledge density (i.e., more information stored in a smaller space).

Since the discovery of doped polyacetylene, a range of polymer-intense semiconductor devices have been studied including normal transistors and field-effect transistors (FETs), and photodiodes and light-emitting diodes (LEDs). Like conductive polymers, these materials obtain their properties due to their electronic nature, specifically the presence of conjugated pi-bonding systems.

In electrochemical light-emitting cells, the semiconductive polymer can be surrounded asymmetrically with a hole-injecting material on one side and a low work function electron-injecting metal (e.g., magnesium, calcium, or aluminum) on the other side. The emission of light results from a radiative charge carrier recombining in the polymer as electrons from one side and holes from the other recombine.

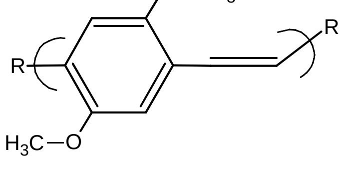
Poly(*p*-phenylene vinylene) (PPV) was the first reported (1990) polymer to exhibit electroluminescence. PPV is employed as a semiconductor layer. As noted earlier, the layer was sandwiched between a hole-injecting electrode and electron-injecting metal on the other. PPV has an energy gap of about 2.5 eV and thus produces a yellow-green luminescence. Today, other materials are available, which give a variety of colors.



(19.2)

Poly(*p*-phenylene vinylene)

A number of poly(arylene vinylene) (PAV) derivatives have been prepared. Attachment of electron-donating substituents, such as dimethoxy groups (structure 19.3), acts to stabilize the doped cationic form and thus lower the ionization potential. These polymers exhibit both solvatochromism (color changes as solvent is changed) and thermochromism (color is temperature-dependent).



(19.3)

Poly(2,5-dimethoxy-*p*-phenylene vinylene)

19.1.2 ELECTRICALLY CONDUCTIVE POLYMERS

The search for flexible, noncorrosive, inexpensive conductive materials has recently focused on polymeric materials. This search has increased to include, for some applications, nanosized fibrils and tubes. The conductivity of common materials is given in Figure 19.1. As seen, most polymers are nonconductive and, in fact, are employed in the electronics industry as insulators. This includes PE and PVC. The idea that polymers can become conductive is not new and is now one of the most active areas in polymer science. The advantages of polymeric conductors include lack of corrosion, low weight, ability to "lay" wires on almost a molecular level, and ability to run polymeric conductive wires in very intricate and complex designs. The topic of conductive carbon nanotubes has already been covered (Section 12.17).

The Nobel Prize in Chemistry for 2000 was given to Alan MacDiarmid, Alan Heeger, and Hideki Shirakawa for the discovery and development of electrically conductive polymers.

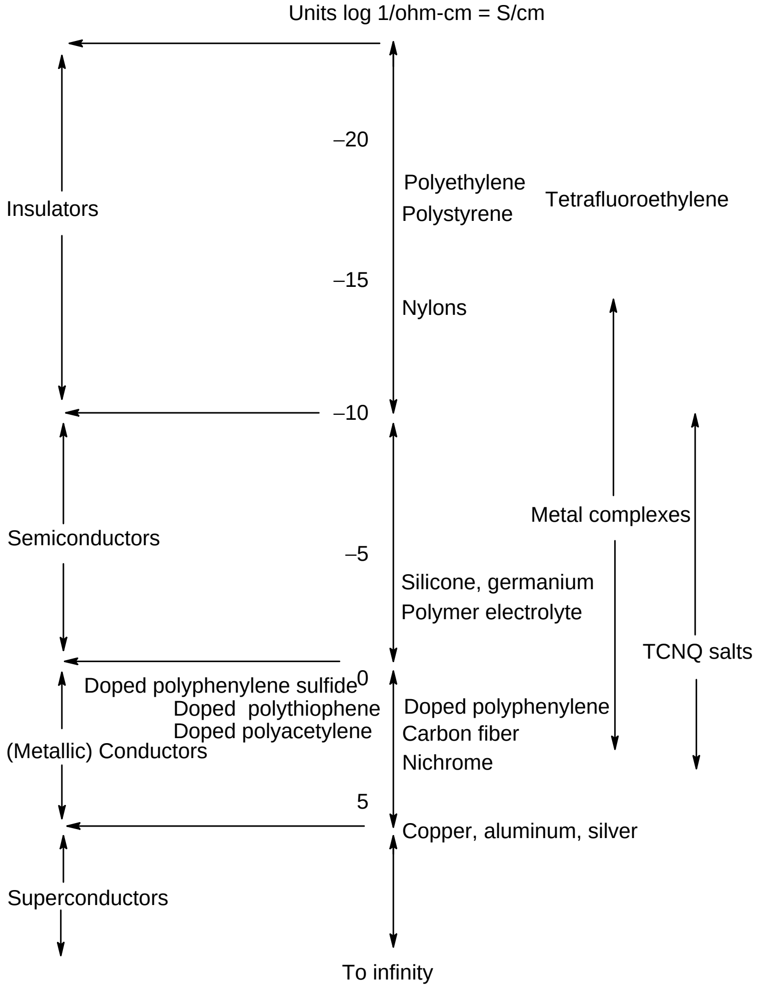


FIGURE 19.1 Electrical conductivity for various materials. S = Siemens = 1/ohm.

In 1975, MacDiarmid and Heeger began studying the metallic properties of inorganic poly(sulfur nitride), but shifted their efforts to polyacetylene after visiting Shirakawa. While the synthesis of polyacetylene was known for years, Shirakawa and coworkers, using a ZNC, prepared it as a silvery film in 1974. But, in spite of its metallic appearance, it was not a conductor. In 1977, using techniques developed by MacDiarmid and Heeger for poly(sulfur nitride), Shirakawa, MacDiarmid, and Heeger were able to increase the conductivity of *trans*-polyacetylene samples, after doping, to a conductivity of about 10^3 S/m or 1 S/cm. They found that oxidation with chlorine, bromine, or iodine vapor made polyacetylene film 10^9 times more conductive than the nontreated film. This treatment with a halogen was called "doping" by analogy with the doping employed with semiconductors. Other oxidizing doping agents have been used such as arsenic pentafluoride. Reducing agents such as metallic sodium have also been successfully used. This chemical doping transforms the polyacetylene from an insulator or semiconductor to a conductor.

A critical structural feature of conductive polymers is the presence of conjugated double bonds. For polyacetylene, every backbone carbon is connected by a stronger localized sigma bond. They are also connected by a network of alternating less localized and weaker pi-bonds. While conjugation is present it is localized enough to prevent ready delocalization of the pi-bond electrons. The dopants cause the introduction of sites of increased or deficiency of electrons (Figure 19.2). When deficiency of electrons, or holes, is created, electrons flow to fill this hole, with the newly created hole causing other electrons to flow to fill the new hole, etc. allowing charge to migrate within and between the polyacetylene chains.

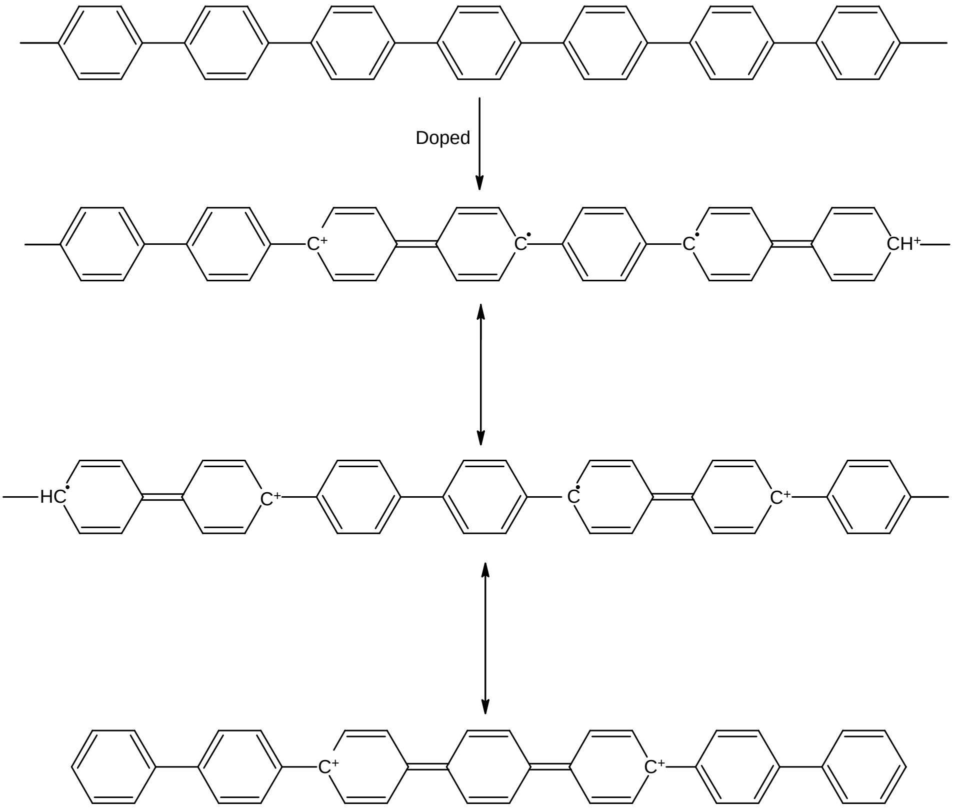


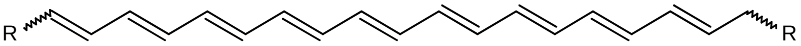
FIGURE 19.2 Poly-*p*-phenylene resonance structures after doping.

In general, the Huckel theory predicts that pi-electrons can be delocalized over an entire chain containing adjacent pi-bonds with the activation energy for delocalization decreasing as the chain length increases. The basic mechanism of electrical conductance is often explained in terms of the band theory borrowed from more classical semiconductors. As noted earlier, for essentially all conductive polymers, pi-bonds are critical for conductance with the overlapping of pi-clouds allowing conductivity of the electric current to occur. Highly delocalized electronic structures with conjugated pi-electrons along the backbones are the norm for good conductivity. The ionization potential to move from the valence band to the conduction band should be small.

Doping provides a ready mechanism for delocalization to occur. Doping is the mode of creating electron sinks or deficiencies and electron excesses that are necessary to breach, or get to, the conductive band. The list of often used oxidant dopants includes I_2 (probably the most widely used because of the ease of using it), AsF_5, $AlCl_3$, Br_2, and O_2. Anionic counterions include $Sb_2F_{11}^-$, I_3, and AsF_6^-. These dopants create defects that can be viewed as either a radical cation for oxidation dopants (the doping agents acting to remove electrons), or radical anion for reduction dopants (the doping agents acting to increase the number of electrons). This is referred to as *polaron* with the oxidation or reduction resulting in the formation of a *bipolaron*. The formation of polarons is shown in Figure 19.2 where resonance structures illustrate the movement of electrons. The bottom resonance structure shows the formation of a bipolaron from the combination of two polarons. While conductance within a single chain is classically used to illustrate the concept, conductance actually occurs between chains as well as within chains. Further, for conductance to be effective, transference between chains is necessary.

Ordinary polyacetylene is composed of small fibers (fibrils) that are randomly oriented. Conductivity is decreased because of the contacts between the various random fibrils. Two approaches have been taken to align the polyacetylene fibrils: the first is to employ a liquid crystal solvent for the acetylene polymerization and to form the polymer under external perturbation; the second is to mechanically stretch the polyacetylene material causing the fibrils to align. The conductivity of polyacetylene is about 100 times greater in the direction of the "stretch" in comparison with that perpendicular to the stretch direction. Thus, the conductivity is isotropic. By comparison, the conductivity of metals such as copper and silver is anisotropic. Of interest is the nonconductivity of diamond, which has only ordered sigma bonds and thus no "movable" electrons and the isotropic behavior of graphite. Graphite, similar to polyacetylene, has a series of alternating pi-bonds (Section 12.15) where the conductivity in the plane of the graphite rings is about 10^6 times that at right angles to this plane.

Polyacetylene has been produced by several methods, many utilizing the Zeigler–Natta polymerization systems. Both *cis* and *trans* isomers exist (structures 19.4 and 19.5). The *cis*-polyacetylene is copper-colored with films having a conductivity of about 10^{-8} S/m. By comparison, the *trans*-polyacetylene is silver-colored with films having a much greater conductivity on the order of 10^{-3} S/m. The *cis* isomer is converted into the thermodynamically more stable *trans* isomer by heating. As noted earlier, conductivity is greatly increased when the *trans*-polyacetylene is doped (to about 10^2-10^4 S/cm). Conductivity is dependent on the microstructure or fine structure of the fibrils, doping agent, extent, technique, and aging of the sample.



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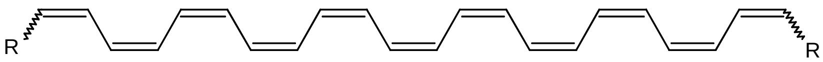
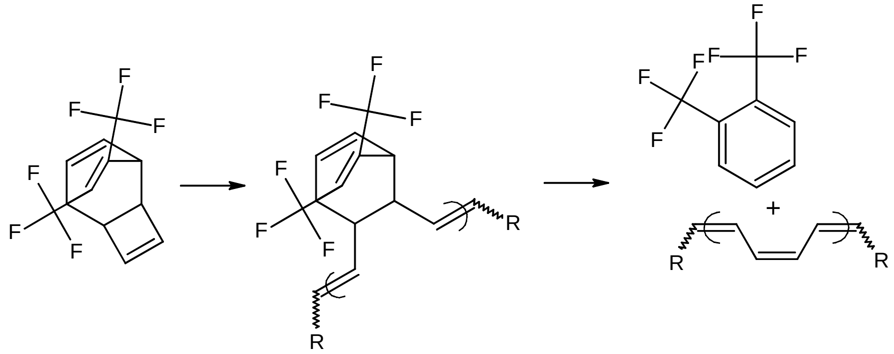


(19.5)

Polyacetylene was initially produced using Ziegler–Natta systems, which resulted in the production of what is now known as Shirakawa polyacetylene. These materials are not easily processable and are mainly fibrillar. Recently, other approaches have been taken. In the

Durham route, the metathesis polymerization of 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0]deca-3,7,9-triene gives a high-molecular weight soluble precursor polymer that is thermally converted to polyacetylene (equation 19.6). The precursor polymer is soluble in common organic liquids and easily purified by reprecipitation. The end product can be aligned giving a more compact material with bulk densities on the order of 1.05 – 1.1 g/cm^3.



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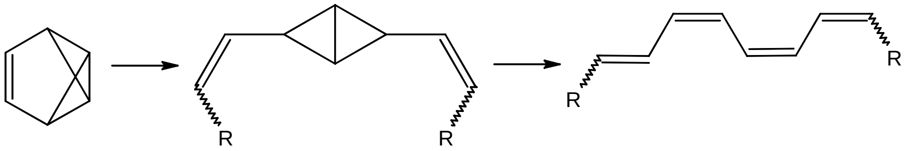
Grubbs and others have used the ring-opening metathesis polymerization to produce thick films of polyacetylene and polyacetylene derivatives (equation 19.7).



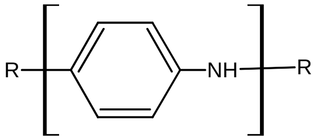
(19.7)

Polyacetylene has good inert atmospheric thermal stability but oxidizes easily in the presence of air. The doped samples are even more susceptible to air. Polyacetylene films have a lustrous, silvery appearance and some flexibility. Other polymers have been found to be conductive. These include poly(*p*-phenylene) prepared by the Freidel–Crafts polymerization of benzene, polythiophene and derivatives, PPV, polypyrrole, and polyaniline. The first polymers commercialized as conductive polymers were polypyrrole and polythiophene because of their greater stability to air and the ability to directly produce these polymers in a doped form. While their conductivities (often on the order of 10^4 S/m) are lower than that of polyacetylene, this is sufficient for many applications.

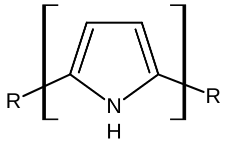
Doped polyaniline is employed as a conductor and as an electromagnetic shielding for electronic circuits. Poly(ethylenedioxythiophene) (PEDOT) doped with polystyrenesulfonic acid is used as an antistatic coating material to prevent electrical discharge exposure on photographic emulsions and is also used as a hole-injecting electrode material in polymer light-emitting devices. Organic soluble-substituted polythiophenes with good conductivities have been prepared. Poly(3-hexylthiophene) has a conductivity of about 100 S/cm at room temperature; poly(3-methylthiophene) has a conductivity of 500 S/cm; and a poly(3-alkylether)thiophene with a conductivity of about 1000 S/cm has been reported. The unsubstituted polythiophene has a conductivity in the range of 50–100 S/cm. The fact that all of these substituted polythiophenes have similar conductivities indicates that there is little twisting of the backbone conjugation as alkyl substituents are added.

Polythiophene derivatives are being used in FETs. Polypyrrole is being used as microwave-absorbing "stealth" screen coatings and in sensing devices. PPV derivatives are being used in the production of electroluminescent displays.

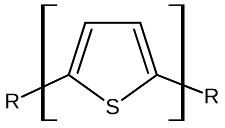
Following are the structures of some of the more common conjugated polymers, along with poly(acetylene), which can be made conductive through doping. As noted earlier, doping causes an electrical imbalance that allows electrons to flow when an electrical potential is applied. The band gap is the energy needed to promote an electron from the valence band to the empty energy or conductive band. Metals have zero band gaps while insulators such as PE have large band gaps, which mean that a lot of energy is needed to promote an electron to an empty band. Semiconductors have small band gaps where valence electrons can be moved into the conductance band through application of relatively small potential energies.



Polyalanine (19.8)



Polypyrrole (19.9)



Polythiophene (19.10)

The optical behavior can be used to help in the understanding of these conductive materials. Pi-conjugation often occurs in the visible region so that most, if not all, of these conductive polymers are colored. Color changes are an important probe in assisting the characterizing effects of various doping agents. Changes in the spectra allow various mechanisms to be studied. Because many of the polythiophene derivatives are organic soluble, spectral changes can be more easily studied. The electronic absorption spectra of a variety of polythiophene derivatives indicate that the band edge for conductivity begins at about 2 eV.

Water-soluble derivatives of polythiophene have been made allowing counterions bound to the polymer backbone to "self-dope" with the protons (e.g., lithium and sodium ions) injecting electrons into the pi-system. Thus, combinations of sodium salts and "proton salts" (e.g., prepared from poly-3-(2-ethanesulfonate)thiophene) have been prepared that are both water-soluble and conducting.

Another area of activity involves the synthesis of material with small band gaps that would allow activation to occur at room temperature without doping. Polyisothianaphthene has been produced with a band gap of about 1 eV. More recently, polymers with alternating donor and acceptor units with band gaps of about 0.5 eV and less have been developed.

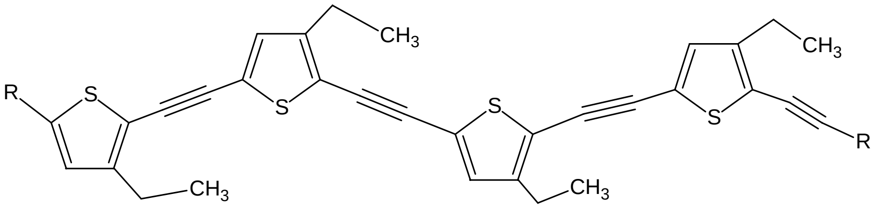
While the amount of electricity that can be conducted by polymer films and "wires" is limited, on a weight basis the conductivity is comparable with that of copper. These polymeric conductors are lighter, some are more flexible, and they can be "laid down" in wires that approach being one-atom thick. They are being used as cathodes and solid electrolytes in batteries, and potential uses include in fuel cells, smart windows, nonlinear optical materials, LEDs, conductive coatings, sensors, electronic displays, and in electromagnetic shielding.

There is a large potential for conducting polymers as corrosion-inhibiting coatings. For instance, the corrosion protection ability of polyaniline is pH-dependent. At lower pH polyaniline-coated steel corrodes about 100 times more slowly than noncoated steel. By comparison, at a pH of about 7 the corrosion protection time is only twice for polyaniline-coated steel. Another area of application involves creation of solid state rechargeable batteries and electrochromic cells. Polyheterocycles have been cycled thousands of times with retention of over 50% of the electrochromic activity for some materials after 10,000 cycles. IR polarizers based on polyaniline have been shown to be as good as metal wire polarizers.

They will also find uses in nonlinear optical devices, such as in optoelectronics, for signal processing and optical communication. Some of the new conducting polymers offer such benefits as flexibility, high damage threshold, ultrafast response in the subpicosecond range, and good mechanical strength. Polyheterocyclic conducting polymers have shown a wide variation in color as they are electronically converted between oxidized and reduced forms. The instability of some of the polymers is being used to monitor moisture, radiation, mechanical, and chemical destruction.

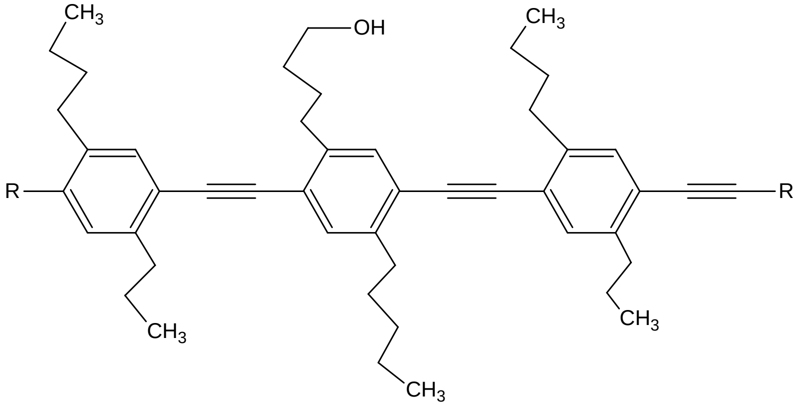
19.1.3 NANOWIRES

Part of the nanorevolution involves the electronics industry and the synthesis of so-called nanowires or molecular wires for electronic applications. Basically, molecular wires contain a series of double or double and triple bonds that have what can be referred to as "whole-chain" resonance. Polyacetylene is an example of a molecule that exhibits whole-chain resonance or delocalization of electrons where the activation energy for delocalization is relatively low. The search is on for nanowires that are more flexible. Often, this flexibility is achieved through a balance of the conductive inner core backbone that is characteristically rigid with a flexible outer core composed of covalently bonded groups that act to decrease the tendency to form highly crystalline structure and which encourage flexibility as illustrated below. As in many of the new areas creativity is important. Often, the molecular wires are created one step at a time with the eventual joining of chains or simply the use of the single chain.



(19.11)

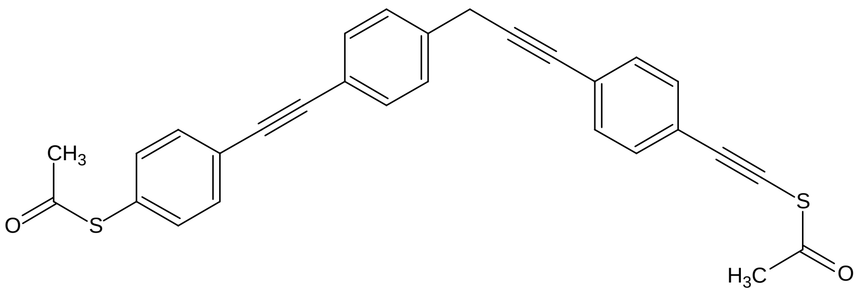
Poly(thiophene ethynylene)



(19.12)

Phenylene–acetylene backbone copolymer

While we call these materials polymeric, in fact they are oligomeric, often intentionally made to be oligomers with specific lengths intended to connect other molecules or molecular devices with the distance between the "gaps" corresponding to the distance of the molecular wires. Thus, we can design molecules with particular lengths, conductivity, and the ability to molecularly connect to other molecules. When needed, nonconductive molecules, such as methylene units, can be added to decrease electronic conductance. These nonconductive moieties are referred to as barriers. Structure 19.13 shows a phenylene–acetylene grouping containing a barrier methylene.



(19.13)

Chain ends are often functionalized with groups that can react with specific sites on another molecule. These functionalized sites are referred to as molecular alligator clips. The chain shown in structure 19.13 has two such functionalized groups or alligator clips, one on each end. These molecular alligator clips are normally designed to attach or anchor to a metal surface. Thus, this molecule is a candidate to connect two electrodes, acting as a molecular wire.

Of importance to their use in electronics, these chains are able to conduct in the microamp region, the same region that most computing instruments operate and individual chains can conduct in the tenth of a microamp range.

19.2 NONLINEAR OPTICAL BEHAVIOR

Nonlinear optics (NLO) involves the interaction of light with materials resulting in a change in the frequency, phase, or other characteristics of the light. Second-order NLO behavior includes second harmonic generation of light that involves the doubling of the frequency of the incident light; mixing of frequencies where the frequency of two light beams is either added or subtracted; and electro-optic effects occurring that results in frequency and amplitude change and rotation of polarization. NLO behavior has been found in inorganic and organic compounds and in polymers. The structural requirement is the absence of an inversion center requiring the presence of asymmetric centers and/or poling. Poling is the application of a high-voltage field to a material that orients some or all of the molecules generally in the direction of the field. The most effective poling is found when the polymers are poled above the T_g (that allows a better movement of chain segments) and then cooled to lock in the "polled" structure. Similar results are found for polymers that contain side chains that are easily poled. Again, cooling helps lock in the polled structure. At times, cross-linking is also employed to help lock in the polled structure.

Third-order NLO behavior generally involves three photons resulting in effects similar to those obtained for second-order NLO behavior. Third-order NLO behavior does not require the presence of asymmetrical structures.

Polymers that have been already found to offer NLO behavior include polydiacetylenes and a number of polymers with liquid crystal side chains. Polymers are also employed as carriers of materials, which themselves are NLO materials. Applications include communication devices, routing components, and optical switches.

19.3 PHOTOPHYSICS

Photophysics involves the absorption, transfer, movement, and emission of electromagnetic, light, energy without chemical reactions. By comparison, photochemistry involves the interaction of electromagnetic energy that results in chemical reactions. Let us briefly review the two major types of spectroscopy with respect to light. In absorption studies, the detector is placed along the direction of the incoming light and the transmitted light measured. In emission studies, the detector is placed at some angle, generally 90°, away from the incoming light.

When absorption of light occurs, the resulting polymer, P*, contains excess energy and is said to be excited.

$$P + h\nu \rightarrow P^* \tag{19.14}$$

The light can be simply reemitted.

$$P^* \rightarrow h\nu + P \tag{19.15}$$

Of much greater interest is the migration, either along the polymer backbone or to another chain, of the light. This migration allows the energy to move to a site of interest. Thus, for plants, the site of interest is chlorophyll. These "light-gathering" sites are referred to as antennae. Natural antennae include chlorophyll, carotenoids, and special pigment-containing proteins. These antenna sites harvest the light by absorbing the light photon and storing it in the form of an electron that is promoted to an excited singlet energy state by the absorbed light.

Bimolecular occurrences can happen leading to an electronic relaxation called quenching. In this approach, P* finds another molecule or part of the same chain, A, transferring the energy to A.

$$P^* + A \rightarrow P + A^* \tag{19.16}$$

Generally, the quenching molecule or site is in its ground state.

Eliminating chemical rearrangements, the end results for quenching are most likely electronic energy transfer, complex formation, or increased nonradioactive decay. Electronic energy transfer involves an exothermic process where part of the energy is absorbed as heat energy, and part is emitted as fluorescence or phosphorescence radiation. Polarized light taken on in fluorescence depolarization is also known as *luminescence anisotropy*. Thus, if the chain segments are moving at about the same rate as the reemission, part of the light is depolarized. The extent of depolarization is then a measure of the segmental motions.

Complex formation is important in photophysics. Two terms need to be described here: first, an *exciplex*, which is an excited state complex formed between two different kinds of molecules, one that is excited and the other that is in its grown state; second, an *excimer*, which is similar to exciplex except that the complex is formed between like molecules. Here, we will focus on excimer complexes that form between two like polymer chains or within the same polymer chain. Such complexes are often formed between two aromatic structures. Resonance interactions between aromatic structures, such as two phenyl rings in PS, give a weak intermolecular force formed from attractions between the pi-electrons of the two aromatic entities. Excimers involving such aromatic structures give strong fluorescence.

Excimer formation can be described as follows where [PP]* is the excimer.

$$P^* + P \rightarrow [PP]^* \tag{19.17}$$

The excimer decays giving two ground state aromatic sites and emission of fluorescence.

$$[PP]^* \rightarrow h\nu + 2P \tag{19.18}$$

Invariably, the energy of the light emitted is less than that originally taken on. By studying the amount and energy of the fluorescence radiation decay rates, depolarization effects, excimer stability, and structure can be determined.

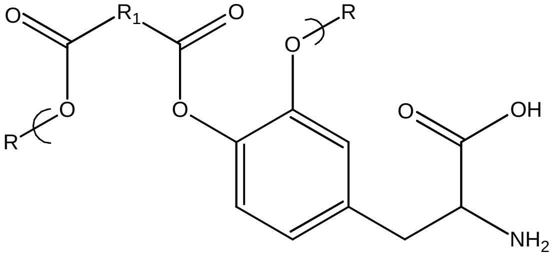
19.4 DRUG DESIGN AND ACTIVITY

There are a number of steps that should be completed before a drug is brought to market. Generally, first a compound should be active in treating some illness. This may be done with cell and bacterial studies followed up with live animal tests. This drug is then modified in an attempt to increase its activity and minimize negative side effects. When possible, the target is identified. The target is typically one that is identified with the illness. The target is validated by determining its function and determining that its activity is modified by association with the drug.

A series of studies are undertaken to evaluate the effectiveness and toxicity of the drug compound. Throughout this process, large decreases in the number of compounds making it successfully through the testing occurs. Generally, extensive animal testing is done. If the drug is believed to be effective in the treatment of the illness, additional steps occur. Initially, a drug company files an Investigational New Drug Application (INDA) with the FDA to get permission to begin testing the drug in humans. A series of clinical trials with the potential drug are conducted in humans. *Phase I* clinical trials involve testing the drug in a small number (20–100) of healthy individuals to test the drug's safety, tolerance, length of activity, effective dosage, and dosing schedule. *Phase II* clinical trials involve testing the drug in large numbers of individuals (100–500) with the particular illness to gain additional information of efficacy, side effects, safety, and appropriate dosage and schedule. *Phase III* clinical trials involve testing the drug in large numbers of volunteers (hundreds to thousands) to again gain more information of the efficacy, side effects, and safety. Generally, only one or two dosage levels and schedules are studied in phase III studies. If results are consistent with the drug successfully treating the illness with only minor side effects, application is submitted to the FDA for marketing it. Even after the drug has come to market, ongoing monitoring occurs for safety and side effects. Accomplishment of such a gauntlet of testing costs from $200 to $800 million.

Most drugs are smaller molecules. Polymer-containing drug formulations are common. Here, the drug is contained within some polymeric matrix that assists in controlling the release either through control of drug diffusion through the chains or by erosion, degradation, or solubility, of the polymer network.

But there are some drugs that are polymeric offering advantages over smaller molecules. Along with polymers being simply depositories of the drugs, polymers can perform active roles in drug therapy. Polymeric drugs can act in two divergent ways: as a control release agent and as a drug itself. The polymeric drug may act in a control release manner. A polymer that contains a known therapeutic portion can degrade releasing this portion over sometime. Thus, a polymer that contains the drug L-dopa (structure 19.19) used to treat Parkinson's disease degrades over time releasing L-dopa over a period of time.

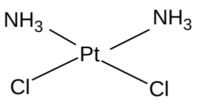


(19.19)

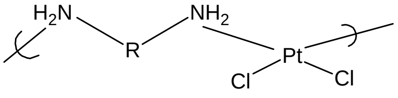
Polymer-containing L-dopa

The polymer may act as a drug itself or the polymer drug may also act in both roles. Following is a brief discussion of advantages of polymeric drugs that may apply to either mode of control release and/or as a drug itself. Because of their size, polymers with chain lengths of about 100 units and greater typically are unable to easily move through biological membranes, thus movement is restricted. This can result in limiting negative side effects, such as damage to the kidneys, because the polymer can reside in only certain body sites. Also, this limited mobility can assist in directing the polymer drug. This also allows the use of lower and more level drug concentrations reducing damages to renal organs. In some cases, multiple attachments by the same polymer chain can be beneficial. Thus, many cancer drugs act to "tie up" the DNA chains inhibiting cell replication. Here, multiple attachments to the DNA, possible for polymer drugs that contain numerous binding units within each single chain, might be beneficial in decreasing the cells' effectiveness in overcoming single DNA "chemical knots" (chemical bonding together of the two DNA strands).

The polymeric nature may inhibit premature drug deactivation. Thus, cisplatin (structure 19.20), the most widely used anticancer drug, is converted into numerous inactive, but more toxic, platinum-containing compounds before it arrives at the targeted cancer cells. Placement of the active platinum-containing moiety into a polymer (structure 19.21) decreases this tendency to hydrolyze into these unwanted cisplatin compounds because of the greater hydrophobic character of the polymeric drug.



Cisplatin (19.20)



Polymer containing a cisplatin-like unit (19.21)

Polymers may also evade the microorganism's defense. Recently, it was found that many cells become drug-resistant after repeated treatment. Cells have groups of molecules that protect it from outside invasion. The small-molecule drugs are considered as "outside" invaders. Thus, drugs introduced into their environment are considered as outside invaders and the cell manufacturers greater number of these "housekeepers" to rid the cell of the invaders. These "housekeeping" agents are often not very specific and remove other similar drugs that intrude their cell. These housekeeping proteins may not be as effective in eliminating polymer drugs.

Polymer drugs are also known to remain within human hosts longer than smaller molecules. Depending on the illness and treatment, this preferential retention may be simply due to physical retention through entanglement with biological outer-layer materials or through some specific additional interaction. Tumor-associated cells are frequently hyper-permeable to plasma proteins and other macromolecules. These "leaky" vasculatures and limited lymphatic drainage, typical of tumor and missing in normal tissue, result in the accumulation of polymers. Thus, such polymers reside in the interstitial space of these cells. This results in *enhanced permeability and retention* (EPR) of large chains.

Drug design, today, typically aims at certain specific biological activities. Thus, for cancer treatments this focus is on controlling cell growth (Figure 19.3). Cell growth can be considered occurring in four dependent steps. Drugs are designed to control cell growth at any one of these steps directly or indirectly. The indirect intervention of cell growth targets any one of these steps that influence the cell growth cycle. Essentially all chemotherapies are based on the continual growth of cancer cells compared with healthy cells generally being in some rest state.

Drugs aiming to control the same problem may target different sites. For instance, in the treatment of breast cancer, tamoxifen acts to control cell growth by blocking estrogen receptors on the cancer cell, while Arimidex acts to reduce the body's estrogen production.

Cancer cells have three main characteristics that are different from healthy cells. First, they are immortal, able to replicate themselves hundreds of times while healthy cells generally replicate themselves less than two dozen times over our lifetime. Second, cancer cells are not

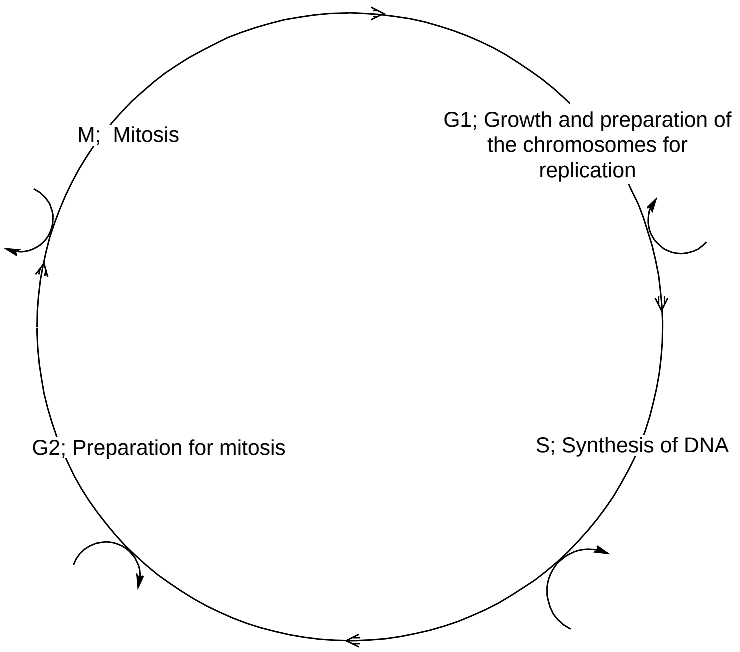


FIGURE 19.3 Cell growth cycle.

contact inhibited, which means that they will continue to grow forming tumors. By comparison, healthy cells replicate until they touch another cell and then stop reproduction. This is called contact inhibition. Finally, cancer cells are normally in a growth mode, whereas healthy cells are generally in a rest mode. For most situations, drug action takes advantage of the cancer cells being in a growth mode needing an intake of various materials to keep growing. Thus, any cell that is growing at the time a chemodrug is administered will get a dose of the chemodrug, most likely a lethal dose. Since the cancer cells are almost always in the growth mode, they will be most affected. Recently, we have found a family of organotin polymers that inhibit a variety of cancer cells but do not affect the growth cycle of healthy cells. This points out another possible avenue to create cancer cell-specific drugs. Healthy cells have their autoimmune system intact, whereas cancer cells have damaged autoimmune systems. These organotin polymers may be warded off by the healthy cells, whereas the cancer cells are inhibited by them.

19.5 SYNTHETIC BIOMEDICAL POLYMERS

Synthetic polymers have been studied for sometime for their use in the general field of medicine. Initial results were average. More recently, because of a better understanding of the importance of surface, avoidance of contaminants, control of molecular weight, and molecular weight distribution, the use of synthetic polymers in the biomedical sciences is increasing. Polymers are viewed as important biomedical materials for a number of reasons, some of which appear contradictory—but only because different uses require different properties. Some of the important properties are the ability to tailor-make structures, surface control, strength, flexibility, rigidity, inertness or reactivity, lightweight, ease of fabrication, ability to achieve a high degree of purity, lack of water solubility or compatibility, bioerodability, and the ability of some of them to withstand long-term exposure to the human body—a truly hostile environment. Fighting against some of the biomaterials is their limited (by volume) use—thus, researchers are often limited to using commercial materials made for other applications, but as the use of these important materials increases, manufacturers will become more interested in tailor-making materials, if for no other reason, than the high-cost per unit volume.

Long-term inertness without loss of strength, flexibility, or other necessary physical property is needed for use in artificial organs, prostheses, skeletal joints, etc. Bioerodability is needed when the polymer is used as a carrier such as in controlled release of drugs, removal of unwanted materials, or where the materials' purpose is short-lived, such as in their use as sutures and frames for natural growth.

While the nature of the material is important, the surface of the material is also often critical. The human body wants to wrap around or connect to bodies within its domain. In some cases, the desired situation is little or no buildup on the polymer. Here, surface "slickness" is needed. Siloxanes and fluorinated materials such as PTFE are generally slick materials, but other materials can be made slick through surface treatments that present to the body few voids and irregularities at the atomic level. In other cases, body buildup, and surfaces and materials that assist this growth are preferred. Surface hydrophobicity or hydrophilicity, presence or absence of ionic groups, and chemical and physical (solid or gel) surfaces are all important considerations as one designs a material for a specific application.

Ability to function long term is an ongoing problem. In general, PUs degrade after about 1.5 years, nylons lose much of their mechanical strength after about 3 years, and polyacrylonitrile loses about 25% strength after 2 years. On the other hand, PTFE loses less than 10% strength after about 1 year and siloxanes retain most of their properties after 1.5 years.

Following is a brief look at some of the varied uses, real and projected, for synthetic polymers. These are intended to be only illustrative. The field of biomedical materials is rapidly growing and it is extensive.

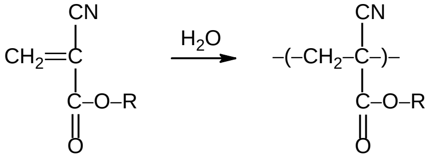
There have been a lot of efforts to construct artificial hearts for human use. These are largely composed of polymeric materials. Even with the problems associated with organ transplant, the use of artificial hearts may never be widespread. This is because of several trends. First, many solutions to biological problems reside in the use of biological materials. With the advent of increased effectiveness of cloning and related advances, suitable biological replacements may be grown from a person's cells, thus ensuring compatibility. Second, related to the first, regeneration of essential parts of vital organs is becoming more practical. Third, because of nanotechnology and related electrical and optical advances, surgery to locate and repair imperfections is improving. Fourth, our autoimmune system is divided into two main systems: one guards against "small" invading organisms such as viruses, bacteria, and pollen; the other guards whole organs such as the heart through rejection of foreign body tissue. Purine nucleoside phosphorylase (PNP) is a human enzyme that serves at least two major functions. First, PNP acts to degrade unleashed molecules, such as foreign nucleic acids. PNP is necessary for our immune system as it fights disease. Some anticancer drugs are synthetic nucleosides and nucleotides, such as polyIpolyC, that are employed to directly attack selected cancerous tumors. PNP degrades such nucleic acid-related materials before they reach the tumor. Neutralization of PNP just prior to administration of the synthetic nucleic acid-related material would allow lower dosages to be used. Second, PNP is an integral part of the body's T-cell immunity system that rejects foreign tissue. Effort is currently underway to effectively inhibit only the PNP action allowing the first autoimmune system to work, while allowing organ transplantation without rejection. Recently, through the use of zero gravity conditions, crystals of PNP have been grown of sufficient size to allow structural determination. With this structure determined, efforts are underway to detect sites of activity and drugs that would allow only these sites to be neutralized when needed.

Even so, synthetic polymers are important in replacing parts of our essential organs. Thus, silicon balls are used in the construction of mechanical heart valves. Many of these fail after sometime and they are being replaced by a flap valve made from pyrolytic carbon or POM.

Aneurysms can be repaired through reinforcement of the artery wall with a tube of woven PTFE or polyester. Replacement of sections of the artery can be done using a tube of porous PTFE. One remaining problem is the difference in elasticity between the woven and porous materials and the arteries themselves.

Carbon fiber composites are replacing screws for bone fracture repair and joint replacements. These fiber composites are equally strong and chemically inert. By comparison, the metals they replace are often alloys, which may contain metals that the patient may be allergic to.

Polymers are also used as sutures. Fighters and other athletes have used poly(alpha-cyanoacrylates), super glues, to quickly stop blood flow in surface cuts. Today, super glue is also used for, in place of or along with, more traditional polymeric suture threads for selected surface wounds, internal surgery, and retinal and corneal surgery. The alpha-cyanoacrylate polymers (structure 19.22) undergo anionic polymerization in the presence of water. More about sutures is explained in Section 19.6.



$$CH_2{=}\overset{\overset{CN}{|}}{\underset{\underset{\underset{O}{\|}}{C-O-R}}{\underset{|}{C}}} \xrightarrow{H_2O} -(-CH_2-\overset{\overset{CN}{|}}{\underset{\underset{\underset{O}{\|}}{C-O-R}}{\underset{|}{C}}}-)- \qquad (19.22)$$

Poly(alpha-cyanoacrylate)

Siloxanes are the most extensively used synthetic biomaterial due to several reasons such as flexibility, chemical and biological inertness, low capacity to bring about blood clotting, overall low degree of biological toxicity, and good stability within biological environments.

Artificial skin had been made from a bilayer fabricated from a cross-linked mixture of bovine hide, collagen, and chondroitin-B-sulfate derived from shark cartilage with a thin top layer of siloxane. The siloxane layer acts as a moisture- and oxygen-permeable support and to protect the lower layer from the “outer world” allowing skin formation to occur in conjunction with the lower layer. Poly(amino acid) films have also been used as an “artificial” skin. Research continues in search of a skin that can be effectively used to cover extensive wounds and for burn patients.

Elastomeric siloxanes have also been used in encapsulating drugs, implant devices, and in maxillofacial applications to replace facial portions lost through surgery or trauma. Transcutaneous nerve simulators are made from “conductive” siloxanes. These are employed in the treatment of chronic severe pain through application of low-level voltage to the nerves, disrupting transmission of pain impulses to the brain. Siloxanes are also used in extracorporeal blood oxygenation employed in the heart–lung assist machine that is routinely used in open heart surgery. The “heart” of the apparatus is the membrane, which allows ready transport of oxygen and carbon dioxide yet retain moisture and the blood cells. The siloxane membranes can be made using a polyester or PTFE screen in an organic dispersion of silicon rubber. When dried, thin films are obtained, which are used in the heart–lung assist device.

Siloxane-containing devices have also been used as contact lenses, tracheostomy vents, tracheal stents, antireflux cuffs, extracorporeal dialysis, ureteral stents, tibial cups, synovial fluids, toe joints, testes penile prosthesis, gluteal pads, hip implants, pacemakers, intra-aortic balloon pumps, heart valves, eustachian tubes, wrist joints, ear frames, finger joints, and in the construction of brain membranes. Almost all the siloxane polymers are based on various polydimethylsiloxanes.

The kidney removes waste materials from our blood. Because of partial or total kidney failure, many persons are on hematolysis. The first hemodialysis units were large and by today’s standards were not very effective and the semipermeable tubes, made mainly of cellophane, had very limited lifetime. Initially, dialysis treatment was expected to be for only terminal patients but as the life expectancy of dialysis patients increased as did the demand for dialysis, smaller, more efficient dialysis machines have emerged. At the heart of these advances is the filtering material. Today, bundles of microhollow fibers are used in the construction of hemodialysis cells. The fibers are "heparinized" to discourage blood clotting. The fibers are mainly made of polyacrylonitrile. Polycarbonate, cellulose acetate, and rayon fibers are also being used.

The most widely used hip joint replacement is largely a polished cobalt–chromium alloy that moves against a specially designed UHMWPE. This UHMWPE is highly crystalline and highly cross-linked through gamma radiation. Tests have shown that the UHMWPE wears out at an average of 0.1 mm each year. Since most assemblies employ about a 10 mm thick layer of UHMWPE, the lifetime of the hip joint replacement based only on the wear of the UHMWPE is about 100 years.

Controlled release of drugs can be envisioned as occurring via three major routes. One approach utilizes diffusion-controlled release through membranes or matrices. Here, the rate of release is controlled by the permeability of the membrane or matrix. In the second approach, the drug is captured within a matrix that undergoes degradation, usually through aqueous-assisted solubilization or degradation (including hydrolysis). Here, the rate of drug release is dependent on the break up of the typically polymeric matrix. For the second approach, a number of polymers have been used including poly(glycolic acid) and polyanhydrides. The third approach involves simple degradation of a drug-containing polymer where the drug moiety is present as part of the polymer backbone or as side chains. Degradation of the polymer results in the release of the drug in some fashion.

Controlled release of drugs using polymer intensive materials is becoming more commonplace. The release "pack" can be attached externally such as many of the "nicotine patches" that deliver controlled amounts of nicotine transdermally. The release pack can also be introduced beneath the skin or within the body as is the case with many diabetes treatment assemblies.

A number of siloxane-containing controlled release packs have been devised and used. Glaucoma, motion sickness, and diabetes have been treated using drugs dispersed in a silicon matrix. This kind of pack needs to be placed near the site of intended activity for greatest effectiveness.

Implant materials can be divided into two general categories depending on the time requirement. Those that are present for release of a drug or to hold a broken bond in place until sufficient healing occurs are termed short-term implant materials. The second group includes materials that function over a longer period such as for the life of the patient. In the first case, degradation is generally required, while for the long-term material inertness and long-term stability are typically required. There are times when this is not true. For instance, some of the newer biomaterials act as scaffolds that promote tissue growth by providing a three-dimensional framework with properties that encourage favorable cell growth. This material may be designed to be either short or long term. One approach to designing scaffolding material involves placing certain amino acid-containing units on the polymeric scaffold that encourages cell growth.

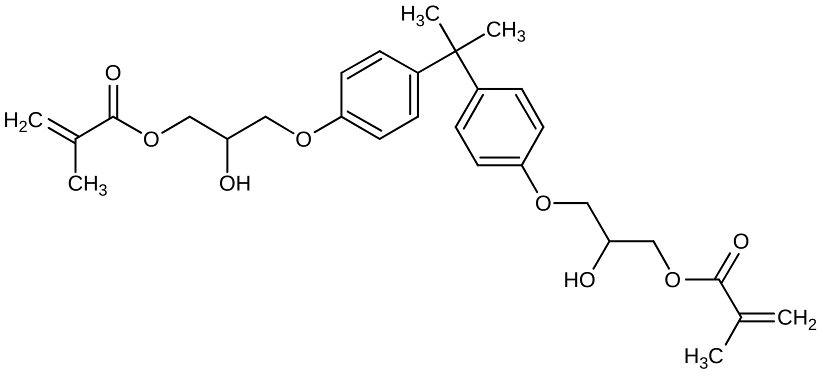
Another aspect related to control release of drugs concerns the type of structures that currently appear to be working. Not unexpectedly, because of compatibility and degradation purposes, most of the effort on the control release formulations includes polymers that have both a hydrophobic and hydrophilic portion with the material necessarily containing atoms in addition to carbon. Another concern is that the products of degradation are not toxic or do not form toxic materials. It has also been found that amorphous materials appear to be better since they are more flexible and permit more ready entrance of potential degradative compounds.

Another area of activity involves the synthesis of supermolecular layers that are connected through cross-linking giving essentially one-molecule thick micelles. Depending upon the particular template and solvents employed these monolayers can be designed to have almost any combination of hydrophilic and hydrophobic sites. Again, specific control of release rates, degradation times and routes, biocompatibility, or incompatibility is possible. Many of these micelle-based delivery systems are based on a poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock or on a polypeptide and PEO combination. Drug delivery has also been achieved using conducting electroactive polymers formed through controlled ionic transport of counterions (dopants) in and out of membranes.

Hydrogels have been used to shepherd drugs through the stomach into the intestine. Hydrogels are cross-linked, hydrophilic polymer networks that allow the smaller drugs access to their interior and that can be designed to inflate, swell at the desired site, to deliver the drug. These hydrogels have been formed largely from materials with a poly(acrylic acid) backbone. More about hydrogels is given in Section 19.14.

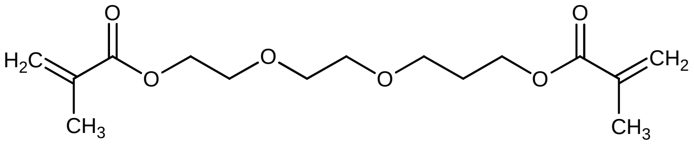
19.5.1 DENTISTRY

Polymers are used extensively in dentistry. Dental restorative composites generally consist of difunctional and trifunctional monomer systems, which provide the cross-linking necessary to form a strong matrix once polymerized. Reinforcing fillers such as silanized quarts and ceramics, hybrid fillers such as prepolymerized resins on fumed or pyrogenic silica, and ceramics act as the dispersed phase of the composite. The diluent or continuous phase is the monofunctional and difunctional monomer that decreases the viscosity of difunctional and trifunctional monomers, which finally act to form the stable composite matrix. Dental sealants are similar except that the filler material is either not present or present in lesser concentration. Many of the restorative composites are based on modified dimethacrylates, the most common being 2,2-bis[p-(2′-2-hydroxy-3′-methacryloxypropoxy)phenyl]-propane, bis-GMA (structure 19.23), and triethyleneglycol dimethacrylate (TEGDMA) (structure 19.24).



(19.23)

bis-GMA



(19.24)

TEGDMA

These two are used either separately or as a mixture. Because of the presence of the somewhat flexible ethylene oxide and related units and use of appropriate fillers, these materials give composite fillings with lower polymerization shrinkage, enhanced mechanical properties, lower solubility and water adsorption, better thermal expansion characteristics, and good biocompatibility with aesthetic properties closely matching those of the tooth itself.

Some other fillings employ urethanedimethacrylate (1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane) (UDMA) in place of bis-GMA. This is an active area of research with new monomer systems being introduced in an ongoing manner.

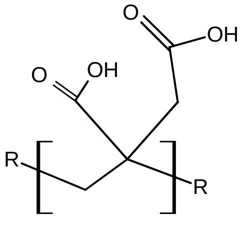
Cavity varnishes are used to seal the exposed dentinal tubules and protect the pulp from the irritation of chemicals in the filling materials. They are generally largely NR or a synthetic polymeric resin such as 2-hydroxyethyl methacrylate (HEMA).

Almost all denture bases are made of methacrylic (acrylic) resins, which give a good fit and a natural appearance. A compression molding process is used where the monomer–polymer dough or slurry contain PMMA or poly(methyl acrylate). Often, there is a change in the contour of the soft tissue and a liner is fitted onto the denture base. Silicon reliners are often used for this purpose.

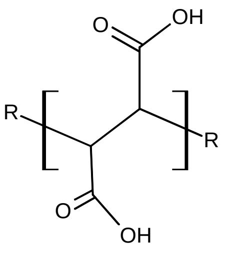
Plastic acrylic denture teeth are made by injection or transfer molding. Acrylic teeth have a higher strength than porcelain teeth and break less readily. However, they resist cold flow, have greater water absorption, and have higher wear rate than porcelain teeth.

Many of the dental polymer cements are glass–ionomer combinations made from ionomer-forming polymers that contain acid groups such as poly(acrylic acid), poly(itaconic acid) (structure 19.25), poly(maleic acid) (structure 19.26), and poly(2-butene-1,2,3-tricarboxylic acid) (structure 19.27). These polyalkenoate cements are set up through reaction with an aluminosilicate fluoride glass with the polyacids hydrolyzing the glass network releasing the aluminum and calcium ions, and forming a siliceous hydrogel. The acid groups chelate with the released metal cations forming a cross-linked matrix.

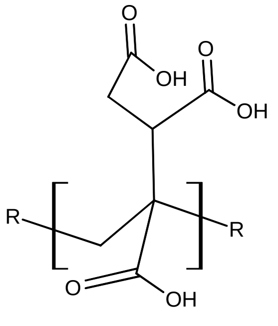
Also included in the general grouping of biomaterials are the new electronics that are being developed including nanotechnology. These electronic biomaterials need to be encapsulated sufficiently to protect them from the body and to protect the body from hostile actions against the presence of the foreign object or they need to be made with a coating material that will act as an encapsulating material to the electronics device. Special care will be taken with respect to adhesive materials that connect the electrical device to the particular site for activity and/or interactions between the electromagnetic messages and surrounding tissue. Again, adhesive, encapsulating, and shielding materials will be largely polymeric.



Poly(itaconic acid) (19.25)



Poly(maleic acid) (19.26)



Poly(2-butene-1,2,3-tricarboxylic acid) (19.27)

19.6 SUTURES

Since surgery began, about 5000 B.C., tying together the surgical site required a stitching material, which is now called sutures. Surgery, combat, accidents, and hunting could result in wounds requiring closure with sutures.

As time progressed, various suture materials were used, essentially all polymeric, and initially all natural. Early materials included linen strips, grasses, mandibles of pincher ants, silk, animal hair, and parts of animals including muscles, tendons, and intestines. The earliest use of so-called catgut was by the ancient Greek physician Galen. The 18th century brought along the use of animal hide and silver wire. By the 20th century, synthetic sutures began to dominate as sutures of choice. The introduction of polyglactin structures in the 1970s started the transition from natural to more synthetic adsorbable sutures.

Sutures are the largest group of devices implanted into humans. At present, there is a wide variety of materials available, each with known advantages and limitations.

Today, sutures are available in different kinds and sizes. The standard sizes of sutures (with diameters in inches) follow a system set by the United States Pharmacopeia. The scale originally was 0–3 with zero being the smallest. As the ability to make strong thin sutures is increased, smaller suture diameters were indicated by additional zeros, thus a 00 was smaller than 0. Today, suture size is given by a number representing the diameter ranging in general order from 10 to 1 and then from 1/0 to 12/0 with 1/0 being the largest and 12/0 being the smallest with a diameter smaller than a human hair strain. A 4/0 corresponds to a 0000 sized suture and a 6/0 corresponds to a 000000 suture. Thus, in the $x/0$ series, the x corresponds to the number of zeros that reflect suture diameter.

Table 19.1 contains a listing of suture sizes and typical uses.

As expected, smaller sutures of the same material generally exhibit lower tensile strengths and can break more easily.

Suture size has some correspondence to the tissue being bound together with thinner tissues like the face requiring thinner sutures. Thinner sutures are also required for facial surgery to limit scar formation.

A surgeon considers the following factors while choosing a suture: (a) knot security, (b) tensile strength and its lifetime, (c) minimal tissue drag and inflammation, (d) handling, (e) size, (f) inhibition of infection, and (g) potential of allergenic reaction.

Other less obvious factors are also considered while choosing a suture. For instance, the age and health of the patient. An older person in poor health generally requires a longer period to heal, thus for absorbate sutures, the required degradation time needs to be increased. Conversely, for an active child, while the degradation time may be less, the suture may be exposed to more frequent sudden stresses and the body tissues are generally thinner. The presence of immunodeficiency is also an important factor since they are more susceptible

TABLE 19.1
Suture Sizes and Typical Uses

Size	Typical Uses
0 and larger	Abdominal wall closure, drain sites, arterial lines, fascia, orthopedic uses
2/0	Blood vessels, viscera, fascia
3/0	Trunk, limbs, gut
4/0	Neck, hands, tendons, mucosa
5/0	Face, neck, blood vessels
6/0	Face
7/0 and smaller	Microsurgery, ophthalmology

to infection. Patients who have taken steroids, undergone chemotherapy, infected with HIV, etc. where the immunosystem is stressed are included in this grouping. In some way, all of us fit into this category, to some extent, because the surgery or action that has inflected the need for the suture compromises our immune system. Thus, where possible, a health picture or history should be taken prior to scheduled surgery.

Sutures can be a single strand called a monofilament, or many filaments twisted or braided together. The importance of specific factors that may not be initially important may actually be of greater importance. For instance, braided sutures offer advantages of being stronger, more flexible, and offer a more secure knot formation, but they offer disadvantages such as the presence of crevices where infection can find a home and they may inflect a sawing action on the tissue, cutting the tissue with each movement. Further, braided sutures, because of their rough morphology, cause tissues to swell more. While knotting or tying off is generally required to maintain suture location and ability to hold the tissues together, the stresses on the suture caused by the formation of the knot result in the knotted material typically being the least resistant to hydrolysis and are generally the sites where the initial break occurs.

Sutures are sold and packaged with specific needles already threaded and the sutures already cut top length. They can be colored (dyed) or clear and coated or uncoated. Black-colored sutures are typical in instances where ready identification of the suture is important, e.g., internal surgery. Other coatings can also be applied that make the surface smoother or give the surface some therapeutic activity.

The United States Pharmacopeia is the agency that determines standard procedures and parameters for suture testing. In Europe, it is the British Pharmacopeia (for the United Kingdom) and European Pharmacopoeia that specify the test procedures and parameters for suture testing. Product testing involves both biological, such as biocompatibility, and physical examinations. Unlike many material areas, most of the testing is done on suture materials already being used. A number of factors are responsible for this trend. A major factor involves the lack of understanding between the test results and materials because of the complex hostile environment where the sutures operate. Researchers believe that it is important to understand these relationships using known materials before looking at newer candidates. This does not mean that the area of sutures is static. New suture materials are continually being introduced, but most of these advances involve modification of existing materials.

Biocompatibility is an important consideration. Again, many unintended consequences are often found, unfortunately after the fact. In the areas of synthetic hip and knee replacement, use of alloys is often called for, yet some patients are found to have long-term allergies to certain metals present in minute amounts that eventually require replacement of the joint material. Thus, extensive testing is required before a new suture becomes commercially available.

Much of the testing involves looking at real-time biodegradation results on physical properties. There is an effort to develop standardized tests that can be done outside a patient with this effort now being done by comparing the tests done outside the patient with results found with the patient.

Stress–strain properties, often described in terms of tensile strength, are usually used to describe the ability of a suture to withstand various surgical (such as pulling together the materials to be held together) and postsurgical stresses. Postsurgical abrupt stresses, e.g., a cough, are important considerations. Long-term failure of a suture, caused by even small leakages, can result in the formation of an edema or hemorrhage. Thus, both long-term and abrupt behaviors need to be considered while choosing a suture. For example, a suture used in a lung needs to have a high elasticity, slow degradation, and high tensile strength.

Diameters are measured using a dead-weight gauge with a specific foot pressure of weight applied with diameters measured to within 0.02 mm. The diameter is measured at three points on the suture, about $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$ of the strand length. Since the knot strength is so important, knot pull strength is measured. Here, the suture is tied around a flexible rubber tubing of 6.5 mm inside diameter and 1.6 mm wall thickness. The suture is attached to the testing machine and tested at a specified rate of elongation. A similar needle attachment test is done.

Suture manufacture is specialized. In the production from raw materials or isolation from natural materials, purification is especially important because small amounts of by-products and contaminants can have a serious effect of the properties of the suture and the behavior within the patient. Processes for suture fabrication include melt spinning, extrusion, and braiding.

With the exception of sutures made from steel, all others are polymeric. Sutures are generally divided into two broad categories: (1) absorbable sutures, which are absorbed by the healing tissue through proteolysis or hydrolysis and (2) nonabsorbable sutures, which remain in the tissue, often for the lifetime of the patient.

In general, absorbent sutures are composed of materials that are natural to mammals, such as catgut, and to materials that are either quite susceptible to hydrolysis and/or polymers derived from natural materials such as polyglactin, which is a copolymer of lactic and glycolic acid. Nonabsorbent sutures can be made from natural materials such as cotton, which is a plant material, polymers that range from being hydrophobic to hydrophilic, and steel.

There is a difference between what is called permanent or nonabsorbent and the actual degradation rate of the material. Silk, polyester, nylon, and cotton sutures generally degrade with time, while steel sutures remain reasonably intact throughout the patient's lifetime. Further, there is a difference between such physical properties as tensile strength and absorbent and nonabsorbent sutures. Silk, polyester, nylon, cotton, and, in fact, most nonabsorbent sutures lose tensile strength with time, time being a month, year, or longer.

Because only a little suture is generally employed and it is important in the overall surgical procedure, cost is not a major consideration. Following are brief discussions of the major kinds of suture material.

Cotton and *linen* are not widely used today as sutures. Cotton is usually used as a twisted monofilament, such as thread. It is used where rapid healing is expected because of its short-term resistance to degradation. Atramat surgical cotton, unlike "ordinary" cotton, has good strength and a uniform diameter, but it is weaker than silk. It offers good handling and good knot security. Linen is obtained from linen fibers and is similar to surgical cotton in most ways.

Catgut sutures are seldom actually catgut. The name is derived from past practices. Today, so-called catgut is derived from the submucosa of sheep jejunum and the ileum or serosa of beef intestine that is cut into longitudinal ribbons.

For *plain catgut*, the ribbons are treated with dilute formaldehyde to increase tensile strength and resistance to enzymatic lysis. They are sterilized using cobalt 60 irradiation. Plain catgut is, in fact, highly purified collagen. It is generally used only with wounds that heal rapidly because of its rapid degradation with the necessary tensile strength remaining for only 1 week. It can also give adverse tissue reaction because it is a protein. It is seldom used today because of the adverse tissue reactions and rapid degradation.

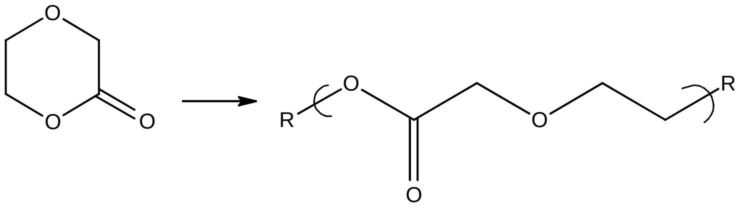
Chromic catgut is created by treatment of plain catgut with basic chromium salts that result in the catgut being more resistant to absorption and stronger. Chromic catgut retains a reasonable tensile strength for 2–3 weeks. It is often the suture of choice for Pomeroy tubal ligation procedures because it dissolves quickly decreasing the opportunity for a fistula to form between the two ends of the bisected tube.

Both varieties of catgut are not employed for facial or surface use because of their tendency for scar formation and inflammatory response.

Silk, used for sutures, is obtained from the cocoon of the silk worm, *Bombyx mori*. Tension force is gradually lost until tissue encapsulation occurs. Tissue reactivity may be moderate because silk is a protein and its interaction with the body is not benign. It is classified as nonabsorbent because it retains much of its strength for more than 2 months and 50% to half a year, but loses most of its strength after 2 years. While stronger than cotton, surgical silk is weaker than the synthetic nonabsorbable sutures. Much of the silk is coated with silicon allowing a smooth travel through tissue and avoiding a saw-cutting effect. It is widely used in general surgery, gastroenterology, gynecology, obstetrics, ophthalmology, etc.

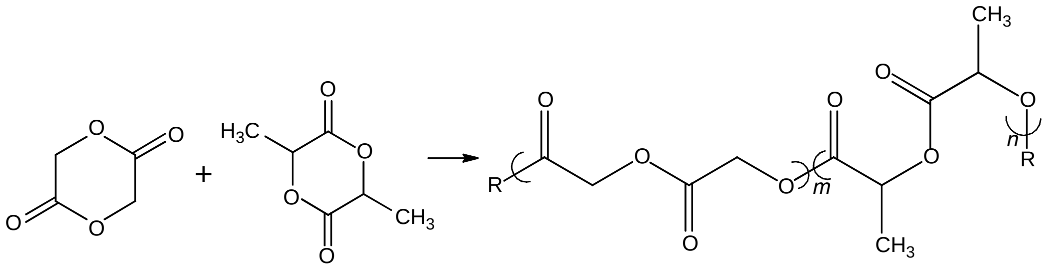
While natural sutures can undergo enzymatic-induced degradation, synthetic sutures generally undergo only physical hydrolysis as the major path of degradation.

Polydioxanone (structure 19.29) is made from the ROP of *p*-dioxanone (structure 19.28). Polydioxanone sutures are generally offered as a monofilament in a variety of sizes. They offer a minimum tissue reactivity with absorption occurring over about a 200-day process. The original tensile resistance holds to about 70% after 4 weeks and 50% after 6 weeks. It is often employed in tissue coaptation that heals slowly. It offers adequate tissue support and good knot security. While it offers good initial tissue support, it is not used where long-term tissue support is necessary. It is used in general surgery, gastroenterology, gynecology, and urology, as well as subdermal plastic surgery procedures. As with many sutures, it is colored by application of a dye for easy identification during the surgical procedure.



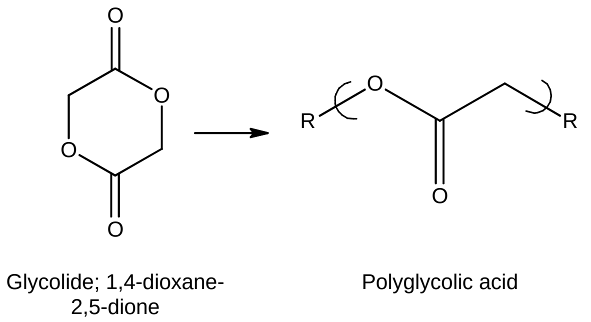
p-Dioxanone (19.28) Polydioxanone (19.29)

Polyglactin (structurally the same as *polyglyconate*) is a structural copolymer of lactic and glycolic acid synthesized from glycolide (structure 19.30) and 3,6-dimethyl-1,4-dioxane (structure 19.31). Polyglactin (structure 19.32) was the second synthetic suture offered commercially, beginning in 1975. It is usually sold as a braided material offered in a wide variety of sizes. A variety of copolymer compositions are offered under varying trade names. For instance, Vicryl is a 90/10 composition of poly(glycolide-co-lactide) while Panacryl is a 5/95 copolymer composition. Vicryl Rapide is a new polyglactin suture introduced into usage in the United States, but it has been used for sometime in Europe. It retains 50% strength for 5 days and is essentially absorbed in 40 days. Coated Vicryl Rapide is used for skin closure in small superficial areas, and in the vulvar and episiotomy areas because it falls off in about 1 week to 10 days eliminating the necessity for suture removal. It is also being used in gynecological surgery to tie bleeders in areas close to vital structures because of its fast absorption and minimal tissue reaction decreasing the opportunity for kinking and obstruction formation.



1,4-dioxane-2,5-dione; glycolide (19.30) 3,6-dimethyl-1,4-dioxane (19.31) Polyglactin (19.32)

Polyglycolic acid is a homopolymer of glycolide and was the initial synthetic suture offered for sale under the trade name of Dexon. It is formed into monofilaments from the melt with the filaments stretched as they are formed to assist in aligning the polymer chain, thus increasing the filament strength. Polyglycolic acid (structure 19.33) is also braided into sutures.



(19.33)

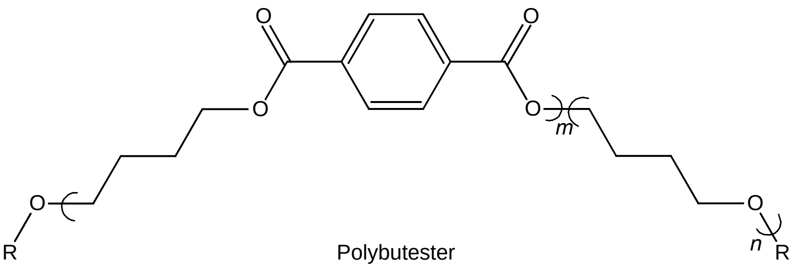
The *polyamide* (nylon) material that is employed as a suture material is the standard nylon-6,6. It is usually used as a monofilament. Tissue reaction is minimal and, in time, it is encapsulated by connective tissue. Hydrolysis decreases the chain length and strength by about 10% per year. It is used in neurology, ophthalmic, and plastic surgery. It has good tensile strength and little elongation change. It offers good knot security and low tissue drag. It is the suture material of choice for chainsaw leg wounds since it offers good strength and flexibility needed for knee and leg action.

Polyester sutures are made from PET. They show better handling than nylon offering greater initial strength than nylon, polypropylene, and silk with only stainless steel being stronger. It offers less skin reaction than silk and is equally manageable, offering good knot security and ease in tying the knot. It is often employed as a braided material. Uncoated polyester sutures, such as Dacron, Mersilene, and Surgidac, offer the best knot security. Teflon-coated sutures, such as Tevdek, Polydek, and Ethiflex, handle better.

Polyethylene sutures are used for general surgery offering a smooth surface area that produces little tissue drag. They are inert.

Polytetrafluoroethylene, Teflon, is often impregnated into sutures and used as a coating promoting reduction of tissue drag and biological inertness. Gore-Tex sutures are a monofilament PTFE and part of a grouping of PTFE biological implants called ePTFE. Gore-Tex is 50% air by volume. It has good tensile strength, inertness, slipperiness, ties like silk, and offers good knot security. Suture-related bleeding is reduced because they can be swaged to needles that closely approximate the thread diameter. It is especially used for vaginal reconstructive surgery for perivesical and sacrospinous ligament support.

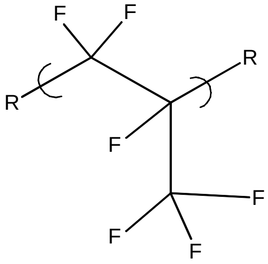
Polybutester (structure 19.34) is a segmented block copolymer of butylene terephthalate units and tetramethylene ether glycol units. The terephthalate portion is rigid giving the butylene terephthalate blocks a semirigid or hard property. The tetramethylene ether glycol or tetramethylene ether oxide units are flexible and contribute to the "softness" of the polymer. Thus, polybutester makes use of the hard or soft concept often employed in polymer science to give a material with some strength that acts flexible or soft. It is used with soft tissue applications including ophthalmic and cardiovascular surgeries, but not microsurgery and neural tissue surgery. It offers minimal acute inflammatory reaction and is gradually encapsulated. It offers long-term strength retention. Polybutester-coated Ethibond sutures also handle well causing less tissue reaction in comparison with the other polyester sutures.



Polybutester (19.34)

Isotactic *polypropylene* is employed as a suture material. It is extruded as a monofilament. Tissue reaction is minimal and, *in vivo*, it offers outstanding stability making it a good candidate when permanent support is needed. It resists repeated bending over a longer time period, retains good strength, and offers minimal rejection and good controlled elongation, making it a suture of choice for cardiovascular and cuticular applications. It also offers minimal resistance or drag as it is moved through tissues creating a minimal tear and tissue dragging. It provides good knot security. It is also used in plastic reconstruction, gynecology and obstetrics, orthopedics, and general surgery.

Polyhexafluoropropylene (structure 19.35) is a recently available suture material used for soft tissue neurological, cardiovascular, vascular, and ophthalmic surgeries. It offers the inertness of PTFE. It is available as a monofilament.



Polyhexafluoropropylene (19.35)

Stainless steel wire offers the greatest strength and knot security and it seldom promotes tissue reaction. But, it is difficult to handle with a tendency of puncturing gloves and tissues, kinks, deforms, and undergoes fatigue. Thus, it is not widely used and with the availability of the new high-strength synthetic sutures, continues to be replaced.

In summary, there exists a variety of suture materials with only one that is not polymeric. They serve as essential materials in surgery.

19.7 GEOTEXTILES

Because of the recent rash of hurricanes like Katrina and tsunamis, we have become more aware of the need for protection against their violence. Geotextiles play a major role in this protection. Reinforced soil was used by Babylonians 3000 years ago in the construction of their pyramid-like tower, ziggurats. One of these famous towers, the Tower of Babel, collapsed. For thousands of years, the Chinese used wood, straw, and bamboo for soil reinforcement including the construction of the Great Wall. In fact, the Chinese symbol for civil engineering can be translated as "earth and wood." The Dutch have made extensive use of natural fibrous materials in their age-old battle with the sea. The Romans employed wood and reed for foundation reinforcement. By the 1920s, cotton fabrics were tested as a means for strengthening road pavements in the United States, but these field trials were not followed up by application.

The modern materials for geotextiles are those produced by the textile industry, since the early 1900s. In the 1950s, the original technology for manufacturing plastic nets was developed by the packaging industry. The 1960s saw manufacturing capabilities for nonwoven fabrics made from continuous filaments being developed. The stage was set for the birth of the geotextiles industry. In 1957, as part of the Netherlands project to reclaim and protect its ocean-side, nylon-woven fabric sandbags were used. In 1958, PVC-woven fabric was used for coastal erosion in Florida. In 1958 and 1959, sandbags made from synthetic polymers were used in West Germany and Japan for the control of soil erosion.

Geotextiles are available as mats, textiles, webs, nets, grids, and sheets. When retention of the contained material is desired synthetic polymers such as polypropylenes, polyesters, nylons, PEs, and PVCs are used because they resist rapid degradation. When only short-term retention is needed natural materials such as cotton are used. Geotextiles are not always made from fibers, but include film materials such as PE and polypropylene sheets used to retain moisture but retard weed growth in gardens.

Geotextiles perform a number of functions. They help control fluid transmission such as helping to direct the flow of rain water to an outlet. They are used to separate materials for containment and to stop mixing such as highway embankment retention. It can be used for filtration control that allows for liquid and small particulates to pass through, but to retain larger materials such as rocks. In sandbags for flood control, geotextiles simply hold together a material such as sand for breach control.

19.8 SMART MATERIALS

We have had smart materials as materials for a long time though the term is relatively new. Some of the first smart materials were piezoelectric materials, such as poly(vinylene fluoride), which emit an electric current when pressure is applied and change volume when a current is passed through it. Most smart materials are polymeric or have a critical portion of the smart system that is polymeric.

Today, research involves not only the synthesis of new smart materials, but also the application of already existing ones. Much of the applications of smart materials involve the assemblage of it and envisioning its uses. Thus, it is possible that since application of pressure to a piezoelectric material causes a discharge of current, a portion of a wing could be constructed such that apparent “warpage” of a wing would result from an “electronic feedback” mechanism employing a computer coupled with a complex system of electronic sensing devices. Almost instantaneous, self-correcting changes in the overall wing shape would act to allow safer and more fuel-efficient air flight. Piezoelectric sensors could also be used to measure application of “loads” through reaction of the piezoelectric sensors to stress or strain.

Smart materials are materials that react to applied force—electrical, stress or strain (including pressure), thermal, light, and magnetic. A smart material is not smart simply because it responds to external stimuli, but it becomes smart when the interaction is used to achieve a defined engineering or scientific goal. Thus, most materials, such as ceramics, alloys, and polymers, undergo volume changes as they undergo phase changes. While the best known phase changes involve changes in state such as melting or freezing, many materials, specifically polymers, offer more subtle phase changes. For polymers, the best known subtle phase change is associated with the glass transition, T_g, where local segmental mobility occurs. Volume changes associated with T_g are well known and used as a measure of the amount of crystallinity present in a polymer. Thus, when this volume change is used to affect some desired change, such as switching on and off an electric circuit, the polymer becomes a smart material. Multiple switching devices can be constructed using polymers with varying T_g values.

The use of smart materials as sensing devices and shape-changing materials has been enhanced because of the increased emphasis on composite materials that allow the introduction of smart materials as components.

A smart material assembly might contain:

- Sensor components that monitor changes in some parameters such as temperature, light, magnetic field, and/or current
- Communication networks that relay changes detected by the sensor components through fiberoptics or conductive "wire"
- Actuator parts that react to the external stimuli such as changes in temperature, current, etc.

The actuator part may also be a smart material, such as a piezoelectric bar, placed in a wind foil that changes orientation according to a current imputed by the computer center allowing a machine such as an automobile to handle better and be more fuel efficient.

Muscles contract and expand in response to electrical, thermal, and chemical stimuli. Certain polymers, such as synthetic polypeptides, are known to change shape on application of electric current, temperature, and chemical environment. For instance, selected bioelastic smart materials expand in salt solutions and may be used in desalination efforts and as salt concentration sensors. Polypeptides and other polymeric materials are being studied in tissue reconstruction, as adhesive barriers to prevent adhesion growth between surgically operated tissues, and in controlled drug release, where the material is designed to behave in a predetermined matter according to a specific chemical environment.

Most current efforts include three general types of smart materials: piezoelectric, magnetostrictive (materials that change their dimension when exposed to a magnetic field), and shape memory alloys (materials that change shape and/or volume as they undergo phase changes). Conductive polymers and liquid crystalline polymers can also be used as smart materials since many of them undergo relatively large dimensional changes when exposed to the appropriate stimulus such as an electric field.

New technology is being combined with smart materials called micromachines, machines that are smaller than the width of a human hair. Pressure and flow meter sensors are being investigated and commercially manufactured.

As with so many areas of polymers smart materials have our imagination as the limit.

19.9 HIGH-PERFORMANCE THERMOPLASTICS

Engineering plastics are also referred to as high-performance thermoplastics or advanced thermoplastics. An *engineering plastic* is simply one that can be cut, sawed, drilled, or similarly worked with. Along with the ability to be worked with, high-performance thermoplastics generally can also be used at temperatures exceeding 200°C. These materials are also referred to as high-temperature thermoplastics. As the advantages of polymeric materials become evident in new areas, the property requirements, such as thermal stability, will increase causing the polymer chemist to seek new materials or "old" materials produced in new ways to meet these demands.

Table 19.2 contains some of the new advanced thermoplastics that are currently available.

Many of these polymers are being utilized as lightweight replacements for metal because of their strength, high-dimensional stability, and resistance to chemicals and weathering.

Nylon-6,6 was the first engineering thermoplastic and till 1953 represented the entire annual engineering thermoplastic sales. Plastic nylon-6,6 is tough, rigid, and need not be lubricated. It has a relatively high use temperature (to about 270°C) and is used in the manufacture of many items from hair brush handles to automotive gears.

TABLE 19.2
Advanced High-Temperature Thermoplastics and Applications

Material	Heat Deflection Temperature (°C)	Properties
Poly(arylene carbonates)	—	Leaves no degradation residue
Polyamideimides	280	Good wear and good friction and solvent resistance
Polyanilines	70	Electrical conductor
Polyarylates (aromatic polyesters)	175	Good toughness, UV stability, flame retarder
Polybenzimidazoles	440	Good hydrolytic, dimensional, and compressive stability
Polyetherimides	220	Good chemical, creep, and dimensional stability
Polyethersulfones	200	Good chemical resistance and stability to hydrolysis
Polyimides	360	Good toughness
Polyketones	330	Good chemical resistance, strength, and stiffness
Poly(phenylene ether)	170	Often alloyed with polystyrene
Poly(phenylene sulfide)	260	Good dimensional stability and chemical resistance
Polyphenylenesulfone	260	Good chemical resistance
Polyphthalamide	290	Good mechanical properties
Polysulfone	175	Good rigidity

Nylon-4,6 was developed by DSM Engineering Plastics in 1990 and sold under the trade name Stanyl giving a nylon that has a higher heat and chemical resistance for the automotive industry and in electrical applications. It has a T_m of 295°C and can be made more crystalline than nylon-6,6. A number of other nylons, such as the aromatic nylons and aramids, are strong and can operate at high temperatures, and they have good flame-resistant properties.

The next general grouping of polymers to enter the engineering thermoplastic market was the polyacetals derived from formaldehyde and known as POMs. While formaldehyde can be easily polymerized, it also depolymerizes easily through an unzipping mechanism. Most industrial polyacetals are capped preventing ready unzipping. POMs are highly crystalline, creep-resistant, rigid, fatigue-resistant, mechanically strong and tough, solvent-resistant, and self-lubricating. Unfortunately, even when capped, care must be taken since they have a tendency to unzip at high temperatures. Polyacetals are used in the manufacture of rollers, housings, bearings, gears, and conveyor chains.

While a number of polyesters have been considered as engineering thermoplastics, only a few have been widely used. Although PET is widely used, it does not crystallize rapidly discouraging its use in rapid molding processes. Polyester engineering thermoplastics require a high degree of crystallinity. Thus, PET is widely used as a fiber, but not widely employed as an engineering thermoplastic.

By comparison, poly(butyl terephthalate) (PBT) is widely used as an engineering thermoplastic since it crystallizes rapidly allowing rapid fabrication. It has low moisture absorption, good self-lubrication, good retention of mechanical properties at elevated temperatures, and offers good solvent resistance and fatigue resistance. It is used in numerous "under-the-hood" automotive applications including ignition systems. It is also used in athletic goods, small- and large-appliance components, power tools, and electrical applications.

Polycarbonates have been made using a variety of bisphenols, but the most widely produced materials are derived from bisphenol A. Polycarbonates, which exhibit good impact strength, are heat-resistant, have good electrical properties, and high-dimensional stabilities. They also offer good transparency that allows their use in replacing glass where good transparency is needed such as in safety glazing, automotive headlamps and taillights, CDs, and in ophthalmic applications. They also offer inherent flame resistance due in part to the presence of the carbonate moiety that is already largely oxidized so as not to act as a fuel.

Poly(alkylene carbonates) leave no residue when decomposed. Thus, they are used in binders for holding ceramic and metal powders together, long enough for them to be made into the desired products. These polymers also give good moisture and oxygen barriers and they are abrasion resistant, offer good clarity and give tough films, and are being considered in food and medical packaging applications.

PPE or PPO shows total compatibility with PS allowing a number of different combinations to be formed giving rise to the Noryl family of blends and alloys. These two combine, each offering needed properties. The PPO brings fire retardancy and contributes to a high heat distortion temperature above 100°C allowing the products to be cleaned and used in boiling water. PS contributes ease of fabrication to the combination. Both contribute to the blends outstanding electrical properties and good water resistance. Furthermore, the blends give materials with a lower density than most engineering materials.

Polyarylsulfones offer materials with good thermal–oxidative stability, solvent resistance, creep resistance, and good hydrolytic stability. Their low flammability and smoke evolution encourage their use in aircraft and transportation applications. They hold up to repeated steam sterilization cycles and are used in a wide variety of medical applications such as life support parts, autoclavable tray systems, and surgical and laboratory equipment. Blow-molded products include suction bottles, surgical hollow shapes, and tissue culture bottles. PPS has a number of automotive uses including as an injection-molded fuel line connector and as part of the fuel filter system.

The aromatic polyketones offer good thermal stability, good environmental resistance, good mechanical properties, resistance to chemicals at high temperatures, inherent flame retardancy, good friction and wear resistance, and good impact resistance. PEEK became commercialized in 1980 under the name Victrex. It is used in the chemical process industry as compressor plates, pump impellers, bearing cages, valve seats, and thrust washers; in the aerospace industry as aircraft fairings and fuel valves; and in the electrical industry as semiconductor wafer carriers and in wire coatings.

PEI was first announced by General Electric scientists in 1982. It offers good stiffness, impact strength, transparency, low smoke generation, broad chemical resistance, good heat resistance, good electrical properties, and good flame resistance. It also offers good processability and a good resin can be made from it allowing easy molding. It is also used in internal components of microwave ovens, electrical applications, and in transportation.

With the advent of the soluble stereoregulating catalysts, so-called older polymers have been synthesized with additional control over the structure giving products with enhanced strength and dimensional stability. Amorphous PS is relatively brittle, requiring a plasticizer to allow it to be flexible. The use of soluble stereoregulating catalysts allowed the synthesis of sPS with a T_m of about 270°C and a T_g of about 100°C with good solvent and chemical resistance. DOW commercialized sPS under the trade name Questra in 1997. It is used in specialty electrical and under-the-hood automotive applications.

19.10 CONSTRUCTION AND BUILDING

The use of polymeric materials as basic structural materials is widespread and of ancient origin. In the past, building materials were largely rocks and plant materials, both largely polymeric. Today, the major structural building materials are concrete, and in many places wood, again, both largely polymeric. The proportion of concrete to wood varies on the type of building and location. Generally, the structural materials are concrete and steel for large buildings. For home dwellings it may be almost only concrete such as in the Middle East where wood is not abundant, with more wood used for framing in the United States.

For home building, the first material is concrete for the slab, here in Florida, or some form of concrete for the basement. Frames consisting of wooden boards are generally the next

TABLE 19.3
Use of Materials in Building and Construction

Material	Weight (Billions of Pounds)	Percentage by Weight
Concrete[a]	250	50
Lumber[a]	60	12
Ceramic[a]	50	10
Wood panels[a]	20	4
Iron and steel	15	3
Plastics[a]	10	2
Others[b]	95	19

[a] Indicates a polymeric material.

[b] Some of these are polymeric, such as paints, sealants, and coatings.

major addition. This is followed by a plywood roof covered by roofing material, again the major choices of fiberglass shingles, wood shakes, and ceramic and concrete tiles are all polymeric. Shortly, the structure is enclosed with the addition of a wooden door and glass windows. Table 19.3 shows the proportion of materials used in building and construction and is an average of homes and large buildings for the United States for 2000. Of these basic materials, over three quarters are polymer intensive. Table 19.4 shows general use categories of polymers in home construction.

The use of synthetic polymers in building and construction is also increasing at a rapid rate. Flooring is a mixture of wood, synthetic and clad wood, carpet, and tile, all polymeric. While carpets were once derived from natural materials such as cotton and wool, today almost all of them are derived from synthetic polymers and include nylon, polyester, olefins, and polyacrylonitrile.

Uses of plastics are given in Table 19.5.

As lighter and stronger polymeric materials are available, their impact on the building and construction industry and on other industries will increase. Further, as materials that perform specific tasks are available, they too will become integrated into the building and construction industry. This includes devices for gathering and storage of solar energy and smart materials including “smart windows.”

TABLE 19.4
Common Applications of Polymers in Home Construction

Application	Typical Polymers Used
Foundation	Cement (concrete)
Framing	Wood
Thermal insulation	Foamed polystyrene, polyurethane, Fiberglas®
Vapor barrier	Polyethylene
Siding	Wood, polyvinyl chloride
Paints	Acrylics, polyurethanes
Electrical insulation	Polyisoprene (rubber), chlorinated polyethylene
Flooring	Wood, complex silicates (cement or ceramic tile), carpet (nylon, polyester, polyolefin)
Roofing	Plywood (sheathing), fiberglas (shingles), complex silicates (cement, ceramic tile)

TABLE 19.5
Major Plastic Applications in Building and Construction

Plastic	Use(s)
ASA	Window frames
Acrylics	Lighting fixtures and glazing
PVC and chlorinated PVC	Hot and cold water pipe; moldings, siding, window frames, floor tiles
Melamine and urea formaldehyde	Laminating for counter tops, adhesives for wood, plywood, and particle board
Phenol formaldehyde	Electrical devices and plywood adhesive
Poly(ethylene terephthalate)	Counter tops and sinks
Polycarbonates	Window and skylight glazing
Polyethylene	Pipes, wires, and cable coverings, plastic lumber, vapor barriers
Poly(ethylene oxide)	Roofing panels
Polystyrene	Insulation and sheathing
Polyurethane	Insulation and roofing systems
Polypropylene	Vapor barrier sheeting, pallets, brushes

19.11 FLAME-RESISTANT TEXTILES

Combustion generally occurs through a burning process where there is a fuel, here a polymer, and oxygen. Because most organic polymers have high hydrocarbon content and/or contain only carbon, hydrogen, and oxygen, the major products of combustion are carbon dioxide and water, or when there is an insufficient amount of oxygen, carbon monoxide and water. For some polymers such as PS and PVC, formation of fused ring compounds results in the formation of char that acts as a barrier to oxygen acting to impede the combustion process. In fact, the burning process is more complex occurring in at least three environments: the surface where oxidation is predominant; the inner surface where the amount of oxygen is depleted yet where evolution of created gases occurs; and the bulk where there is a lack of oxygen and produced gases are trapped. Even so, as combustion continues, more of the polymer sample is exposed becoming surfaces as the old surface is burnt away. These new surfaces generally react with incoming oxygen forming mainly the typical combustion products.

Most combustion is exothermic feeding on itself. Table 19.6 shows the heats of combustion of selected polymers. Those polymers containing large amounts of oxygen typically have lower heats of combustion because they are already partially oxidized. Thus, POM and PET have low heats of combustion.

Heats of combustion are not indicators of the tendency to burn or the rate of burning. Other indicators are employed as markers with respect to their tendency to burn. The limiting oxygen index (LOI) is one of these markers. Briefly, the sample, in a predescribed standard

TABLE 19.6
Heats of Combustion of Selected Polymers

Polymer	ΔH (kJ/g)	Polymer	ΔH (kJ/g)
POM	17	Nylon-6,6	32
Cellulose	18	PS	42
PVC	20	NR	45
PET	22	PP	46
PMMA	26	PE	47

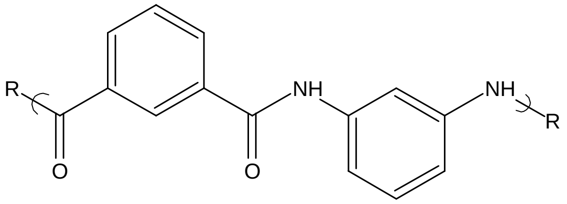
TABLE 19.7
Limiting Oxygen Index (LOI) of Selected Polymers

Polymer	LOI
PP	0.17
PE	0.17
PMMA	0.17
PS	0.18
PC	0.27
PVC	0.48
PTFE	0.95

form, is set afire in an upward-flowing oxygen–nitrogen gas mixture and a stable flame is established. The oxygen/nitrogen ratio is reduced until the sample flame becomes unstable and is extinguished. The minimum oxygen content which supports combustion is the LOI of the sample. Such tests are quantitative but must be considered first approximations.

Table 19.7 lists the LOIs of selected polymers. Materials with LOI values above 0.25 are considered to be self-extinguishing under normal atmospheric conditions. Addition of flame retardants increases the LOI. While most polymers decompose mainly to carbon dioxide and water, some give off harmful gases. Thus, PVC splits hydrogen chloride when burning. Some compounds such as polyacrylonitrile might be suspected to give off hydrogen cyanide, but, in fact, they form complex fused ring systems incorporating the cyanide moiety into the system resulting in the emission of little or no hydrogen cyanide.

Asbestos was the first flame-resistant material used but because of its negative health effects, it has been replaced by other materials. Today, the most widely used flame-resistant textile is Nomex™ (structure 19.36). It is inherently flame resistant, not requiring an additional application or need to worry that the coating may be removed through cleaning. Nomex is an aramid or aromatic nylon material. Along with being flame resistant, it is very strong and so is also used in tire cord. Because of its stiffness and high cost, it is seldom used as a general textile material. Here, we will focus on fiber-intensive uses of such aromatic nylons.



(19.36)

Cost of a material depends on many factors. Some polymers retain unwanted materials, such as unreacted monomer that must be removed. Removal is generally done by dissolving the polymer and reprecipitating it leaving the unwanted material in solution. Aramid polymers are difficult to dissolve, so did not become commercially available until the 1980s. Paul Morgan and Charles Carraher noticed that some materials stay dissolved when produced in rapidly stirred systems. Morgan turned this observation into use when he noticed that aromatic nylons, when made in rapidly stirred systems, stayed dissolved long enough so that the solution can be run into a nonsolvent that turned the aromatic nylons to solids as they passed through spinnerets into the nonsolvent. Thus, the aramid fibers were formed without needing to redissolve them. This allowed aromatic nylons to be available at a competitive cost.

Aramids resist melting, dripping, supporting combustion in air, or burning. These are all positive characteristics. It is employed by firefighters for both routine firefighting materials and also as a common station wear. Clothing made from aramids is durable and comfortable. The "firefighting" outerwear is thicker than that employed as innerwear by the firemen. Racers also take advantage of the durability and flame-resistant characteristics of aramids by wearing clothing made of it. In a pileup, it provides valuable seconds that allow the drivers to be pulled safely from the burning wreckage.

19.12 WATER-SOLUBLE POLYMERS

The solubility rules governing polymers are similar to that governing water solubility of smaller organic molecules except that the extent of polymer solubility and range of polymeric structures are more limited. Figure 19.4 presents structures of some of the commercially available water-soluble polymers. As with smaller molecules, the presence of highly electronegative atoms that can participate in hydrogen bonding is normal for water-soluble polymers. Such groups include alcohols, amines, imines, ethers, sulfates, carboxylic acids and associated salts, and to a lesser extent, thiols. For charged species, such as sulfates, pH and the formation of charged species are also important factors. Thus, the copolymer derived from vinylamine and vinyl sulfonate is not water-soluble, but the corresponding sodium salt of this copolymer is water-soluble.

The amount and rate of water solubility is decreased by the presence of cross-linking and the substitution of nonpolar units for polar units within the polymer. Most water-soluble polymers possess both hydrophobic and hydrophilic portions and this combination affects the shape of the polymer chains in solution. Many water-soluble polymers exist in random or partially helical chains in water solution where the chains are partially extended allowing further hydrogen bonding with water. Since polar groups present in similar configurations and conformations repeal one another, many water-soluble polymers approach rigid rods. Such structures are somewhat favored because the organic backbones tend to reside within the interior of the polymer chain with the polar groups thrust outwards towards the water.

There also exist a number of water-soluble copolymers. Thus, copolymers containing about 80% ethylene units with units of sodium acrylate are water-soluble and used in the formation of many materials including ionomers.

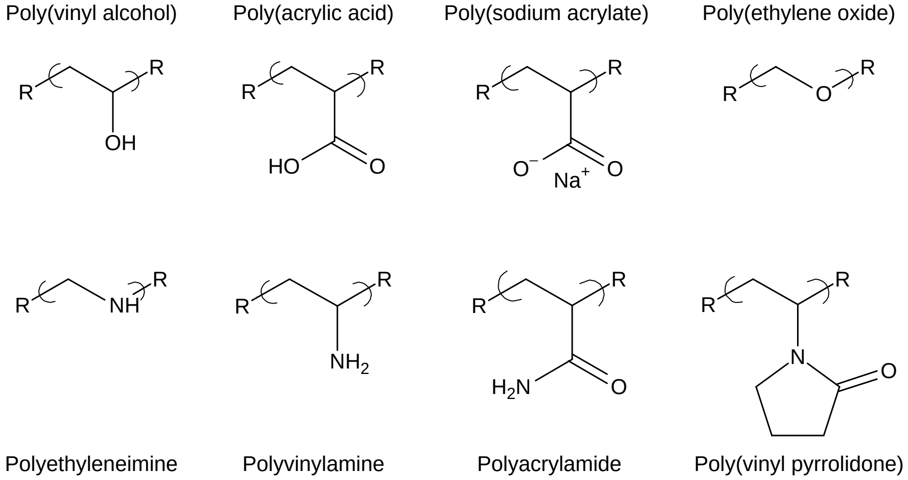

Poly(vinyl alcohol)
Poly(acrylic acid)
Poly(sodium acrylate)
Poly(ethylene oxide)
Polyethyleneimine
Polyvinylamine
Polyacrylamide
Poly(vinyl pyrrolidone)

FIGURE 19.4 Structures of commercially available water-soluble polymers.

19.13 ANAEROBIC ADHESIVES

Almost everything we use daily has adhesives connected with them. Our soda bottles use adhesives to attach the label; our tables—wooden, glass, metal, or a mixture—are connected by adhesives; our shoes are held together by adhesives; our automobiles, trucks, airplanes, trains, all are connected by adhesives; our tires, stoves, and washers, all contain adhesives as essential materials.

Ancient adhesives involved and generally required oxygen to affect the adhesion. Today, there are many application areas where adhesion is required but in the absence of oxygen. These adhesives are called *anaerobic adhesives*. Most anaerobic adhesives are based on dimethyl acrylates. Thus, adhesive is applied to the threads of a bolt. As long as the screw surface remains in contact with oxygen, curing does not occur. On screwing the bolt into the channel or nut, the adhesive's contact with oxygen is cut off and its contact with a metal, typically iron or copper, begins the adhesion process.

An often employed adhesive material for anaerobic adhesives is tetraethyleneglycol dimethacrylate (TEGMA). Reaction begins through the free radical polymerization of TEGMA. This reaction is inhibited by the presence of oxygen as shown in Figure 19.5. Thus, as long as oxygen is present, any TEGMA molecules that become unintentionally active react either with another TEGMA molecule (not preferred) or with oxygen rendering it largely inactive. The second reaction can occur at any point leading to passive oligomers. In fact, anaerobic adhesives are shipped with a blanket of oxygen layered over the adhesive to be sure that a ready supply of oxygen is present to prevent premature polymerization from occurring. Even on application, the monomer is exposed to oxygen until it is married in such a manner as to cut off the supply of oxygen. At this point a hardener comes into play.

The hardener systems are complex. The most employed hardener system contains a three-part system: the actual radical-producing molecule, here a cumene hydroperoxide,

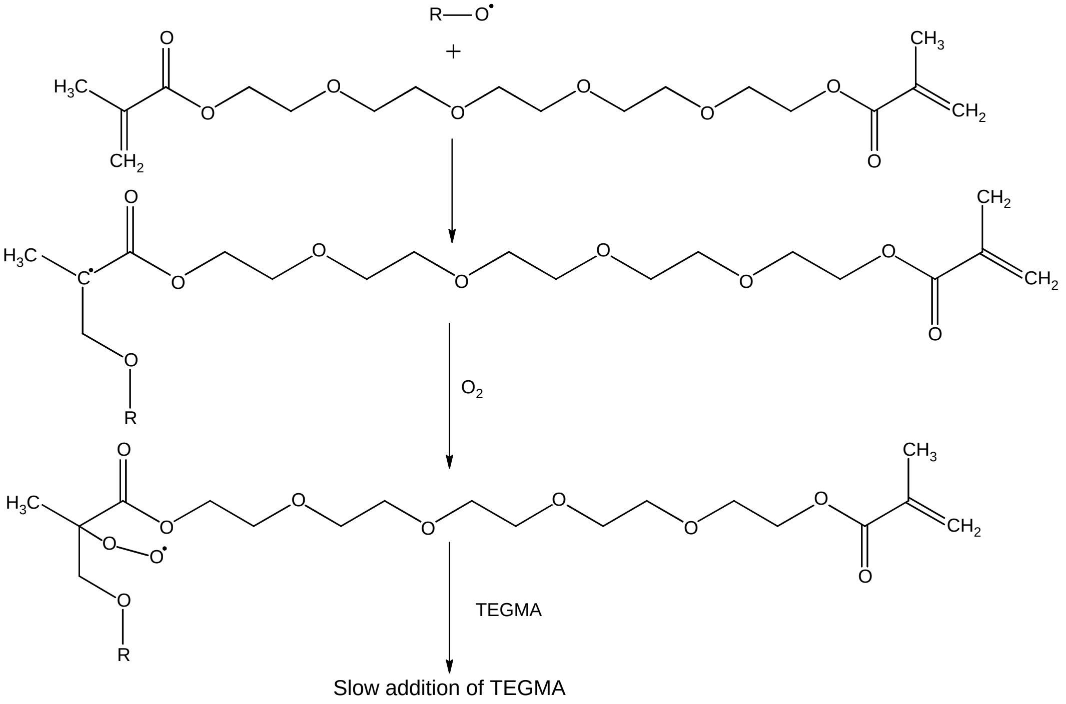


FIGURE 19.5 Formation of passive monomer-derived molecules.

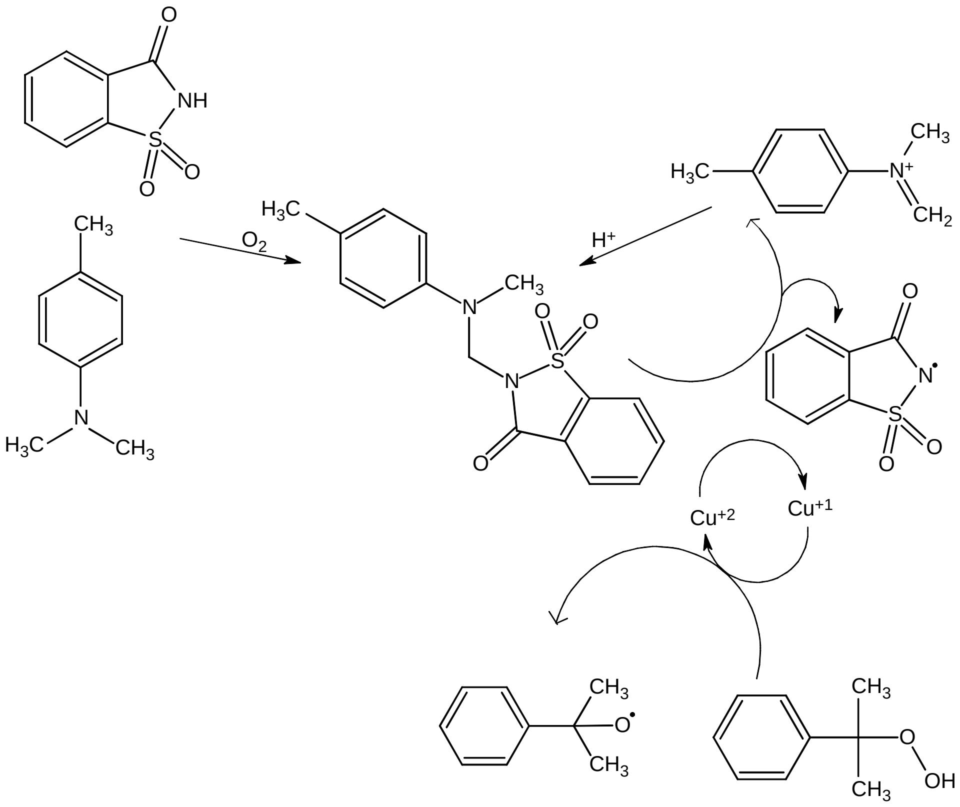


FIGURE 19.6 Reactions involved in the hardening process.

an accelerator, here *N*,*N*-dimethyl-*p*-toluidine, and saccharin which acts as a metal complexing material and a reducing agent for metal ion, here copper (Figure 19.6). The reaction between the saccharin and *N*,*N*-dimethyl-*p*-toluidine consumes any remaining oxygen (Figure 19.6, top left). An aminal is produced, which dissolves surface metal ions reducing them to a lower oxidation number.

$$Cu^{+2} \rightarrow Cu^{+1} + e^{-} \tag{19.37}$$

The Cu^{+1} catalyzes the formation of radicals from the cumene hydroperoxide, which then begins the polymerization of the TEGMA and TEGMA molecules with only one reactive end (Figure 19.7). Those with two active ends result in the formation of cross-linked materials. A similar reaction occurs with iron and several metals such as zinc, gold, silver, cadmium, magnesium, titanium, and alloys that contain any of these metals.

The ‘‘aminal’’ reaction is cyclic ensuring the formation of an abundance of radicals that effect the polymerization of TEGMA.

Because the vast majority of the monomers react at both ends, these adhesives are thermosets and brittle. Thus, such adhesives are not suitable for areas requiring flexibility. Because they are thermosets, they are typically resistant to oils, water, and solvents. Thus, the adhesive plays two roles: bonding and protection. These properties make anaerobic adhesives suitable for automotive and truck motor mounts and electric engines.

Along with their use with bolts, they are also employed in securing screws in various mechanical and electrical applications.

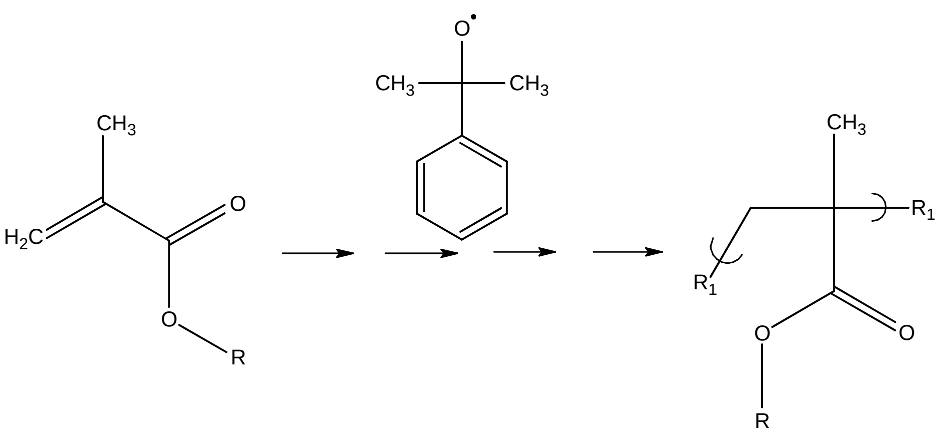


FIGURE 19.7 Polymerization of one end of the tetraethyleneglycol dimethacrylate (TEGMA).

Bolts are generally disconnected by heating to about 400°C thereby thermally degrading the adhesive matrix allowing the bolt to become disengaged.

Different mixtures of anaerobic adhesives are available that offer a variety of curing times, strengths, and compatibilities. A typical cure time is 20 min for cure to begin, vibration resistance in about 1 h. Some fast cure systems will have about 20% cure in a few minutes and are almost cured in about 2 h. Some instant cure systems are ready for use within seconds.

19.14 HYDROGELS

Hydrogels are simply water-filled gels. They are characterized by being hydrophilic yet not completely soluble in water. Those hydrogels that are able to absorb large amounts of water are referred to as superwater adsorbents.

Hydrogel structures may contain the hydrophilic units in the polymer backbone or as side chains. Those polymers that contain the hydrophilic units in the backbone include acrylic, PVA, *N*-vinyl-2-pyrrolidone, and acrylamide-containing materials, derivatives of PEO, and ionomers and glycopolymers. Polymers that contain such functional groups as —OH, —COOH, —SO_3H, and —$CONH_2$ can act as foundations for hydrogels. These polymers generally contain some cross-linking that locks in a three-dimensional structure, which prevents water solubility and also helps retain water. The cross-links can be chemical or physical.

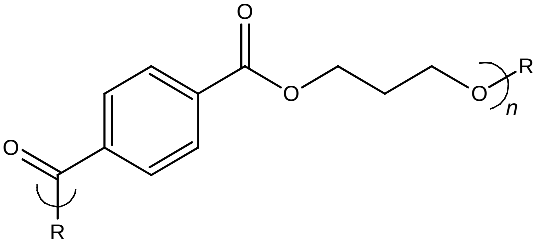
Applications of hydrogels include highly absorbent diapers based on poly(sodium acrylate), contact lenses based on poly(2-hydroxyethyl methacrylate) (polyHEMA), and switches based on variations of swelling of the hydrogels. A number of drug delivery systems have also been based on hydrogels.

19.15 EMERGING POLYMERS

A number of small-scale polymeric materials will continue to enter the marketplace on a regular basis. These include biomaterials and electronic materials where the cost per pound is high and the poundage is low, generally less than 100 t per year. These are materials that fulfill specific needs.

The number of new large-scale giant molecules that enter the marketplace will be small. It has been estimated that it takes about $1 billion to introduce and establish a new material. It is a daunting task with no guarantee of success. In the past, new giant molecules could be introduced that offered improvements in a number of areas and thus would attract a market share in a number of application areas. Today, there are already a wide range of materials for most large-scale application areas that compete for that particular market share so that it is difficult for any material to significantly break into any market area. A new material needs a "flagship" property that a particular market needs.

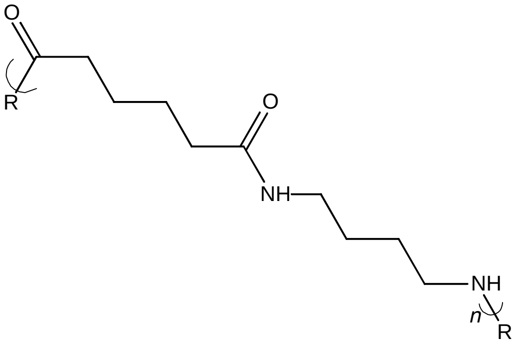
DuPont and Shell have developed a new polyester, poly(trimethylene terephthalate) (PTT) (structure 19.38) that is structurally similar to PET, except that 1,3-propanediol (PDO) is used in place of ethylene glycol. The extra carbon in Sorona allows the fiber to be more easily colored giving a textile material that is softer with greater stretch. Further, it offers good wear and stain resistance for carpet use. The ready availability of the monomer PDO is a major consideration with efforts underway to create PDO from the fermentation of sugar through the use of biocatalysts for this conversion. Sorona and Lycra blends have already been successfully marketed. Sorona is also targeted for use as a resin and film.



(19.38)

Poly(trimethylene terephthalate)

In 1990, DMS introduced nylon-4,6 called Stanyl (structure 19.39), based on the reaction between adipic acid and 1,4-diaminobutane. Stanyl can withstand temperature of about 310°C allowing it to create a niche between conventional nylons and high-performance materials. It was not able to break into the film market and has only now begun to be accepted for tire cord applications. About 22 million pounds of Stanyl was produced in 2001.



(19.39)

Nylon-4,6

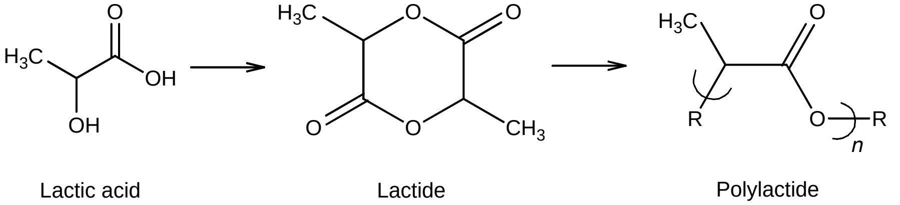
In 1997, Dow introduced sPS under the trade name Questra. The production of Questra is based on relatively new technology and science involving soluble stereoregulating catalysts that produce PS, which has a fixed and repeating geometry as each new styrene monomer unit is added to the growing PS chain. Targeted areas include medical, automotive, and electronic applications.

Several other produces have been developed based on the relatively new soluble stereoregulating catalysis systems. Index, an ethylene–styrene interpolymer, was introduced in 1998 and is intended to compete with block copolymers such as styrene–butadiene–styrene, flexible PVC, PUs, and polyolefins. It is being used as a modifier for PS and PE. Dow is also developing soundproofing and packaging foam applications for Index. Hoechst Celanese (now Ticona) developed Topas, a cycloolefin copolymer, in the 1980s and began its commercial production in 2000. Topas has high moisture barrier properties and is being considered for use in blister packaging for pharmaceuticals. It is also being used in resealable packages where it provides stiffness to the sealing strip. It is also being used in toner resin applications and is being blended with LLDPE and LDPE providing stiffness and improving sealing properties.

A number of new materials are likely to be involved in the upcoming move towards blue-light CDs. For any of these to become important materials in this area they will need to improve on the present polycarbonate-based materials.

GE introduced, in 2000, a new polyester carbonate based on resorcinol arylates called W-4. It is now marketed as Sollx. Sollx does not need to be painted, it offers good weather, chip, scratch, and chemical resistance and is being used as the fenders for the new Segway Human Transporter. It is also aimed at automotive uses including body panels. Sollx is coextruded into two layers: clear and colored, to simulate automotive paint. It is then thermoformed and molded into the finished product.

Several new ventures are based on using natural, renewable materials as the starting materials instead of petrochemicals. These products are known as "green" products since they are made from renewable resources and they can be composted. Along with the production of 1,3-propanediol by Shell and DuPont to produce nylon-4,6, Cargill Dow is making polylactide (PLA) beginning with corn-derived dextrose. The PLA (structure 19.40) is made from corn-derived dextrose, which is fermented forming lactic acid. The lactic acid is converted into lactide, a ring compound that is polymerized through ring opening.



(19.40)

PLA looks and processes like PS. It has the stiffness and tensile strength of PET, and offers good odor barrier and resists fats, oils, and greases. PLA is being considered for use in fibers and packaging. As a film, PLA has good deadfold properties, i.e., it has the ability to be folded and to stay folded. It is being used as a fiber for apparel and carpeting applications. It is being sold as a bridge between synthetic and natural fibers in that it processes like synthetic fibers but has the touch, comfort, and moisture management of natural fibers.

As noted earlier, new materials must "fight-it-out" with existing materials for existing and developing areas. This is particularly true in the automotive area. Thus, PE–PE-copolypropylene panels and bumpers have replaced "rubber" HIPS as automotive bumpers. Other materials were available with greater toughness and scratch resistance, but they were also more expensive. Here, classical monomers were employed to develop nonclassical materials.

In the automotive industry, the rule of thumb is that every 10% reduction of vehicle weight gives about a 5% increase in fuel economy. Weight reduction is only one of the driving forces for the replacement of metals with polymeric materials. It is worth mentioning other driving forces because these are also involved in the selection of certain polymers over other polymers. Reduction in cost is also a factor. Reduction in cost involves a number of factors including, but not exclusive of, simple pound per pound cost. Polymers are outperforming metals because of the ease with which complex structures can be made. Some polymers lend themselves to easy fabrication and this represents both cost savings and enhances the opportunity for the material to become an automotive material. Interestingly, the number of parts also is involved in deciding what material to be used. For instance, if the number of part to be used is less than about 100,000 annually, then injection-molded plastic parts are less expensive than ones stamped from steel. Injection-molded parts also provide aesthetics that are hard to obtain from steel and glass. In fact, many of the plastics can be made to resemble chromes and gold, so are used to enhance the look of some automobiles. Polycarbonate tail lenses are favored over glass for a number of reasons including ability to make more complex and attractive shapes. No longer are only circular taillights the only option.

Flexibility of design as well as material flexibility favors polymers. Again, plastics can be made into almost any shape and when necessary even bent a little to fit them into almost impossible spaces within the automobile's interior.

Along with traditional plastics, composites are also becoming more widely employed. GM has traditionally employed fiberglass composites for the Corvette's body panels (now using carbon–fiber composites for some of these panels), but is now looking to use composites for the body panels of other automobiles.

Performance is also a consideration and in some instances favors polymers over steel. DuPont developed a nylon water jacket spacer for the 2006 Toyota Crown and Lexus GS-300. It did not reduce weight, but did increase the heat-transfer efficiency between the engine coolant system and the cylinders lowering the fuel consumption by 1% or an equivalence of over 50 lb.

Another indirect way that polymers can assist fuel economy is by allowing alternative fuel uses. Plastics can ''create'' free space needed to store bulky batteries encouraging their use as alternative fuel sources.

Along with the more classical polymers some new ones have been developed for automotive use. Thus, GE developed Noryl GTX resins that are being used on the fenders of some cars including the Volkswagen New Beetle and Hummer H3. The Noryl GTX resins are alloys of PPO and nylon-6,6.

The automotive industry is continuing looking for new materials and new uses for more classical materials.

19.16 SUMMARY

1. Polymers are major materials in the nanotechnology revolution including as conductive (photo and electronic) materials. Delocalization of electrons throughout a polymer chain or matrix is important for electronic conductance. This is often accomplished through doping that encourages flow of electrons. Doping provides a ready mechanism for delocalization to occur. Doping is the mode of creating electron sinks or deficiencies and electron excesses that are necessary to breach, or get to, the conductive band.
2. Polymers are also major materials in the biomedical areas and the delivery of drugs. Polymeric drugs can act as control agents to deliver specific biologically active agents or can act as drugs themselves. Polymeric drugs have advantages over smaller drugs because of their size and are being used in the field of medicine.
3. Polymers are used extensively in dentistry as composites, fillings, dental bases, teeth, cements, and as adhesives.
4. Sutures are the largest group of devices implanted into humans. Sutures are employed to hold together parts of the body generally through the use of fibers. A wide variety of materials are available today, each with known advantages and limitations and all are essentially polymeric.
5. Smart materials are materials that react to applied force—electrical, stress or strain (including pressure), thermal, light, and magnetic. A smart material is not smart simply

because it responds to external stimuli, but it becomes smart when the interaction is used to achieve a defined engineering or scientific goal.

6. Engineering plastics are also referred to as high-performance thermoplastics or advanced thermoplastics. An engineering plastic is simply one that can be cut, sawed, drilled, or similarly worked with. Many of those must have a relatively high use temperature generally above 200°C. Many of these polymers are being utilized as lightweight replacements for metal because of their strength, high-dimensional stability, and resistance to chemicals and weathering. Illustrations of high-performance thermoplastics are a number of nylons and polyesters, polycarbonates, polyimides, PPO, and polysulfones.
7. The use of polymeric materials as basic structural materials is widespread and of ancient origin. These materials include concrete, wood, glass, and a wide variety of plastics and elastomers. In fact, with the exception of steel, most of a house is polymeric.
8. Polymers form the basis for fire-resistant textiles. For instance, many of the firefighters and race car drivers wear clothing made from aromatic nylons because these materials resist melting, dripping, supporting combustion in air, or burning.
9. For new polymeric materials to enter the marketplace, many things must be in place including a flagship property that meets a particular market need, ready availability, and money. It takes about $1 billion to introduce and establish a new polymer into the marketplace.

GLOSSARY

anaerobic adhesives Adhesives that cure or set in the absence of oxygen.

biological compatibility No negative biological interactions.

bioerodability Material degradation caused by biological means.

cisplatin (cis-diaminedichloroplatinum II) Most widely used anticancer drug.

doping Addition of materials that create electron sinks or deficiencies and electron excesses that are necessary to create electrically conductive polymers.

engineering plastics Also referred to as high-performance thermoplastics or advanced thermoplastics. An engineering plastic is simply one that can be cut, sawed, drilled, or similarly worked with.

excimer Similar to an exciplex except that the complex is formed between like molecules.

exciplex An excited state complex formed between two different kinds of molecules, one is excited and the other is in its grown state.

hydrogels Cross-linked, hydrophilic polymer networks that allow smaller drugs access to their interior and can be designed to inflate, swell at the desired site, to deliver a drug.

limiting oxygen index (LOI) Minimum oxygen level where burning is sustained.

magnetostrictive material Materials that change their dimension when exposed to a magnetic field.

nanowires Oligomeric molecules that contain an electrical conducting core with chemically functional groups on each end.

nonlinear optics (NLO) Involves the interaction of light with materials resulting in a change in the frequency, phase, or other characteristics of the light.

photochemistry Area of study involving the interaction of electromagnetic energy that results in chemical reactions.

photoconductive Material that is conductive when exposed to light.

photophysics Area of study involving the absorption, transfer, movement, and emission of electromagnetic, light, energy without chemical reactions.

photoresponsive Material whose properties change when exposed to light.

piezoelectric material Materials that emit a current when pressure is applied. The pressure may be applied by simply exposing the material to an electromotive force.

shape memory alloys Materials that change shape and/or volume as they undergo phase changes.

smart materials Materials that react to applied force—electrical, stress or strain (including pressure), thermal, light, and magnetic.

transdermal Across the skin.

EXERCISES

1. Compare and contrast cancer and healthy cells.
2. Describe what a smart material is.
3. What are the properties that make aromatic fibers good material for fire-resistant materials?
4. Which of the following would you expect might become electrically conductive if doped and why? PE, PVC, PS, poly-*p*-phenylene, and PPV.
5. What advantages might conductive carbon nanotubes have over polyacetylene?
6. What disadvantages do conductive carbon nanotubes have in comparison with some of the newly developed conductive polymers?
7. Describe briefly how doping works.
8. Give one advantage polymeric drugs might have over small-molecule drugs.
9. Polymer hearts have been devised and tested for sometime. What are several reasons for this area of research may not produce widespread use of synthetic hearts?
10. Most suture material is colorless. Why is color added?
11. What are some important considerations in developing a biomaterial?
12. What are denture bases made of?
13. You cut yourself using a chain saw. Which of the following sutures might be used and why? Catgut, cotton thread, or nylon filament.
14. Which of the following polymers might be water-soluble? PE, nylon-6,6, PEO, copolymer containing about 50% ethylene and about 50% acrylic acid units, PVC, and PET.
15. Which of the following is not an emerging thermoplastic? Nylon-6,6, PET, PPO, polypropylene.
16. Since PVC has a much higher LOI than PC, why is it not employed to make fire retardant fabric?
17. Would you predict PEO, $—(CH_2—CH_2—O—)—$, to be water-soluble?
18. Why is PTFE not employed as a general high-bulk-used construction material?
19. Why is there such a wide variety of polymers employed in biomedical applications?
20. Why are there a number of fluorine-containing polymers employed in industry and biomedicine?

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Appendix A
Symbols

A	Arrhenius constant
ABS	copolymer of acrylonitrile, butadiene, and styrene
AIBN	2,2′-azobisisobutyronitrile
ANSI	American National Standards Institute
ASTM	American Society for Testing Materials
ATR	attenuated total reflectance spectroscopy
AU	polyurethane
BPO	benzoyl peroxide
BSI	British Standards Institute
bp	boiling point
CA	cellulose acetate
CAB	cellulose acetate butyrate
CED	cohesive energy density
CMC	carboxymethylcellulose
CN	cellulose nitrate
CR	neoprene
C_p	specific heat
C_s	chain transfer constant
DNA	deoxyribonucleic acid
DP	degree of polymerization
DRS	dynamic reflectance spectroscopy
DS	degree of substitution
DSC	differential scanning calorimetry
DTA	differential thermal analysis
E	Young's modulus
E_a	activation energy or energy of activation
EGG	Einstein–Guth–Gold equation
EP	epoxy resin
EPDM	poly(ethylene-co-propylene) cross-linked
EPM	poly(ethylene-co-propylene)
EPR	electron paramagnetic resonance spectroscopy
ESR	electron spin resonance spectroscopy
ET	thiokol
ETA	electrothermal analysis
f	aspect ratio
G	Gibbs free energy; modulus; molar attraction constant
GPC	gel permeation chromatography
GRS	poly(butadiene-co-styrene)
HDPE	high-density polyethylene
HIPS	high-impact polystyrene

IIR	butyl rubber
IR	infrared
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
K	constant in Mark–Houwink equation; Kelvin
LDPE	low-density polyethylene
LLDPE	linear, low-density polyethylene
MF	melamine–formaldehyde resin
MWD	molecular weight distribution
M_n	number-average molecular weight
M_v	viscosity-average molecular weight
M_w	weight-average molecular weight
M_z	z-average molecular weight
NBR	poly(butadiene-co-acrylonitrile)
NBS	National Bureau of Standards
NMR	nuclear magnetic resonance spectroscopy
NR	natural rubber
OI	oxygen index
PA	polyamide
PBI	polybenzimidazole
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCB	polychlorinated biphenyls
PE	polyethylene
PEEK	poly(ether ether ketone)
PET	poly(ethylene terephthalate)
PF	phenol–formaldehyde resin
PGC	pyrolysis gas chromatography
PMMA	poly(methyl methacrylate)
PMR	proton magnetic resonance spectroscopy
PNF	poly(phosphonitrilic fluorides)
PolyEd	Polymer Education Committee
POM	polyoxymethylene, polyformaldehyde, acetals
PP	polypropylene
PPO	poly(phenylene oxide)
PPS	poly(phenylene sulfide)
PS	polystyrene
PTFE	polytetrafluoroethylene, Teflon
PU	polyurethane
PVA	poly(vinyl alcohol)
PVAc	poly(vinyl acetate)
PVB	poly(vinyl butyral)
PVC	poly(vinyl chloride)
PVDC	poly(vinylidene chloride)
RIM	reaction injection molding
RNA	ribonucleic acid
S	entropy; radius of gyration
SAM	poly(styrene-co-acrylonitrile)
SBR	poly(butadiene-co-styrene) elastomer
SEM	scanning electron microscopy
Si	silicon

SMA	poly(styrene-co-maleic anhydride)
SMC	sheet-molding compound
SN	sulfur nitride
SPE	Society of Plastics Engineering
SPI	Society of the Plastics Industry
SR	synthetic rubber
TDI	toluenediisocyanate
TGA, TG	thermal gravimetric analysis
TMMV	threshold molecular weight value
TPE	thermoplastic elastomer
TPX	poly-4-methylpentene
T_c	ceiling temperature; cloud point temperature
T_g	glass transition temperature
T_m	melting point
UF	urea–formaldehyde resin
UHMWPE	ultrahigh molecular weight polyethylene
UV	ultraviolet
WLF	Williams–Landel–Ferry equation

Appendix B Trade Names

Trade or Brand Name	**Product**	**Manufacturer**
Abafil	Reinforced ABS	Rexall
Abalyn	Abietic acid derivative	Hercules
Absafil	ABS polymers	Fiberfil
Absinol	ABS polymers	Dart
Abson	ABS polymers	B.F. Goodrich
Accepta	Polyester	KoSa
Acctuf	PP copolymer	Amoco Polymers
Acelon	Cellulose acetate	May & Baker
Acetophane	Cellulose acetate films	UCB-Sidac
Aclar	Polyfluorocarbon film	Allied
Aclon	Fluoropolymer	Allied Signal
ACP	PVC	Alpha Gary
Acralen	Styrene–butadiene latex	Farbenfabriken Bayer AG
Acrilan	Acrylic fibers	Solutia
Acrilan	Polyacrylonitrile	Chemstrand
Acronal	Polyalkyl vinyl ether	General Aniline Film
Acrylacon	Fibrous glass-reinforced polymers	Rexall
Acrylafil	Reinforced polymers	Rexall
Acrylaglas	Fibrous glass-reinforced styrene–acrylonitrile copolymer	Dart
Acrylicomb	Acrylic honeycomb	Dimensional Plastics
Acrylite	Acrylic	Cyro Inds.
Acrylux	Acrylic plastics	Westlake
Acryrex	Acrylic	Chi Mei
Acrylan-Rubber	Butyl acrylate–acrylonitrile copolymer	Monomer Corp
Acrylite	PMMA	American Cyanamide
Acrysol	Thickeners	Rohm & Haas
Actol	Polyethers	Allied
Adell	Thermoplastic resin	Adell
Adipol	Plasticizer	FMC
Adiprene	Urethane elastomers	DuPont
Adpro	PP	Huntsman
Aerodux	Resorcinol–formaldehyde resin	Ciba
Aerpflex	PE	Anchor

Aeron	Plastic coated nylon	Flexfilm
Afcolene	PS and SAV copolymers	Pechiney–Saint-Gobain
Afcoryl	ABS polymers	Pechiney–Saint-Gobain
Affinity	PE copolymers with poly(alpha-olefins)	Dow
Agro	Rayon fibers	Beaunit Mills
Akulon	Nylon-6; nylon-6,6	AKU, DSM
Akuloy	Nylon-6; nylon-6,6 alloys	DSM
Aim	PS	Dow
Alathon	HDPE and copolymers	DuPont/Lyondell Polymers
Albertols	Phenolic resins	Chemische Werke Huls AG
Albis	Nylon-6; nylon-6,6	Albis Canada
Alcryn	TP elastomer	DuPont
Aldocryl	Acetal resin	Shell
Alfane	Epoxy resin cement	Atlas Minerals
Algil	Styrene copolymer monofilament	Shawinigan; Polymer Corp.
Algoflon	Polytetrafluoroethylene	Montecatini/Auismont
Alkathene	PE	Imperial
Alkon	Acetal copolymers	Imperial
Alkor	Furan resin cement	Atlas Minerals
Alloprene	Chlorinated natural rubber	Imperial
Alphatec	TP elastomer	Alpha Gary
Alphalux	Poly(phenylene oxide)	Marbon
Alsibronz	Muscovite mica	Franklin Mineral
Alsilate	Clay	Freeport Kaolin
Alsynite	Reinforced plastic panels	Reichhold
Amberlac	Modified alkyd resins	Rohm & Haas
Amberlite	Ion-exchange resins	Rohm & Haas
Amberol	Phenolic resins	Rohm & Haas
Amco	Olefin fiber	Sampson Rope Tech.
American	Olefin fiber	Sampson Rope Tech.
Ameripol	Polyisoprene	Firestone
Amerith	Cellulose nitrate	Celanese
Amer-Plate	PVC sheets	Ameron Corrosion Control
Amilan	Nylon	Tojo Rayon/Toray
Amoco	TP resin	Amoco Polymers
Amodel	Polyphthalamide, PPA	Amoco Polymers
Ampcoflex	Rigid PVC	Atlas Minerals
Ancorex	ABS extrusions	Anchor
Angel Hair	Olefin fiber	Wayn-Tex
Anso (group of tradenames)	Nylon-6	Honeywell Nylon
Antron (and related trade names)	Nylon-6,6 fiber	DuPont/INVISTA
Anvyl	Vinyl extrusions	Anchor
Apec	High temperature PC	Bayer
Apex N	PVC blend with nitrile rubber	Teknor Apex
API	PS	American Polymers
Apogen	Epoxy resins	Apogee

Aqualoy	Nylon-6/12; nylon-6,6; PP	ComAlloy
Aquathene	PE	Quantum
Araclor	Polychlorinated polyphenyls	Monsanto
Aralac	Protein fiber	Imperial
Araldite	Epoxy resins	Ciba
Ardel	Polyarylate	Amoco Polymers
Ardil	Protein fiber	Imperial
Armite	Vulcanized fiber	Spaulding Fibre
Armorite	Vinyl coating	Armitage
Arnel	Cellulose triacetate	Celanese
Arnite	PET	Algemene Kuntstzijde, DSM
Arnitel	Polyester block copolymer with polyester	DSM
Arochem	Modified phenolic resins	Ashland
Aroclor	Chlorinated polyphenyls	Monsanto
Arodure	Urea resins	Ashland
Arofene	Phenolic resins	Ashland
Aroplaz	Alkyd resins	Ashland
Aropol	Polyester resins	Ashland
Aroset	Acrylic resins	Ashland
Arpak	Expandable PP bead	JSP
Arpro	Expandable PP bead	JSP
Arothane	Polyester resins	Ashland
Artfoam	Rigid urethane foam	Strux
Arylon, Arylon T	Polyaryl ethers	Uniroyal
Asaparene	Linear block styrene copolymer with butadiene	Asahi
Ascot	Polyolefin sheet-coated spunbonded	Appleton Coated Paper
Ashlene	Nylon-6; nylon-6,6; nylon-6/12	Ashley Polymers
Astralit	Vinyl copolymer sheets	Dynamit Nobel
Astrel	Polyarylsulfone	3M
Astroturf	Synthetic turf–nylon and PE	Monsanto
Astryn	PP alloy, co-homopolymers, TPO	Montell
Astyr	Butyl rubber	Montecatini
Atlac	Polyester cast resin	ICI
Attane	ULDPE	Dow Plastic
Aurum	TP polyimide	Mitsui Toatsu
Avisco	PVC film	FMC
Avistar	Polyester film	FMC
Avisun	PP	Avisum Corp.
Avora (and related trade names)	Polyester	KoSa
Avron	Rayon fiber	American Viscose
Azdel	Fibrous glass–reinforced ABS copolymer sheet	Azdel
Bakelite	Phenol–formaldehyde	Union Carbide
Bapolene	PE	Bamberger
Barden	Kaolin clay	Huber

Barex	Barrier resin/Acrylonitrile copolymers	Vistron/BP Chemicals
Barricaut	Polyester	Honeywell
Basofil	Melamine fibers and materials	Basofil Fibers, LLC
Bayblend	PC/ABS	Bayer
Baydur	Structural foam PUR RIM	Bayer
Baygal	Polyester casting resin	Farbenfabriken Bayer AG
Baylon	Polycarbonate	Farbenfabriken Bayer AG
Baypren	Polychloroprene	Farbenfabriken Bayer AG
Beckacite	Modified phenolic resin	Reinhhold; Beck, Koller
Beckamine	Urea–formaldehyde resin	Reichhold; Beck, Koller
Beckopox	Epoxy resins	Reichhold
Beckosol	Alkyl resins	Reichhold
Beetle	Urea–formaldehyde resin	American Cyanamid/Cytec Inds.
Beltec	Polyester	Honeywell
Bemberg	Rayon fiber	Beaunit Mills
Benvic	PVC	Solvay
Benvic	PVC	Solvay & Cie
Bexloy	Ionomer	DuPont
Bexone F	Poly(vinyl formal)	British Xylonite
Bexphane	PP	Bakelite Xylonite
Biobarrier	Olefin	Reemay
BioFresh	Acrylic fibers	Sterling Fibers
Blanex	Cross-linked PE	Richhold
Blapol	PE	Richhold
Blendex	ABS resin	BorgWarner
Bolta Flex	Vinyl sheeting and film	General Tire & Rubber
Bolta Thene	Rigid oldfin sheets	General Tire & Rubber
Boltaron	Plastic sheets	General Tire & Rubber
Bondstrand	Filament wound fiberglass reinforced plastics	American Corrosion Control
Bondtie	Olefin	Sampson Rope Tech.
Borofil	Boron filaments	Texaco
Boronol	Polyolefins with boron	Allied Resinous
Bostik	Epoxy and polyurethane adhesives	Bostik-Finch
Bounce-Back	Acrylic fibers	Solutia
Bronco	Supported vinyl or pyroxyline	General Tire & Rubber
Budene	*cis*-1,4-Polybutadiene	Goodyear
Butacite	Poly(vinyl acetal) resins	DuPont
Bukaton	Butadiene copolymers	Imperial
Butaprene	Styrene–butadiene elastomers	Firestone
Butarez CTL	Telechelic butadiene polymers	Phillips Petroleum
Buton	Butadiene–styrene resin	Enjay
Bu-Tuf	Polybutene	Petrotex
Butvar	Poly(vinyl butyral) resin	Shawinigan Products
BXL	Polysulfone	Union Carbide
Cab-O-Sil	Colloidal silica	Cabot
Cabot	TP resin	Cabot
Cadco	Plastic rod	Cadillac

Cadon	Nylon filament	Chemstrand
Calprene	Linear and branched styrene copolymers with butadiene	Repsol
Capran	Nylon-6	Allied Signal
Carbaglas	Fiberglass-reinforced polycarbonate	Dart
Carbopol	Water soluble resins	B.F. Goodrich
Carboset	Acrylic resins	B.F. Goodrich
Carbospheres	Hollow carbon spheres	Versar
Carbowax	Poly(ethylene glycols)	Union Carbide
Cariflex I	*cis*-1,4-Polyisoprene	Shell
Cariflex TR	Linear and branched styrene block copolymers	Shell
Carillon	Aliphatic PK	Shell
Carinex	PS	Shell
Caroma	PVC	Shell
Caromastic	Epoxyl coal tar coating	Carboline
Carolux	Flexible polyurethane foam	North Carolina Foam
Castear	Cast polyolefin films	ExxonMobil
Castethane	Castable polyurethanes	Upjohn
Catalac	Phenol–formaldehyde	Catalin
Cefor	PP	Shell
Celanex	Thermoplastic foam and sheeting	Celanese
Celatron	PS	Celanese
Celbond	Polyester	KoSa
Celcon	Acetal copolymers	Celanese
Celgard	Microporous PP film	Celanese
Cellasto	Microcellular urethane elastomer	North American Urethane
Cellofoam	PS foam board	United States Mineral Products
Cellon	Cellulose acetate	Dynamit Nobel
Cellonex	Cellulose acetate	Dynamit Nobel
Cellosize	Hydroxyethyl cellulose	Union Carbide
Celluliner	Expanded PS foam	Gilman Brothers
Cellulite	Expanded PS foam	Gilman Brothers
Celluloid	Plasticized cellulose nitrate	Celanese
Celpak	Rigid polyurethane foam	Dacar
Celstar	Acetate fibers	Celanese Acetate
Celramic	Glass nodules	Pittsburgh Corning
Centrex	ASA, ASA + AES	Bayer
Cerex	Styrene copolymers	Monsanto
Cevian	ASA, ASA + PBT, SAN	Daicel
C-Flex	Linear block styrene copolymer with ethylene–butylene	Consolidated Polymer Tech.
Chemigum	Urethane elastomer	Goodyear
Chemlon	Nylon-6; nylon-6,6	Chem Polymer
Chem-o-sol	PVC plastisol	Chemical Products
Chempro	Ion-exchange resin	Freeman

Celthane	Rigid polyurethane foam	Dacar
Chemfluor	Fluorocarbon plastics	Chemplast
Chemglaze	Polyurethane-based coating	Lord
Chemgrip	Epoxy adhesives for TFE	Chemplast
Chlorowax	Chlorinated paraffins	Diamond Alkali
Chromspun	Acetate fibers	Voridian
Cibanite	Aniline–formaldehyde resin	Ciba
Cimglas	Fiberglass-reinforced polyester	Cincinnati Milacron
Cis-4	*cis*-1,4-Polybutadiene	Phillips Chemical
Claradex	ABS	Shin-A
Clocel	Rigid polyurethane foam	Baxenden Chemical
Clopane	PVC tubing and film	Clopay
Cloudfoam	Polyurethane foam	International foam
Co-Rexyn	Polyester resins, coatings, pastes	Interplastic
Cobex	PVC	Bakelite Xylonite
Cobocell	Cellulose acetate butyrate tubing	Cobon
Coboflon	Teflon tubing	Cobon
Cobothane	Ethylene–vinyl acetate tubing	Cobon
Collodion	Cellulose nitrate solution	Generic name
Colovin	Calendered vinyl sheeting	Columbus Coated Fabrics
Comforel	Polyester	INVISTA
ComFortrel (and related trade names)	Polyester	Wellman
Comshield	PP	ComAlloy
Comtuf	Impact resistant resins	ComAlloy
Conathane	Polyurethane compounds	Conap
Conductrol	Acrylic fibers	Sterling Fibers
Conolite	Polyester laminate	Woodall
Coolmax	Polyester fiber	INVISTA
Coperba	Linear styrene block copolymers with butadiene	Petroflex
Coral rubber	*cis*-Polyisoprene	Firestone
Cordo	PVC foam and film	Ferro Corp.
Cordoflex	Poly(vinylidene fluoride) solutions	Ferro Corp.
Cordura	Nylon-6,6 fibers	INVISTA
Cordura	Regenerated cellulose	DuPont
Corfam	Poromeric film	DuPont
Corlite	Reinforced foam	Snark
Coro-Foam	Urethane foam	Cook Paint & Varnish
Corval	Rayon fiber	Courtaulds
Corvel	Plastic coating powders	Polymer Corp.
Corvic	Vinyl polymers	Imperial
Courlene	PE fiber	Courtaulds
Coverlight HTV	Vinyl-coated nylon fabric	Reeves Brothers
Covol	Poly(vinyl alcohol)	Corn Products
Crastin	PBT	DuPont
Creslan	Acrylonitrile–acrylic ester	American Cyanamid
Creslite	Acrylic fibers	Sterling Fibers

Cresloft	Acrylic fibers	Sterling Fibers
Cronar	PE	DuPont
Crowelon	Olefin fiber	Crowe Rope Inds.
Crown Fiber	Olefin fiber	Nexcel Synthetics
Cryowrap	Thermoplastic sheets and films	W.R. Grace
Cryovac	PP film	W.R. Grace
Crystalex	Acrylic resin	Rohm & Haas
Crystalon	Rayon fiber	American Enka
Crystalor	Polymethylpentene	Phillips Chemical
Crystic	Polyester resins	Scott Bader
CTI	Nylon-6,6	M.A. Hanna
Cumar	Coumarone–indene resins	Allied Chemical
Curithane	Polyaniline polyamines	Upjohn
Curon	Polyurethane foam	Reeves Brothers
Cyanaprene	Polyurethane	American Cyanamid
Cyanolit	Cyanoacrylate adhesive	Leader, Denis, Ltd.
Cycloset	Cellulose acetate fiber	DuPont
Cycogel	ABS	Nova Polymers
Cycolac	ABS, ABS + PBT	GE Plastics
Cycolac	Acrylonitrile–butadiene–styrene copolymer	BorgWarner
Cycolin	ABS/PBT	GE Plastics
Cycoloy	PC/ABS blend	GE Plastics
Cycopoac	ABS and nitrile barrier	BorgWarner
Cyglas	TS polyester	Cytec Inds.
Cymac	Thermoplastic molding materials	American Cyanamid
Cymel	Melamine molding compound	Cytec Inds.
Cyovin	Self-extinguishing ABS graft polymer blends	BorgWarner
Cyrex	Acrylic/PC alloy	Cyro Inds.
Cyrolite	Acrylic	Cyro Inds.
Dacovin	Rigid PVC	Diamond Alkali
Dacron	Polyester fiber	Dupont/DAK Americas, LLC
Dapon	Diallyl phthalate prepolymer	FMC
Daponite	Dapon–fabric laminates	FMC
Daran	PVC emulsion coatings	W.R. Grace
Daratak	PVC emulsions	W.C. Grace
Darex	Styrene copolymer resin	W.R. Grace
Darlon	Polyacrylonitrile fiber	Farbenfabriken Bayer AG
Darvan	Poly(vinylidene cyanide)	Celanese
Darvic	PVC	Imperial
Davon	Tetrafluoroethylene polymer	Davies Nitrate
Degalan	PMMA	Degussa
Delcron	Polyester fiber	DAK Americas, LLC
Delrin	Acetal polymers	DuPont
Densite	Urethane foam	Tenneco Chemical
Derakane	Polyester resin	Dow
Desmopan	Polyurethanes	Farbenfabriken Bayer AG
Desmophen	Polyesters and polyethers for polyurethanes	Farbenfabriken Bayer AG

Devran	Epoxy resins	Devoe & Reyaolds
Dexel	Cellulose acetate	British Celanese
Dexon	PP–acrylic	ExxonMobil
Dexplex	TPO	D & S Polymers
Dexsil	Polycarboranesiloxane	Olin Mathieson
Diakon	PMMA	Imperial
Diaron	Melamine resins	Richhold
Dielux	Acetals	Westlake Plastics
Diene	Polybutadiene	Firestone
Dimension	Nylon-6 alloy	Allied Signal
Diolen	PET	ENKA-Glazstoff
Dion	Polyester resins	Diamond Alkali
Dolphon	Epoxy and polyester resins	John C. Dolph
Dorlastan	Spandex fiber	Dorlastan Fibers LLC
Dorvon	PS foam	Dow
Doryl	Poly(diphenyl oxide)	Westinghouse Electric
Dow Corning	Silicons	Dow Corning
Dowex	Ion-exchange resinis	Dow
Dowlex	HDPE, LLDPE	Dow Plastics
Drexflex	TP elastomer	D & S Plastics
Dri-Lite	Expanded PS	Poly Foam
Dry Step	Nylon-6	Honeywell Nylon
DSDN	Nylon-6,6 fibers	INVISTA
DSP	Polyester fiber	Honeywell
Duco	Cellulose nitrate lacquers	DuPont
Dulac	Lacquers	Sun Chemical
Dulux	Polymeric enamels	DuPont
Duolite	Ion-exchange resins	Diamond Alkali
Duracel	Lacquers	Mass & Waldstein
Duracon	Acetal copolymers	Polyplastics
Duraflex	Polybutylene	Shell
Dural	Acrylic modified PVC	Alpha Gary
Duralon	Furan molding resins	U.S. Stoneware
Durane	Polyurethanes	Raffi & Swanson
Duramac	Alkyd resins	Commercial Solvents Corp.
Duraplex	Alkyd resins	Rohm & Haas
Duraspan	Spandex fibers	Carr-Fulflex
Durel	Polyarylate	Hoechst-Celanese
Durelene	PVC tubing	Plastic Warehousing
Durethan	Nylon-6	Farbenfabriken Bayer AG
Durethan U	Polyurethanes	Farbenfabriken Bayer AG
Durethene	PE film	Sinclair-Koppers
Durez	Phenolic resins	Occidental
Durathon	Polybutylene resins	Witco
Durite	Phenolic resins	Borden
Duron	Phenolics	Firestone Foam
Duron	Olefin fibers	Drake Extrusion
Dural	Ethylene–propylene copolymers	Montecatini
Duraspun	Acrylic fibers	Solutia
Dyal	Alkyd resins	Sherwin-Williams

Dyalon	Urethane elastomers	Thombert
DyeNAMIX	Nylon-6,6 fiber	Solitia
Dylark	SMA copolymer	Nova Chemicals
Dylene	PS	Nova Chemicals
Dylite	Expandable PS	Nova Chemicals
Dynaflex	SBS, SEBS	GLS Plastics
Dyneema	Olefin fiber	DSM High Performance Fibers
Dyroam	Expanded PS	W.C. Grace
Dylan	PE resins	Sinclair-Koppers
Dylel	ABS copolymers	Sinclair-Koppers
Dylene	PS resins	ARCO Polymer
Dylite	Expandable PS	Sinclair-Koppers
Dynafilm	PP film	U.S. Industrial Chemical & National Distillers & Chemical Corp.
Dynaflexl	Linear block styrene copolymers	GLS
Dynel	Modacrylic fiber	Union Carbide
Dynel	Vinyl chloride–acrylonitrile copolymers	Union Carbide
Dyphene	Phenol–formaldehyde resins	Sherwin-Williams
E-Foam	Epoxies	Allied
Eastabond	PET	Eastman Chemical
Eastalloy	PC + polyester	Eastman Chemical
Eastapak	PET	Eastman Chemical
Eastar	Polyesters	Eastman Chemical
Eastman	Thermoplastic resin	Eastman
Easypoxy	Epoxy adhesive kits	Conap
Ebolan	TEF materials	Chicago Gasket
Ecavyl	PVC	Kuhlmann
Eccosil	Silicon resins	Emerson & Cummings
Ecdel	Polyester block copolymer with polyether	Eastman Kodak
Ecoprene	TP elastomer	Rubber & Plastics Solutions
Edistir	PS	EniChem
Ektar	PET, PBT, PCT polyesters	Eastman
Elastalloy	TP elastomer	Eastman
Elastolit	Urethane engineering thermoplastic	North American Urethanes
Elastollan	Polyurethane block copolymer with polyether/polyester	BASF
Elastollyx	Urethane engineering thermoplastic	North American Urethanes
Elastolur	Urethane coating	BASF
Elastonate	Urethane isocyanate prepolymers	BASF
Elastonol	Urethane polyester polyols	North American Urethanes
Elastopel	Urethane engineering thermoplastic	North American Urethanes

Elastothane	Polyurethane elastomer	Thiokol
Electrafil	Electrically conductive polymers	DSM
Electroglas	Cast acrylic	Glasflex
Elexar	Linear styrene block copolymer with ethylene–butylene	Teknor Apex
El Rexene	Polyolefin resins	Rexall
El Rey	LDPE	Rexall
Eltex	HDPE	Teknor Apex
Elustra	Olefin fibers	FiberVisions Products
Elvace	Acetate–ethylene copolymer	DuPont
Elvacet	Poly(vinyl acetate) emulsion	DuPont
Elvacite	Acrylic resins	DuPont
Elvamide	Nylon resins	DuPont
Elvanol	Poly(vinyl alcohol) resins	DuPont
Elvax	Poly(ethylene-co-vinyl acetate)	DuPont
Elvic	PVC	Solvay
Emac	EMA copolymer	Chevron Chemical
Empee	PE, PP	Monmouth
Enathene	Ethylene–butyl acrylate polymer	Quantum
Engage	Polyethylene copolymer with Poly(alpha-olefins)	Dow
Enka	Nylon-6,6 fiber	Polyamide Ind. Fibers
Enkalure	Nylon fiber	American Enka
Enrad	Preirradiated PE	Enflo
Enrup	Thermosetting resin	U.S. Rubber Co.
Ensocote	PVC lacquer coatings	Uniroyal
Ensolex	Cellular plastic sheets	Uniroyal
Ensolite	Cellular plastic sheets	Uniroyal
Epibond	Epoxy adhesive resin	Furane Plastics
Epikote	Epoxy resins	Shell Chemical
Epilox	Epoxy resins	Leuna
Epi-Rez	Epoxy cast resins	Celanese
Epi-Tex	Epoxy–ester resins	Hoechst-Celanese
Epikote	Epoxy resins	Shell Chemical
Epocap	Two-part epoxy compounds	Hardman
Epocryl	Epoxy acrylate resins	Shell Chemical
Epodite	Epoxy resins	Showa Highpolymer
Epolast	Two-part epoxy compounds	Hardman
Epolene	Low-melt PE	Eastman Chemical
Epolite	Epoxy compounds	Hexcel
Epomarine	Two-part epoxy compounds	Hardman
Epon	Epoxy resins	Shell Chemical
Eponol	Linear polyether resins	Shell Chemical
Eposet	Two-part epoxy compounds	Hardman
Epotuf	Epoxy resins	Reichhold
Epoxylite	Epoxy resins	Epoxylite Corp.
Eref	PA/PP alloy	Solvay
Escalloy	Crack resistant PP	ComAlloy
Escon	PP	Enjay

Escor	Acid terpolymer	ExxonMobil
Escorene	PP	ExxonMobil
ESP	Polyester fiber	KoSa
Essera	Olefin fibers	American Fibers & Yarns
Estane	Polyurethane resins	B.F. Goodrich
Estron	Cellulose acetate filament	Eastman Chemical
Ethafoam	PE foam	Dow
Ethocel	Ethyl cellulose	Dow
Ethofil	Fiberglass-reinforced PE	Dart
Ethoglas	Fiberglass-reinforced PE	Dart
Ethosar	Fiberglass-reinforced PE	Dart
Ethron	PE	Dow
Ethylux	PE	Westlake Plastics
Europrene Sol T	Linear and branched styrene copolymers	EniChem
Evalca	EVA copolymer	Eval
Evenglo	PS	Sinclair-Koppers
Everflex	PVA copolymer emulsion	W.C. Grace
Everlon	Polyurethane foam	Stauffer Chemical
Evolutia	Acrylic fibers	Solutia
Exact	Polyethylene copolymer with poly(alpha-olefins)	ExxonMobil
Excelite	PE tubing	Thermoplastic Processes
Exon	PVC	Firestone Plastics
Extane	Polyurethane tubing	Pipeline Service
Extrel	Plastic film	ExxonMobil
Extren	Fiberglass-reinforced polyester	Morrison Molded Fiber Glass
Fabrikoid	Pyroxylin-coated fabrics	Dupont
Facilon	Reinforced PVC fabric	Sun Chemical
Fassgard	Vinyl-coated nylon	M.S. Fassler
Fasslon	Vinyl coating	M.S. Fassler
Felor	Nylon filaments	DuPont
Ferrene	PE	Ferro
Ferrex	PP	Ferro
Ferrocon	Polyolefin	Ferro
Ferroflex	PP blend with EPDM or EPR	Ferro
Ferroflo	PS	Ferro
Ferropak	PP/PE alloy	Ferro
Fertene	PE	Montecatini
Fibercast	Reinforced plastic pipe	Fibercast
Fiberfil	Fiber reinforced material	DSM
Fiberglas	Fibrous glass	Owens-Corning Fiberglass
Fiberite	Phenolic molding compounds	Fiberite
FiberLoc	Nylon-6,6 fiber	INVISTA
Fibermesh	Olefin fibers	SI Corp.
Fibro	Rayon	Courtaulds NA
Fina	Polyolefin	Fina Oil
Filabond	Unsaturated polyester	Reichhold
Finaclear	PS, SBS	Fina Oil
Finaclear	PS, SBS	Fina Oil

Fillwell (and related trade names)	Polyester	Wellman
Finaprene	Linear styrene block copolymers with butadiene	Fina Oil
Flakeglas	Glass flakes for reinforcements	Owens-Corning Fiberglas
Flexalloy	PVC	Teknor Apex
Flexane	Polyurethanes	Devcon
Flexomer	ULDPE	Union Carbide
Flexprene	Linear block styrene copolymer with butadiene	Teknor Apex
Flexprene	TP elastomer	Teknor Apex
Flesocel	Polyurethane foams	Baxenden Chemical
Flexomer	PE copolymer with poly(alpha-olefins)	Union Carbide
Flexothene	PP blend with EPDM or EPR	Quistar
Floranier	Cellulose	Rayonier
Floterrope	Olefin fiber	Sampson Rope Tech.
Flovic	Poly(vinyl acetate)	Imperial
Fluokem	Teflon spray	Bel-Art Products
Fluon	Polytetrafluoroethylene and powders	Imperial
Fluorel	Poly(vinylidene fluoride)	3M
Fluorglas	PTEF-impregnated materials	Dodge Industries
Fluorobestos	Asbestos–Teflon composite	Raybestos Manhattan
Fluorocomp	Reinforced fluoropolymer	LNP
Fluorocord	Fluorocarbon materials	Raybestos Manhattan
Fluorofilm	Cast Teflon fioms	Dilectrix Corp.
Fluoron	Polychlorotrifluoroethylene	Stokes Molded Products
Fluoroplast	PTFE	U.S. Gasket
Fluororay	Filled fluorocarbon	Raybestos Manhattan
Fluorored	TFE compounds	John L. Dore
Fluorosint	TFE–fluorocarbon composites	Polymer Corp.
Foamex	Poly(vinyl formal)	General Electric
Foamthane	Polyurethane foam	Pittsburgh Corning
Foamspan	TP foam	ComAlloy
Foraflon	PVDF	Atochem
Formadall	Polyester premix	Woodall Industries
Formaldafil	Fiberglass-reinforced acetals	Dart
Formaldaglass	Fiberglass-reinforced acetals	Dart
Formaldasar	Fiberglass-reinforced acetals	Dart
Formex	Poly(vinyl acetal)	General Electric
Formica	Thermosetting laminates	Formica Corp.
Formion	Ionomer	A. Schulman
Formrezel	Liquid resins for urethane elastomers	Witco Chemical
Formvar	Poly(vinyl formal)	Shawinigan Resins Corp.
Forticel	Cellulose propionate	Celanese
Fortiflex	PE	Solvay
Fortilene	PP	Solvay
Fortisan	Saponified cellulose acetate	Celanese

Fortrel (and related trade names)	Polyester fiber	Fiber/Wellman
Fortron	PPS	Hoechst-Celanese
Fostacryl	Poly(styrene-co-acrylonitrile)	Foster Grant
Fostalene	Plastic	Foster Grant
Fosta-Net	PS foam mesh	Foster Grant
Fosta Tuf-Flex	High-impact PS	Foster Grant
Fostafoam	Expandable PS beads	Foster Grant
Fostalite	Light stabilized PS	Foster Grant
Fostarene	PS	Foster Grant
FPC	PVC resins	Firestone
FR-PC	PC	Lucky
FTPE	Fluorelastomer	3M
Furname	Epoxy and furan resins	Atlas Minerals
Futron	Polyester	Fusion Rubbermaid
Galalith	Casein plastics	Generic name
Gantrez	Poly(vinyl ether-comaleic anhydride)	General Aniline Film
Gantrez	Fibrous glass roving	Johns-Manville
Gapex	Nylon	Ferro
Garan Finish	Sizing for glass fibers	Johns-Manville
Gedamine	Unsaturated polyester	Charbonnages
Geloy	ASA, ASA + PC, ASA + PVC	GE Plastics
Gelva	Poly(vinyl acetate)	Shawinigan Resins Corp.
Gelvatex	Poly(vinyl acetate) emulsions	Shawinigan Resins Corp.
Gelvatol	Poly(vinyl alcohol)	Shawinigan Resins Corp.
Genaire	Poromeric film	General Tire & Rubber
Genal	Thermosets	General Electric
Genthane	Polyurethane elastomers	General Tire & Rubber
Genetron	Fluorinated hydrocarbon monomers and polymers	Allied Chemical
Gentro	Butadiene copolymer	General Tire & Rubber
Geolast	TP elastomer	Advanced Elastomer Sys.
Geon	PVC	Geon
Geon	PVC	B.F. Goodrich
Gil-Fold	PE sheets	Gilman Brothers
Ginny	Acrylic fibers	Solutia
Glaskyd	Glass-reinforced alkyd resins	American Cyanamid/Cytec Inds.
Glastic	Thermoset resins	Glastic
Glospan	Spandex fiber	RadiciSpandex Corp.
Glyptal	Alkyd coating	General Electric
Goldrex	Acrylic	Hanyang Chemical
Gracon	PVC	W.C. Grace
GravoFLEX	ABS sheets	Hermes Plastics
GravoPLY	Acrylic sheets	Hermes Plastics
Grex	PE	W.R. Grace
Grilamid	Polyamide copolymer with polyether/polyester; nylon-12	EMS America Grilon
Grilon	Nylon-6; nylon-6,6	EMS America Grilon

Grivory	Nylon	EMS America Grilon
Halar	Polyfluorocarbons	Allied/Ausimont
Halex	Polyfluorocarbons	Allied Chemical
Halon	Polyfluorocarbons	Ausimont
Hanalac	ABS	Miwon
Haysite	Polyester laminates	Synthane-Taylor/Haysite
Heaveaplus	Copolymer of methyl methacrylate and rubber	Generic name
Hercocel	Cellulose acetate	Hercules Powder
Hercose	Cellulose acetate–propionate	Hercules Powder
Herculoid	Cellulose nitrate	Hercules Powder
Herculon	PP	Hercules Powder
Hercuprene	Thermoset resins	J-Von
Herox	Nylon	DuPont
Heterofoam	Fire-retardant urethane foam	Hooker Chemical
Hetron	Fire-retardant polyester resins	Ashland
Hex-One	HDPE	Gulf Oil
H-film	Polyamide film from pyromellitic anhydride and 4,4-diaminodiphenyl ether	DuPont
Hi-Blen	ABS polymers	Japanese Geon
Hifax	PP blend with EPDM or EPR	Himont
Hi-fax	HDPE	FMC; Hercules Powder
HiGlass	Glass filled PP	Himont
Hipack	PE	Showa Highpolymer
Hi-Sil	Amorphous silica	PPG
Hi-Styrolux	High-impact PS	Westlake Plastics
Hitalex	PE	Hitachi Chemical
Hitanol	Phenol–formaldehyde resins	Hitachi Chemical
Hivalloy	PP alloy	Montell
HiWal	HDPE	General Polymers
Hollofiber	Polyester fiber	Wellman
Hostacom	Reinforced PP	Hoechst-Cellanese
Hostadur	PET	Farbwerke Hoechst AG
Hostaflon C2	Polychlorotrifluorethylene	Farbwerke Hoechst AG
Hostaflon TF	PTFE	Farbwerke Hoechst AG
Hostaform	Acetal copolymer	Hoechst-Cellanese
Hostalen	PE	Farbwerke Hoechst AG
Hostalen GC	HDPE/LDPE	Hoechst
Hostalloy	Polyolefin alloy	Hoechst-Cellanese
Hostyren	PS	Hoechst
Huntsman	Thermoplastic	Huntsman
Hurcuprene	Linear block styrene copolymer with butadiene or ethylene–butylene	J-Von
Hy (and related trade names)	Olefin fibers	Fiber Vision Prods.
Hycar	Butadiene acrylonitrile copolymer	B.F. Goodrich
Hydrepoxy	Water-based epoxys	Allied Products
Hydrin	Epichlorohydrin rubber	Goodrich–Hercules

Hydro Foam	Expanded phenol–formaldehyde	Smithers
Hydropol	Hydrogenated polybutadiene	Phillips Petroleum
Hydrotec	Polyester fibers	DAK Americas, LLC
Hyflon	Fluoropolymer	Auismont
Hylar	PVDF	Auismont
Hypalon	Chlorosulfonated PE	DuPont
Hytrel	Polyester block copolymer with polyether/polyester	DuPont
Imbue	Polyester fibers	KoSa
Impet	PET	Hoechst-Cellanese
Implex	Acrylic resins	Rohm & Haas
Impressa	Olefin fibers	American Fibers & Yarns
Innova	Olefin fibers	American Fibers & Yarns
Insurok	Phenol-formaldehyde molding compounds	Richardson Company
Intamix	Rigid PVC	Diamond Shamrock
Interpol	Polyurethane	Cook Composites
Ionac	Ion-exchange resins	Permutit Company
Iotek	Ionomer	ExxonMobil
Ipuiace	PPO/PPE	Mitsubishi
Irrathene	Irradiated PE	General Electric
Irvinil	PVC resins	Great American Chemical
Isoderm	Urethane integral–skinning foam	Upjohn
Isofoam	Polyurethane foam resins	Isocyanate Products
Isomid	Polyester–polyamide film magnet wire	Schenectady Chemicals
Isoplast	TPU	Dow
Isoteraglas	Isocyanate elastomer–coated Dacron glass fabric	Natvar Corp.
Isothane	Polyurethane foam	Bernel Foam Products
Iupilon	Polycarbonate	Mitsubishi Edogawa
Iupital	Acetal	Mitsubishi
Ixan	PVDF	Solvay
Ixef	Polyacrylamide	Solvay Polymers
Jetfoam	Polyurethane foam	International Foam
Jet-Kote	Furane resin coatings	Furane Plastics
J-Plast	TP elastomer	J-Von
Kadel	PAEK	Amoco Polymers
Kalex	Urethane resin	Di-Acro Kaufman
Kalspray	Rigid urethane foam	Baxenden Chemical
Kamax	Acrylic copolymer	AtoHaas
Kapton	Polyamide	DuPont
Kardel	PS film	Union Carbide
Kaurit	Phenol–formaldehyde resins	Badische Anilin & Coda
Kelburon	PP/EP	DSM
Kel-F	Trifluorochloroethylene resins	3M
Keltrol	Copolymers	Textron
Kematal	Acetal copolymers	Imperial
Kematal	Acetal copolymer	Hoechst-Celanese

Kemcor	LDPE, HDPE	Kemcor Australia
Kenflex	Hydrocarbon resins	Kenrich Petrochemicals
Ken-U-Thane	Polyurethane	Kenrich Petrochemicals
Ketac	Ketone–aldehyde resins	American Cyanamid
Kevlar	Aramid materials	DuPont
Kibisan	SAN	Chi Mei
Kibiton	SBS	Chi Mei
Koblend	Polycarbonate/ABS	EniChem America
Kodacel	Cellulose acetate film	Eastman Chemical
Kodapak	PET	Eastman
Kodar	Copolyesters	Eastman Chemical
Kohinor	Vinyl	Rimet
Kollidon	Poly(vinyl pyrrolidone)	General Aniline Film
Kolorbon	Rayon fiber	American Enka
Kopa	Nylon-6; nylon-6,6	Kolan America
Kopox	Epoxy resins	Koppers
Korad	Acrylic films	Rohm & Haas
Korez	Phenolic resin cements	Atlas Minerals
Koroseal	PVC	B.F. Goodrich
Kosmos	Carbon black	United Carbon Company
Kotol	Resin solutions	Uniroyal
Kralac	ABS resins	Uniroyal
Kralastic	ABS	Uniroyal
Kralon	HIPS and ABS resins	Uniroyal
Kraton	Butadiene block copolymers and linear and branched styrene block copolymers	Shell Chemical
Kraton D	SBS or SIS terpolymers	Shell Chemical
Kraton IPN	SEBS–polyester	Shell Chemical
Krene	Plasticized vinyl film	Union Carbide
K-Resin	Butadiene–styrene copolymer	Phillips Petroleum
Kriston	Allyl ester casting resins	B.F. Goodrich
Krystal	PVC sheet	Allied Chemical
Krystaltite	PVC shrink film	Allied Chemical
Kydene	Acrylic–PVC powder	Rohm & Haas
Kydex	Acrylic–PVC sheets	Rohm & Haas
Kylan	Chitan	Generic name
Kynar	Poly(vinylidene fluoride)	Atochem
Laden	PS	SABIC
Laguval	Polyester resins	Farbenfabriken Bayer AG
Lamabond	Reinforced PE	Columbia Carbon
Lamar	Mylar vinyl laminates	Morgan Adhesives
Laminac	Polyester resins	American Cyanamid
Lanital	Fiber from milk protein	Shia Viscosa
Last-A-Foam	Plastic foam	General Plastics
Lekutherm	Epoxy resins	Farbenfabriken Bayer AG
Lemac	Poly(vinyl acetate)	Borden Chemical
Lemol	Poly(vinyl alcohol)	Borden Chemical
Levapren	Ethylene–vinyl acetate copolymers	Farbenfabriken Bayer AG

Lexan	Polycarbonate resin	General Electric
Lock Foam	Polyurethane foam	Nopco Chemical
Lofguard	Polyester fiber	KoSa
Lomod	Polyester block copolymer with polyether	General Electric
Lubriloy	Nylon-6; nylon-6,6; nylon-6/12; PBT	ComAlloy
Lucel	Acetal copolymer	Lucky
Lucet	Acetal copolymer	Lucky
Lucite	PMMA and copolymers	DuPont
Ludox	Colloidal silica	DuPont
Lumarith	Cellulose acetate	Celanese
Lumasite	Acrylic sheet	American Acrylic Corp.
Lumax	PBT alloy	Lucky
Lumite	Saran filaments	Chicopee Manufacturing
Lupan	SAN	Lucky
Lupol	Polyolefin	Lucky
Lupon	Nylon-6,6	Lucky
Lupos	ABS	Lucky
Lupox	PBT	Lucky
Lupoy	Polycarbonate/ABS	LG Chemical
Luran	SAN, ASA	BASF
Lusep	PPS	Lucky
Lustran	Molding and extrusion resins, ABS	Bayer
Lustrex	PS	Monsanto
Lutonal	Poly(vinyl ethers)	Badische Anilin & Soda-Fabrik AG
Lutrex	Poly(vinyl acetate)	Foster Grant
Luvican	Poly(vinyl carbazole)	Badische Anilin & Soda-Fabrik AG
Luxis	Nylon-6	Westover
Lycra	Spandix fibers	DuPont/INVISTA
Macal	Cast vinyl films	Morgan Adhesive
Madurik	Melamine–formaldehyde resins	Casella Farbwerke Mainkur
Magnacomp	Nylon-6; nylon-6,10; PP	LPN
Magnum	ABS	Dow Plastics
Makrofol	Polycarbonate film	Naftone
Makrolon	Polycarbonate	Farbenfabriken Bayer AG
Malecca	Copolymers with styrene	Denki Kagaku
Maranyl	Nylon	ICI Americas
Marqesa	Olefin fibers	American Fibers & Yarns
Marquesa Lana	Olefin fibers	Shaw Inds.
Marafoam	Polyurethane foam	Marblette
Maraglas	Epoxy resin	Marblette
Maranyl	Nylons	Imperial
Maraset	Epoxy resin	Marblette
Marathane	Urethane materials	Allied Products
Maraweld	Epoxy resin	Marblette
Marbon	PS and copolymers	BorgWarner
Marlex	Polyolefin resins	Phillips Chemical

Marvibond	Metal–plastic laminates	Uniroyal
Marvinol	PVC	Uniroyal
Mater-Bi	Biodegradable polymers	Novamont
Melan	Melamine resins	Hitachi Chemical
Meldin	Polyimides	Dixon Corp.
Melinex	PET	Imperial
Melit	Melamine–formaldehyde resins	Societa Italiana Pesine
Melmac	Melamine molding materials	American Cyanamid
Melolam	Melamine resin	Ciba-Geigy
Melurac	Melamine–urea resins	American Cyanamid
Meraklon	PP	Montecatini
Merlon	Polycarbonate	Mobay Chemical
Meryl (and related trade names)	Nylon-6; nylon-6,6 fibers	Nylstar
Metallex	Cast acrylic sheets	Hermes Plastics
Methocel	Methylcellulose	Dow
Meticone	Silicone rubber	Hermes Plastics
Metre-Set	Epoxy adhesives	Metachem Resins Corp.
Micarta	Thermosetting laminates	Westinghouse Electric Corp.
Microblocker	Olefin fibers	SI Corp.
Microdenier Sensure	Polyester fiber	Willman
Microlux	Polyester fiber	KoSa
Micro-Matte	Extruded acrylic sheet with matte finish	Extrudaline
Micronex	Carbon black	Columbian Carbon
Micropel	Powdered nylon	Nypel
Microsol	Vinyl plastisol	Michigan Chrome & Chemical
MicroSafe	Acetate fibers	Celanese Acetate
MicroSupreme	Acrylif fibers	Sterling Fibers
Microthene	Powdered PE	Quantum
Milastomer	Thermoplastic elastomer	Mitsui Toatsu
Milmar	Polyester	Morgan Adhesives
Mindel	PSU, PSU alloy	Amoco Polymers
Mini-Vaps	Expanded PE	Malge
Minit Grip	Epoxy adhesives	High Strength Plastics Corp.
Minit Man	Epoxy adhesives	Kristal Draft
Minlon	Reinforced nylon	DuPont
Mipolam	PVC	Dynamit Nobel
Mipoplast	PVC sheets	Dynamit Nobel
Mirafi	Olefin fibers	TenCate Geosynthetics
Mirasol	Alkyd resins	C.S. Osborn Chemicals
Mirbane	Amino resins	Showa Highpolymer
Mirrex	Calendered PVC	Tenneco Chemicals
Mista Foam	Urethane foam	M.R. Plastics & Coatings
Modulene	PE resins	Muehlstein & Co.
Mogal	Carbon black	Cabot Corp.
Molplen	PP	Novamont Corp.
Moltopren	Polyurethane foam	Farbenfabriken Bayer AG
Molycor	Fiberglass-reinforced epoxy tubing	A.O. Smith, Inland Inc.
Monocast	Nylon	Polymer Corp.

Montac	Polyamide copolymer with polyether/polyester	Monsanto
Montrek	Polyethyleneimine	Dow
Moplen	PP	Montecatini
Morthane	Polyurethane block copolymer with polyether/polyester	Morton Int.
Mowiol	Poly(vinyl alcohol)	Farbwerke Hoechst AG
Mowital	Poly(vinyl butyral)	Farbwerke Hoechst AG
Mowlith	Poly(vinyl acetate)	Farbwerke Hoechst AG
Multibase	ABS	Multibase
Multi-Flex	Linear block styrene copolymers with ethylene–propylene	Multibase
Multi-Hips	PS	Multibase
Multi-Pro	PP	Multibase
Multi-San	SAN	Multibase
Multrathane	Urethane elastomer	Mobay Chemical
Multron	Polyesters	Mobay Chemical
Mycalex	Inorganic molded plastic	Mycalex Corp. America
Mylar	Polyester film	DuPont
Napryl	PP	Pechiney–Saint-Gobain
NAS	SMMA acrylic	Nova Chemicals
Natene	PE	Pechiney–Saint-Gobain
Natsyn	*cis*-1,4-Polyisoprene	Goodyear
Naugahyde	Vinyl-coated fabric	U.S. Rubber Co.
NeoCryl	Acrylic resins and emulsions	Polyvinyl Chemicals
Neoprene	Polychloroprene	DuPont
NeoRez	Styrene emulsions & urethane solutions	Polyvinyl Chemicals
NeoVac	PVA emulsions	Polyvinyl Chemicals
Nepoxide	Epoxy resin coating	Atlas Minerals & Chemicals
Nestrite	Phenolic and urea–formaldehyde resins	James Ferguson & Sons
Nevidene	Coumarone–indene resin	Neville Chemical
Nevillac	Modified coumarone–indene resin	Neville Chemical
Niax	Polyol polyesters	Union Carbide
Nimbus	Polyurethane foam	General Tire & Rubber
Nipeon	PVC	Japanese Geon
Nipoflex	Ethylene–vinyl acetate copolymer	Toyo Soda Mfg.
Nipolon	PE	Toyo Soda Mfg.
Nitrocol	Nitrocellulose-based pigment dispersions	J.C. Osburn Chemicals
Noan	Styrene–methyl methacrylate copolymer	Richardson Corp.
Nob-Lock	PVC sheets	Ameron Corrosion Control
Nomex	Aramid nylon	DuPont
Nopcofoam	Polyurethane foam	Nopco Chemical
Norchem	LDPE resin	Northern Petrochemical
Nordel	Ethylene–propylene	DuPont

Norsophen	Phenolic resins	Norold Composites
Nortuff	HDPE, PP	Polymerland
Noryl	Poly(phenylene oxide), PPO alloy	General Electric
Novalast	Thermoplastic elastomers	Nova Polymers
Novalene	Thermoplastic elastomers	Nova Polymers
Novamid	Nylon	Mitsubishi
Novapol	LLDPE, LDPE, HDPE	Nova Chemicals
Novatemp	PVC	Novatec
Novelle	Olefin fibers	FiberVisions
Novodur	ABS polymers	Farbenfabriken Bayer AG
Novon	Starch-based polymer	Novon
NSC	Nylon, PS	Thermofil
Nuclon	Polycarbonate	Pittsburgh Plate Glass
Nucrel	EMMA copolymer	DuPont
Nukem	Acid-resistant resin cements	Amercoat Corp.
Numa	Spandex fibers	American Cyanamid
Nupol	Thermosetting acrylic resin	Freeman Chemical
Nybex	Nylon-6,12	Nova Chemicals
Nydur	Nylon-6	Durethan
Nyglathane	Glass-filled polyurethane	Nypel
Nylafil	Reinforced nylon	DSM
Nylaglas	Fiberglass-reinforced nylon	Dart
Nylamid	Nylon	Polymer Service
Nylasar	Fiberglass-reinforced nylon	Dart
Nylasint	Sintered nylon parts	Polymer Corp.
Nylast	Thermoplastic elastomer	Allied Signal
Nylatron	Filled nylons	DSM
Nylene	Nylon	Custom Resins
Nylind	Nylon-6,6	DuPont
Nylon	Polyamides	DuPont
Nylo-Seal	Nylon-11 tubing	Imperial-Eastman
Nyloy	Nylon-6,6, PC, PP	Nytex Composites
Nylux	Nylons	Westlake Plastics
Nypel	Nylon-6	Allied Signal
Nyplube	TFE-filled nylons	Nypel
Nyreg	Glass-reinforced nylons	Nyper
Nytron	Nylon-6,6	Nytex Composites
Oasis	Expanded phenol–formaldehyde	Smithers
Olefane	PP film	Avisum Corp.
Olefil	Filled PP resin	Amoco Chemicals
Oleflo	PP resin	Amoco Chemicals
Olehard	Filled PP	Chiso America
Olemer	Propylene copolymer	Avisum Corp.
Oletac	Amorphous PP	Amoco Chemicals
Ontex	Thermoplastic elastomer	D & S Plastics
Opalon	PVC	Monsanto
Oppanol B	Polyisobutylene	Badische Anilin & Soda-Fabrik AG

Oppanol C	Poly(vinyl isobutylether)	Badische Anilin & Soda-Fabrik AG
Optema	EMA copolymer	ExxonMobil
Optix	Acrylic	Plaskolite
Orel	Polyester fiber	DuPont
Orevac	Polyamide copolymer with polyether/polyester	Atochem
Orgalacqe	Epoxy and PVC powders	Aquitaine-Organico
Orgamide R	Nylon-6	Aquitaine-Organico
Orlon	Acrylic fibers	DuPont
Ortix	Poromeric film	Celanese
Oxy	Vinyl	Occidental
Oxyblend	Vinyl	Occidental
Oxyclear	PVC	Occidental
Panda	Vinyl and urethane-coated fabrics	Pandel-Bradford
Panelyte	Laminates	Thiokol
Panlite	PC	Teijin Chemical
Papi	Polymethylene, poly(phenyl isocyanate)	Upjohn
Paracon	Polyester rubber	Bell Telephone Labs.
Paracryl	Butadiene-acrylonitrile copolymers	U.S. Rubber Co.
Paradene	Coumarone–indene resins	Neville Chemical
Paralac	Polyester resin	ICI
Parfe	Rayon fiber	Beaunit Mills Corp.
Parlon	Chlorinated rubber	Hercules Corp.
Parylen C	Polymonochloro-p-xylene	Union Carbide
Parylen N	Polyxylene	Union Carbide
Paxon	HDPE	Paxon
Pearlon	PE film	Visking Corp.
Pebax	Polyamide block copolymer with polyether/polyester	Atochem
Pee Vee Cee	PVC	ESB Corp.
Pelaspan	Expandable PS	Dow
Pellethene	Thermoplastic urethane	Dow Plastics
Pentalyn	Abietic acid derivatives	Hercules
Pentec	Polyester fiber	Honeywell
Penton	Chlorinated polyether resins	Hercules
Perbunan N	Butadiene–acrylonitrile copolymers	Farbenfabriken Bayer AG
Peremelite	Melamine resin	Melamine Plastics
Perlon	Polyurethane filament	Farbenfabriken Bayer AG
PermaRex	Cast epoxy	Permali
Permasoft	Nylon-6	Beaulieu
Permutit	Ion-exchange resin	Permutit
Perspex	Acrylic resins	ICI
Petlon	PBT	Albis
Petra	Polyester sheets	Allied Chemical
Petrothene	PE	Quantum

Pevalon	Poly(vinyl alcohol)	May & Baker
Phenoweld	Phenolic adhesive	Hardman
Philjo	Polyolefin film	Phillips-Joana
Philprene	Sytrene–Butadiene rubber	Phillips Petroleum
Pibiter	Poly(butylene terephthalate)	EniChem
Picco	Hydrocarbon resins	Hercules
Piccocumaron	Hydrocarbon resins	Hercules
Piccoflex	Acrylonitrile–Styrene resins	Pennsylvania Industrial Chemical
Piccolastic	PS resin	Pennsylvania Industrial Chemical
Piccolyte	Terpene polymer resins	Hercules
Piccotex	Vinyl–toluene copolymers	Pennsylvania Industrial Chemical
Piccoumaron	Coumarone–indene resins	Pennsylvania Industrial Chemical
Piccovar	Alkyl–aromatic resins	Pennsylvania Industrial Chemical
Pienco	Polyester resins	American Petrochemical
Pil-Trol	Acrylic fibers	Solutia
Plaskon	Amino resins	Allied Chemical
Plastacel	Cellose acetate flake	DuPont
Plastylene	PE	Pechiney–Saint-Gobain
Plenco	Phenolic resins	Plastics Engineering
Pleogen	Polyester resins and gels	Whittaker Corp.
Plexiglas	Acrylic sheets	Rohm & Haas
Plexigum	Acrylate and methacrylate resins	Rohm & Haas
Plicose	PE	Diamond Shamrock
Pliobond	Adhesive	Goodyear
Pliofilm	Rubber hydrochloride	Goodyear
Plioflex	PVC	Goodyear
Pliolite	Cyclized rubber	Goodyear
Pliothene	PE rubber blends	Ametek/Westchester
Pliovic	PVC	Goodyear
Pluracol	Polyethers	Wyandotte Chemicals
Pluragard	Urethane foams	BASF Wyandotte
Pluronic	Polyethers	BASF Wyandotte
Plyocite	Phenol-impregnated materials	Reichhold Chemicals
Plyophen	Phenolic resins	Reichhold Chemicals
Pluronics	Block polyether diols	Wyandotte Corp.
PMC	Melamine formaldehyde	Sun Coast
Pocan	Poly(butylene terephthalate)	Albis
Polarguard (and related trade names)	Polyester fibers	KoSa
Polex	Oriented acrylics	Southwestern Plastics
Pollopas	Urethane–formaldehyde materials	Dynamit Nobel
Polvonite	Cellular plastic materials	Voplex Corp.
Polyallomer	Ethylene block copolymers	Eastman Chemical
Polycarbafil	Fiberglass-reinforced polycarbonates	Dart

Polycure	Cross-linked PE	Crooke Color & Chemical
Poly-Dap	Diallyl phthalate resins	U.S. Polymeric
Poly-eth	PE	Gulf Oil
Poly-eze	Ethylene copolymers	Gulf Oil
Polyflon	Fluoropolymers	Daikin
Polyfoam	Polyurethane foam	General Tire & Rubber
Poly-Gard	Solventless epoxies	Richhold Chemicals
Polyimidal	Polyimide thermoplastics	Raychem Corp.
Polylasting	Olefin fibers	Blue Mountains Inds.
Polylite	Polyester resins	Reichold Chemicals
Polyloom	Olefin fibers	TC Thiolon
Polylumy	PP	Kohjin
Polyman	ABS alloy	Schulman
Polymet	Plastic-filled sintered metal	Polymer Corp.
Polymin	Polyethyleneimine	Badische Anilin & Soda-Fabrik AG
Polymul	PE emulsions	Diamond Shamrock
Poly-pro	PP	Gulf Oil
Polyox	Water soluble resins	Union Carbide
Polysizer	Poly(vinyl alcohol)	Showa Highpolymer
Polystar	Olefin fiber	Nexcel Synthetics
Polyteraglas	Polyester-coated Dacron glass fabric	Natvar Corp.
Polytron	PVC alloy	Geon
Polytrope	PP blend with EPDM or EPR	Schulmam
Poly Tying	Olefin fibers	Blue Mountain Inds.
Polyvin	PVC	Schulman
Polyviol	Poly(vinyl alcohol)	Wacker Chemie GmbH
Powminco	Asbestos fibers	Powhatan Mining
PPO	Poly(phenylene oxide)	Hercules
Premi-glas	Glass reinforced SMC	Premix
Prevail	ABS/Polyurethane	Dow Plastics
Prevex	PE	GE Plastics
Primef	PS	Solvay
Prism	RIM Polyurethane	Bayer
Pro-fax	PP resins	Hercules Powder
Profil	Fiberglass-reinforced PP	Dart
Proglas	Fiberglass-reinforced PP	Dart
Prohi	HDPE	Protective Lining Corp.
Prolan	Olefin fiber	Ronile
Propathene	PP	Imperial
Propax	PP	PolyPacific
Propiofan	Poly(vinyl propionate)	BASF
Propylsar	Fiberglass-reinforced PP	Dart
Propylus	PP	Westlake Plastics
Protectolite	PE film	Protective Lining Corp.
Protron	Ultrahigh-strength PE	Protective Lining Corp.
Pulse	Polycarbonate/ABS	Dow Plastics
Purilon	Rayon	FMC Corp.
PYR-ML	Polyimide	DuPont

Quadrol	Poly(hydroxy amine)	Wyandotte Chemicals
QualiFlo	Polyester fiber	Reemay
Quelflam	Polyurethanes	Baxenden Chemical
Quintac	Linear styrene block copolymer with isoprene	Nippon Zeon
Radel	Poly(ether sulfone)	Amoco Polymers
Radilon	Nylon-6	Radicinovacips
Radipol	Nylon-6,6	Radicinovacips
Ravinil	PVC	ANIC, SPA
Raybrite	Alpha-cellulose filler	Rayonier
Rayflex	Rayon	FMC Corp.
Reflex	PP	Resene
Regalite	Press-polished PVC	Tenneco Advanced Materials
Ren-Flex	PP blend with EPDM or EPR	D&S
REN-Shape	Epoxy materials	Ren Plastics
Ren-Thane	Urethane elastomers	Ren Plastics
Reny	Nylon-6,6	Mitsubishi
Replay	PS	Huntsman
Reprean	Ethylene copolymer	Discas
Resiglas	Polyester resins	Kristal Draft
Resimene	Urea and melamine resins	Monsanto
Resinol	Polyolefins	Allied Resinous
Resinox	Phenolic resins	Monsanto
Resistoflex	Poly(vinyl alcohol)	Resistoflex Corp.
Resolite	Urea–formaldehyde resins	Ciba-Geigy
Resollm	Melamine resins	Monsanto
Restfoam	Urethane foam	Stauffer Chemical
Restirolo	PS	Societa Italiana Resine
Retain	PE	Dsow Plastics
Retrieve	Polyester fiber	Marglen Inds.
Rexolene	Cross-linked polyolefin	Brand-Rex
Rexolite	PS	Brand-Rex
Reynolon	Plastic films	Reynolds Metals
Reynosol	Urethane, PVC	Hoover Ball & Bearing
Reximac	Alkyds	Commercial Solvents Corp.
Rezyl	Alkyd varnishes	Sinclair-Koppers
Rhodiod	Cellulose acetate	M & B Plastics
Rhonite	Resins for textile finishes	Rohm & Haas
Rhoplex	Acrylic emulsions	Rohm & Haas
Riblene	PE	ANIC, SPA
Richfoam	Polyurethane foam	E.R. Carpenter
Rigidex	PE	BP Chemicals
Rigidite	Acrylic and polyester resins	American Cyanamid
Rigidsol	Rigid plastisol	Watson-Standard
Rigolac	Polyester resins	Showa Highpolymer
Rilsan	Nylon-11	Aquitaine-Organico
Rimplast	Blends of TPEs with silicone rubbers	Petrarch Systems
Riteflex	Polyester block copolymer with polyether	Hoechst
Rolox	Two part epoxies	Hardman

Ronfalin	ABS	DSM
Roskydal	Urea–formaldehyde resins	Farbenfabriken Bayer Ag
Royalbrite	Nylon-6	Royal-American
Royalex	Cellular thermoplastic sheets	Uniroyal
Royalite	Thermoplastic sheet materials	Uniroyal
Roylar	Polyurethanes	Uniroyal
Rucoam	Vinyl materials	Hooker Chemical
Rucon	PVC	Hooker Chemical
Rucothane	Polyurethanes	Hooker Chemical
Rulan	Flame-retardant plastic	DuPont
Rynite	Polyester (PET, PBT)	DuPont
Ryton	Poly(phenylene sulfide)	Phillips Petroleum
Sabre	PC + PET	Dow Plastics
Saflex	Poly(vinyl butyral)	Monsanto
Safom	Polyurethane foam	Monsanto
Salus	Olefin fiber	FFT
Santoprene	PP dynamic vulcanizate with nitrile rubber	AES
Saran	PVC and poly(vinylidene chloride) copolymer	Dow Plastics
Sarlink 1000	PP dynamic vulcanizate with nitrile rubber	DSM
Sarlink 3000 and 4000	PP dynamic vulcanizate with EPDM	DSM
Satinflex	PVC	Alpha Grey
Satin Foam	Extruded PS foam	Dow
Scotch	Adhesives	3M
Scotchcast	Epoxy resins	3M
Scotchpak	Polyester film	3M
Scotchpar	Polyester film	3M
Scotchweld	Adhesives	3M
Schulamid	Nylon-6; Nylon-6,6	Schulman
Schulink	Cross-linkable HDPE	Schulman
Sclair	PE	Nova Chemicals
SEF	Modacrylic fibers	Solutia
Seilon	Thermoplastic sheets	Seiberling Rubber
Selar	Nylon, PET	DuPont
Selectron	Polyester resins	PPG
Selecttrofoam	Polyurethane foam	PPG
Sensura	Polyester fiber	Wellman
Serelle	Polyester fiber	KoSa
Serene	Polyester	KoSa
Shareen	Nylon	Courtaulds
Shell	Polyolefins	Shell
Shimmereen	Nylon-6	Honeywell Nylon
Shinite	PBT	Shinkong
Shuvin	Vinyl molding materials	Reichhold Chemicals
Silastic	Silicone materials	Dow Corning
Silkey Touch	Nylon-6 fibers	Honeywell Nylon
Silon-TSR	PDMS/PTFE	BioMed Sciences
Sipon	Alkyl and aryl resins	Alcoloa

Silastomer	Silicones	Midland Silicones
Silbon	Rayon paper	Kohjin
Silocet	Silicon rubber	ICI
Sinite	PBT	EniChem
Sinvet	PC	EniChem
Sirfen	Phenol–formaldehyde resins	Societa Italiana Resine
Sir-pel	Poromeric film	Georgia Bonded Fibers
Sirtene	PE	Societa Italiana Resine
Skinwich	Polyurethane integral-skinning foam	Upjohn
Smart Yarns	Acrylic fibers	Solutia
Soarnol	EVA copolymer	Nichimen
Softlite	Ionomer foam	Gilman Brother
Solarflex	Chlorinated PE	Pantascote
Solef	PVDF	Solvay
Solithane	Urethane prepolymers	Thiokol
Solprene	Branched block copolymer of styrene and butadiene	Phillips Petroleum
Solvic	PVC	Solvay
Sonite	Epoxy resin	Smooth-On
Sovar	Poly(vinyl acetate)	Shawinigan Resins Corp.
Solvic	PVC	Solvay & Cie
Soreflon	PTFE	Rhone-Poulenc
Spandal	Polyurethane laminates	Baxenden Chemical
Spandex	Polyurethane copolymers filaments	DuPont
Spandofoam	Polyurethane foam	Baxenden Chemical
Spandoplast	Expanded PS	Baxenden Chemical
Spectar	Polyester copolymers	Eastman
Spectra (and related trade names)	Olefin fibers and materials	Honeywell
Spectran	Polyester	Monsanto Textiles
S-polymers	Butadiene–styrene copolymers	Esso Labs.
Spraythane	Urethane resin	Thiokol
Spunnaire	Polyester fiber	Wellman
Stainmaster (and related trade names)	Nylon-6,6 fibers	INVISTA
Standlite	Phenol–formaldehyde resins	Hitachi Chemical
Stanyl	Nylon-46	DSM
Starex	Poly(vinyl acetate)	International Latex & Chemical Corp.
Statex	Carbon black	Columbian Carbon
Stay Gard	Nylon-6 fibers	Honeywell Nylon
Stearon	Linear block styrene–butadiene copolymers	Firestone
Stepton	Linear styrene block copolymers	Kurary
Stereon	Styrene–butadiene block copolymer	Firestone
Steripur	Polyester fibers	DAK Americas, LLC
Stretch-aire	Polyester fibers	KoSa

Structo-Foam	Foamed PS slab	Stauffer Chemical
Strux	Cellular cellulose	Aircraft Specialities
Stylafoam	Coated PS sheets	Gilman Brothers
Stymer	Styrene copolymer	Monsanto
Stypol	Urea–formaldehyde resins	Freeman
Styrafil	Fiberglass-reinforced PS	Dart
Styraglas	Fiberglass-reinforced PS	Dart
Styrex	Resin	Dow
Styrocel	Espandable PS	Styrene Products
Styroflex	Biaxially oriented PS film	Natvar Corp.
Styrofoam	Extruded expanded PS	Dow
Styrolus	PS	Westlake Plastics
Styron	PS	Dow
Styronol	PS	Allied Resinous
Styropor	PS	BASF
Substraight	Polyester fiber	Honeywell
Sulfasar	Fiberglass-reinforced polysulfone	Dart
Sulfil	Fiberglass-reinforced polysulfone	Dart
Sullvac	Acrylonitrile–butadiene–styrene terpolymer	O'Sullivan Rubber Corp.
Sumiplex	Acrylics	Sumitomo
Sunlon	Nylon resins	Sun Chemical Corp.
Sunprene	PVC elastomer	Schulman
Suntra	PPS	Sunkyong
Supec	PPS	GE Plastics
Superflow	PS	Gordon Chemical
Superkleen	PVC	Alpha Gary
Super Aeroflex	Linear PE	Anchor Plastic
Super Coilife	Epoxy potting resin	Westinghouse Electric
Super Dylan	HDPE	Arco Polymer
Superflex	Grafted high-impact PS	Gordon Chemical
Supplex	Nylon-6,6 fibers	INVISTA
Suprel	ABS-PVC	Vista Chemicals
Surflex	Ionomer film	Flex-O-Glass
Surlyn	Ionomer resin	DuPont
Syn-U-Tex	Ureathane–formaldehyde and melamine–formaldehyde	Celanese Coatings
Swedcast	Acrylic sheet	Swedlow
Sylgard	Silicon casting resins	Dow Corning
Sylplast	Urea–formaldehyde resins	Sylvan Plastics
Syntex	Alkyd resins	Celanese Corp.
Synthane	Laminated plastic products	Synthane Corp.
Syretex	Styrenated alkyd resins	Celanese Coatings
Tactasse	Nylon-6,6 fiber	INVISTA
Taipol	Linear and branched styrene block copolymers	Taiwan Synthetic Rubber
Tairilin	Polyester fiber	Nan Ya Plastics Corp.
TanClas	Spray or dip plastisol	Tamite Inds.
Technyl	Nylon-6,6	Rhone-Poulenc

Tecoflex	PUR	Thermidics
Tedlar	Polyvinyl fluorocarbon resins	DuPont
Tedur	PPS	Albis
Teflon	Polytetrafluoroethylene and related materials	DuPont
Teflon FEP	TFE copolymer	DuPont
Teflon TFE	PTFE	DuPont
Tefzel	PE–TFE fluoropolymers	DuPont
Teglac	Alkyl coatings	American Cyanamid
Tego	Phenolic resins	Rohm & Haas
Tekon	Linear block styrene copolymer with ethylene–butadiene	Teknor Apex
Tekton	Olefin fiber	Reemay
Telar	Olefin fiber	FFT
Telcar	PP blend with EPDM or EPR	Teknor Apex
Tempra	Rayon fiber	American Enka Corp.
Tempreg	Low-pressure laminates	US Plywood Corp.
Tencel	Lyocell fibers	Tencel
Tenite	Cellulose derivatives	Eastman Kodak
Tenn Foam	Polyurethane foam	Morristown Foam Corp.
Tensylon	Olefin fibers	SI Corp.
Teracol	Poly(oxytetramethylene glycol)	DuPont
Tere-Cast	Polyester casting resins	Reichhold Chemicals
Terluran	ABS polymers	Badisch Anilin & Soda-Fabrik AG
Terluran	ABS	BASF
Terucello	Carboxymethyl cellulose	Showa Highpolymer
Terylem	PET	ICI
Terylene	Polyester fiber	ICI
Tetraloy	Filled TFE molding resins	Whitford Chemical
Tetra-Phen	Phenolic resins	Georgia-Pacific
Tetra-Ria	Amino resins	Georgia-Pacific
Tetronic	Polyethers	Wyandotte Chemical Corp.
Texalon	Nylon	Texapol
Texicote	Poly(vinyl acetate)	Scott Bader
Texileather	Pyroxylin-leather cloth	General tire & Rubber
Texin	Urethane elastomer	Mobay Chemical
Textolite	Laminated plastic	General Electric
Thermaflow	Reinforced polyesters	Atlas Powder
Thermalux	Polysulfones	Westlake Plastics
Thermasol	Vinyl plastisols and organosols	Lakeside Plastics
Thermax	Carbon black	Commercial Solvents Corp.
Thermco	Expanded PS	Holland Plastics
Thiokol	Poly(ethylene sulfide)	Thiokol
Thornel	Graphite filaments	Union Carbide
Thurane	Polyurethane foam	Dow
T-Lock	PVC sheets	Amercoat Corp.
Topas	Cycloolefin copolymer	Hoechst-Celanese
Topel	Rayon fiber	Courtaulds
Topex	PBT	Tong Yang Nylon
Toplex	PC/ABS	Multibase

Toray	PBT	Toray Industries
Torlon	Polyamide–imide	Amoco Polymers
Toyolac	ABS, ABS/PC	Toray Industries
TPX	Poly-4-methylpentane-1	Imperial
Trace	Olefin fibers	American Fibers & Yarns
Trans-4	*trans*-1,4-Polybutadiene	Phillips Petroleum
Trans-Stay	Polyester film	Transiwrap
Trevarno	Resin-impregnated cloth	Coast Mfg. & Supply Corp.
Triax	PC/ABS, ANS/Nylon	Bayer
Tribit	PBT	Sam Yang
Trilene	Nylon-6 fiber	Berkley
Tri-Foil	TFE-coated aluminum foil	Tri-Point Inds.
Trilon	TFE	Dynamit Nobel
Triocel	Rayon acetate	Celanese Fibers
Trirex	PC	Sam Yang
Trithene	TFE	Union Carbide
Trolen	PE	Dynamit Nobel
Trolitan	Phenol–formaldehyde	Dynamit Nobel
Trosifol	Poly(vinyl butyral) film	Dynamit Nobel
Trosiplast	PVC	Dynamit Nobel
Trubyte	Acrylic-based multicomponent dental system	Dentsply
Trulon	PVC resin	Olin Corp.
Trusite	Olefin fibers	Nexcel Synthetics
Tuffak	Polycarbonate	Rohm & Haas
Tufrex	ABS	Bayer
Tuftane	Polyurethane	B.F. Goodrich
Tusson	Rayon fiber	Beaunit Mills Corp.
Tybrene	ABS polymers	Dow
Tygon	Vinyl copolymer	U.S. Stoneware
Tylose	Cellulose ethers	Farbwerke Hoechst AG
Tynex	Nylon bristles and filaments	DuPont
Typar	Olefin fibers	Reemay
Typelle	Olefin fibers	Reemay
Tyril	Styrene–acrylonitrile copolymer	Dow
Tyrilfoam	Styrene/acrylonitrile foam	Dow
Tyrin	Chlorinated PE	Dow
Tyrite	Olefin fiber	Nexcel Synthetics
Tyvec	Olefin fibers	DuPont
Udel	PSO	Amoco Polymers
Uformite	Urea resins	Rohm & Haas
Ultem	Polyetherimide	GE Plastics
Ultradur	PBT	BASF
Ultraform	Acetal	BASF
Ultraline	Olefin fibers	Samson Rope Tech.
Ultramid	Nylon	BASF
Ultrason-E	Poly(ether sulfone)	BASF
Ultrason-S	Polysulfone (PSO)	BASF
Ultrastyr	ABS	EniChem America
Ultrathene	EVA Copolymers	Quantum

Ultrapas	Melamine–formaldehyde resins	Dynamit Nobel
UltraFlo	Polyester fiber	Reemay
Ultra Touch	Nylon-6 fibers	Honeywell Nylon
Ultron (and related trade names)	Nylon-6,6 fibers	Solutia
Ultryl	PVC	Phillips Petroleum
Ultura	Polyester fiber	Wellman
Unichem	PVC	Colorite Plastics
Unifoam	Polyurethane foam	William T. Burnett & Co.
Unipoxy	Epoxy resins and adhesives	Kristal Kraft
Unival	PE	Union Carbide
Unox	Epoxies	Union Carbide
Urac	Urea–formaldehyde resins	American Cyanamid
Urafil	Fiberglass-reinforced polyurethane	Dart
Uraglas	Fiberglass-reinforced polyurethane	Dart
Uralite	Polyurethanes	Hexcel Corp.
Urapac	Rigid polyurethanes	North American Urethanes
Urapol	Polyurethane elastomeric coatings	Gordon Chemicals
Urapol	Polyurethane elastomeric coatings	Poly Resins
Urecoll	Urea–formaldehyde resins	BASF
Uscolite	ABS copolymer	U.S. Rubber Co.
U-Thane	Rigid insulation polyurethane	Upjohn
Uvex	Cellulose acetate butyrate	Eastman Kodak
Valox	Polyesters (PBT, PCT, PET)	General Electric
Valsof	PE emulsions	United Merchants & Manfs.
Valtra	PS	Chevron Chemical
Vandar	Polyester alloy	Hoechst-Celanese
Varcum	Phenolic resins	Reichhold Chemicals
Varex	Polyester	McCloskey Varnish
Varkyd	Alkyd and modified alkyd resins	McCloskey Varnish
Varsil	Silicon-coated fiberglass	New Jersey Wood Finishing
V del	Polysulfone resins	Union Carbide
Vector	Linear styrene block copolymers with butadiene/isoprene	Dexco
Vectra	PP fibers	ExxonMobil
Velene	PS-foam laminates	Scott Paper
Velon	PVC	Firestone Tire & Rubber
Verel	Modacrylic staple fibers	Eastman Chemical
Versamid	Polyamide resins	General Mills
Versel	Polyester thermoplastic	Allied Chemical Corp.
Versi-Ply	Co-extruded film	Pearson Inds.
Vespel	Polymelitimide	DuPont
Vestamid	Nylon-12	Chemische Werke Huls AG
Vestolit	PVC	Chemische Werke Huls AG
Vestyron	PS	Chemische Werke Huls AG

Vibrin	Polyester resins	Uniroyal
Vibrin-Mat	Polyester-glass molding material	W.R. Grace
Vibro-Flo	Epoxy and polyester coating powders	Armstrong Products
Vicara	Protein fiber	Virginia-Caroline Chemical.
Viclan	PVC	Imperial
Victrex	PEEK	ICI
Videne	Polyester film	Goodyear Tire & Rubber
Vinac	Poly(vinyl acetate) emulsions	Air Reduction
Vinapas	Poly(vinyl acetate)	Wacker Chemie GmbH
Vinidur	PVC	BASF
Vinoflex	PVC	BASF
Vinol	Poly(vinyl alcohol)	Air Reduction
Vinsil	Rosin derivative	Hercules
Vinylite	Poly(vinyl chloride-co-vinyl acetate)	Union Carbide
Vinyon	Poly(vinyl chloride-co-acrylonitrile)	Union Carbide
Vipla	PVC	Montecatini Edison S.P.A
Viscalon	Rayon fiber	American Enka
Viskon	Nonwoven fabrics	Union Carbide
Vista	PVC	Vista Chemical
Vistanex	Polyisobutylene	Enjay
Vitel	Polyester resins	Goodyear
Vithane	Polyurethanes	Goodyear
Viton	Copolymer of vinylidene fluoride and hexafluoropropylene	DuPont
Vituf	Polyester resins	Goodyear
Volara	Closed-cell LDPE foam	Voltek
Volaron	Closed-cell LDPE foam	Voltek
Volasta	Closed-cell medium density PE foam	Voltek
Voranol	Polyurethane foam	Dow
Vulcaprene	Polyurethane	Imperial
Vulkollan	Urethane elastomer	Mobay Chemical
Vult-Acet	Poly(vinyl alcohol) latexes	General Latex & Chemical
Vultafoam	Polyurethane foam	General Latex & Chemical
Vultathane	Polyurethane coatings	General Latex & Chemical
Vybak	PVC	Bakelite Xylonite
Vybex	Polyester	Ferro
Vycron	Polyester fiber	DuPont
Vydyne	Nylon resins	Monsanto
Vygen	PVC	General Tire & Rubber
Vynaclor	PVC emulsions	B.F. Goodrich Chemical
Vynaloy	Vinyl sheets	B.F. Goodrich Chemical
Vynex	Rigid vinyl sheeting	Nixon-Baldwin Chemicals
Vyram	PP dynamic vulcanizate with NR	AES
Vyrene	Spandex fiber	U.S. Rubber Co.

Vythene	PVC + PUR	Alpha Gary
Wear-Dated (and related trade names)	Acrylic and Nylon-6,6 fibers	Solutia
WeatherBloc	Acrylic fiber	Sterling fibers
Webril	Nonwoven fabric	Kendall
Weldfast	Epoxy and polyester adhesives	Fibercast
Wellamid	Nylon-6,6; nylon-6 molding resins	Wellman
Wellon	Nylon-66; nylon-6 fibers	Wellman
Wellstrand	Nylon-66; nylon-6 fibers	Wellman
Welltite	Olefin fibers	Wellington
Welvic	PVC	Imperial
Whirlclad	Plastic coatings	Polymer Corp.
Whirlsint	Powdered polymers	Polymer Group
Whitcon	Fluoroplastic lubricants	Whitford Chemical Corp.
Wicaloid	Styrene/butadiene emulsions	Ott Chemical
Wicaset	PVC emulsions	Ott Chemical
Wilfex	Vinyl plastisols	Flexible Products
Xenoy	PC/polyester	GE Plastics
XT Polymer	Acrylics	American Cynamid
Xydar	Liquid crystal polymers	Amoco Polymers
Xylon	Nylon-66; nylon-6	Dart
Xylonite	Cellulose nitrate	B.X. Plastics
Zantrel	Rayon fiber	American Enka
Zee	PE wrap	Crown Zellerback
Zefran	Acrylic fiber	Dow
Zefsport	Nylon-6 fibers	Honeywell Nylon
Zeftron (and related trade names)	Nylon-6 fibers	Honeywell Nylon
Zelux	PE films	Union Carbide
Zemid	PE, HDPE	DuPont Canada
Zendel	PE	Union Carbide
Zeonex	Polymethylpentene (PMP)	Nippon Zeon
Zerlon	Acrylic/styrene copolymer	Dow
Zerok	Protective coatings	Atlas Minerals & Chemicals
Zetafax	Poly(ethylene-co-acrylic acid)	Dow
Zetafin	Poly(ethylene-co-ethyl acrylate)	Dow
Zylar	Acrylic copolymer	Novacor
Zytel series	Nylons	DuPont

Appendix C
Syllabus

Three interrelated questions can be addressed when considering the construction of a course: (1) topics to be covered; (2) order in which these topics should be covered; and (3) proportion of time to be spent on each topic. Just as in any other area of science and engineering, there exists a healthy variety of topics, extent of coverage of each topic, and order of covering the material. There is no "right" answer and this text is developed so that chapters can be dealt with in essentially any order, with the most important topics dealt with near the beginning of most chapters and (possibly) less important material covered later in the chapter.

The field of polymers is expanding at a rapid rate with too much fundamental material to be handled in a single introductory course, yet the basic elements have been included in this text. Some topics that are today considered to be fundamental were not known a decade ago. Each of the fundamental topics are placed into perspective in the current text building upon the core courses of chemistry—organic, physical, inorganic, and analytical.

One assumption agreed upon by most academic and industrial polymer scientists and engineers as well as associated education committees is that there should be both a core of material common to introductory courses and a portion that reflects individual interests and training of teachers, student bodies, and local preferences and circumstances. Thus, not every topic needs to be covered to present a meaningful introductory polymer course. Some years ago, PolyEd, the education arm of Polymer Chemistry and Polymeric Materials: Science and Engineering, developed, with the help of polymer scientists and engineers, a listing of basic topics and preferred coverage. The results are given in Table 1.

TABLE 1
Preferred Topics in Introductory Polymers

Topic	Amount of Course Time (%)	Chapter
Introduction	5	1
Morphology	10	2
Stereochemistry		
Molecular interactions		
Crystallinity/amorphosity		
Molecular weights	10	3
General types		
Solubility		
Testing and characterization	10	13,14
Structure/property relationships		
Physical tests		
Spectral identification		
Stepwise polymerizations and condensation polymers	10	5

(*continued*)

TABLE 1 (continued)
Preferred Topics in Introductory Polymers

Topic	Amount of Course Time (%)	Chapter
Chain-reaction polymerizations and addition polymers Ionic and free radical kinetics of polymerization Polymers produced by chain-reaction polymerization	10	5,6
Copolymerization Kinetics Types of copolymers Blends Principal copolymers	10	7
Optional topics	35	
Natural and biomedical polymers		9,10
Organometallic polymers		11
Inorganic polymers		12
Reactions of polymers	11	
Rheology (flow properties, viscoelasticity)		14
Additives		15
Synthesis of polymer reactants		17
Polymer technology		18

Basically, the committee proposed that all lecture courses include portions of the first seven topics with the level and extent of coverage guided by factors such as available class time, additional topics covered, interest of instructor, student interests, and class composition. It must be emphasized that the “optional topics” listed should not be considered limiting and that additional topics can be introduced.

Appendix D Polymer Core Course Committees

In 1979/80, the American Chemical Society Committee on Professional Training noted the following:

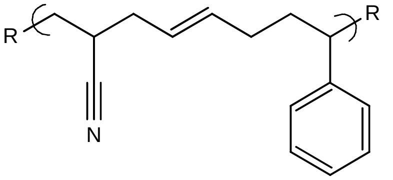
> In light of the current importance of inorganic chemistry, biochemistry, and polymer chemistry, advanced courses in these areas are especially recommended and students should be strongly encouraged to take one or more of these. Furthermore, the basic aspects of these three important areas should be included at some place in the core material.

In light of this directive, the Polymer Education Committee formed committees that focused on the integration of polymer topics in the foundational courses. Committees, hereafter called the Core Course Committees, were formed to develop avenues where polymers would be included in the foundational courses to enhance them. Polymer topics, principles, and illustrations were identified that would help and enhance these courses. The reports of these committee deliberations were published in the *Journal of Chemical Education* as follows:

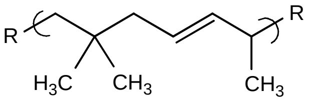
- Introduction (describing the overall project) 60(11):971 (1983)
- General Chemistry 60(11):973 (1983)
- Inorganic 61:230 (1984)
- Physical 62:780 (1985) and 62:1030 (1985)
- Chemical Engineering 62:1079 (1985)

These reports act as a starting point for those teaching the specific foundational courses to introduce polymers.

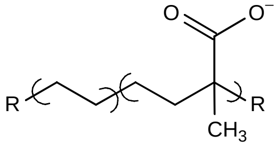
Appendix E
Structures of Common Polymers



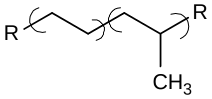
Acrylonitrile–butadiene–styrene (ABS)



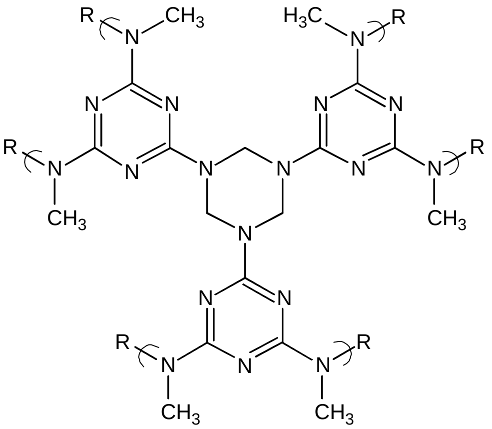
Butyl rubber



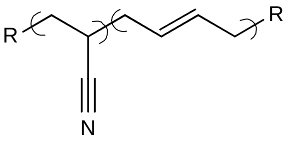
Ethylene–methacrylic acid copolymer (Ionomer)



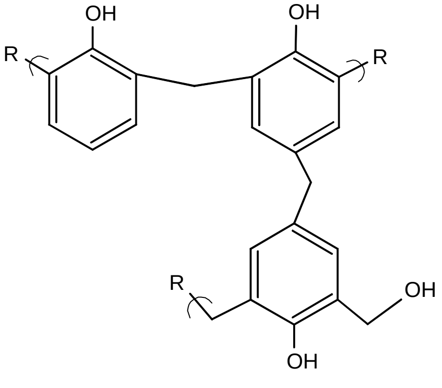
Ethylene–propylene elastomer



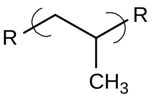
Melamine–formaldehyde resin (MF)



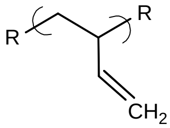
Nitrile rubber (NRB)



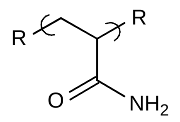
Phenol–formaldehyde resin (PF)



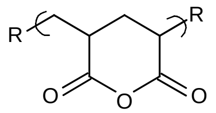
Polyacetaldehyde



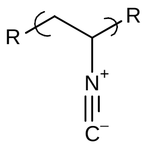
Polyacrolein



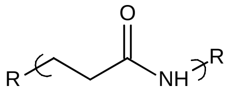
Polyacrylamide



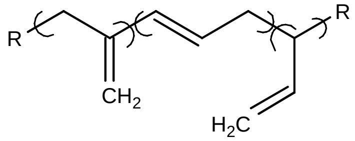
Poly(acrylic anhydride)



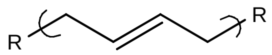
Polyacrylonitrile



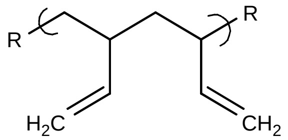
Poly(β-alanine);
nylon-3



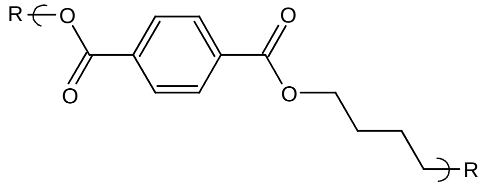
Polyallene



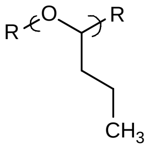
Polybutadiene, butadiene
rubber (BR)



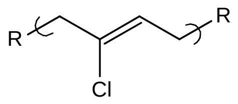
1,2-Polybutadiene



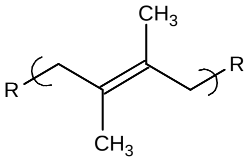
Poly(butylene terephthalate) (PBT)



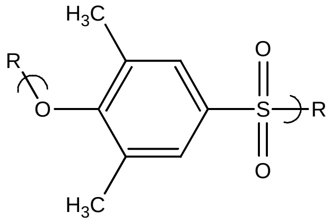
Poly(*n*-butyraldehyde)



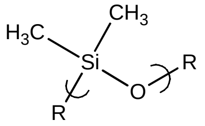
Polychloroprene



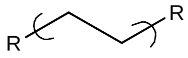
Poly(2,3-dimethylbutadiene)



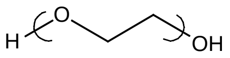
Poly(3,5-dimethyl-1,4-
phenylene sulfonate)



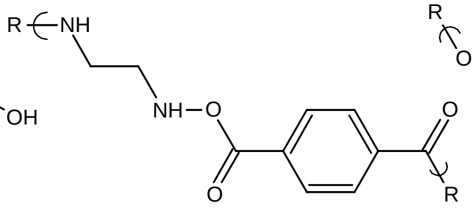
Polydimethylsiloxane



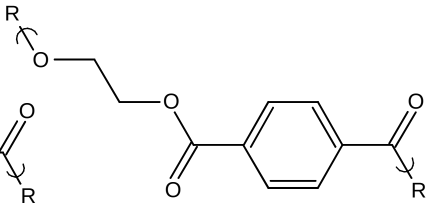
Polyethylene
(PE)



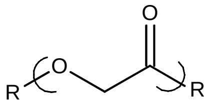
Poly(ethylene glycol) (PEG)



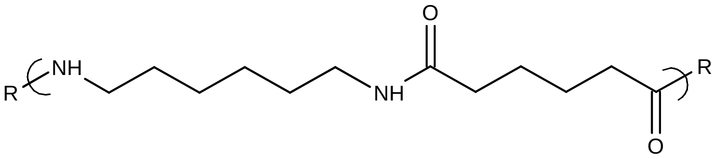
Poly(ethylene terephthalamide)



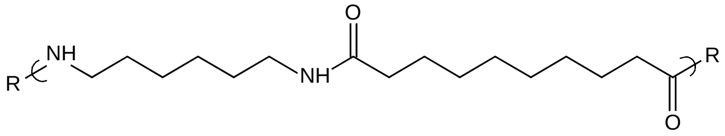
Poly(ethylene terephthalate)



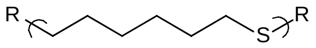
(PET)
Poly(glycolic ester)



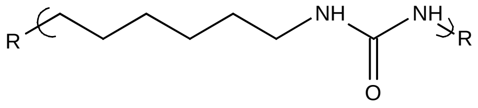
Poly(hexamethylene adipamide) (Nylon-66)



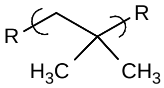
Poly(hexamethylene sebacamide) (Nylon-610)



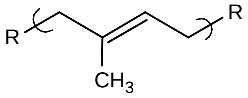
Poly(hexamethylene
thioether)



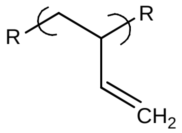
Poly(hexamethylene urea)



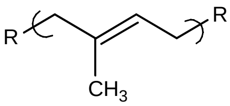
Polyisobutylene (PIB)



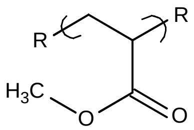
Polyisoprene



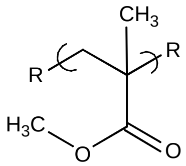
Poly-3,4-isoprene



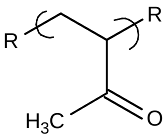
Poly-*trans*-1,4-isoprene



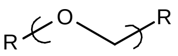
Poly(methyl acrylate)



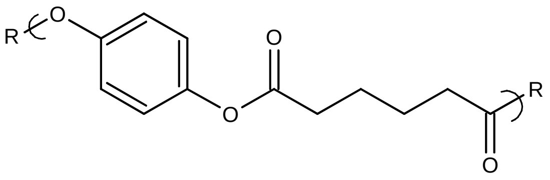
Poly(methylmethacrylate)



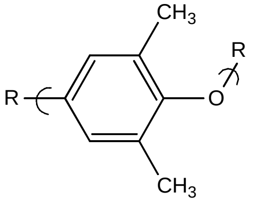
Poly(methyl vinyl
ketone)



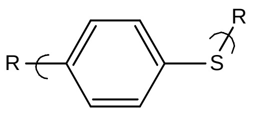
Polyoxymethylene
polyacetal



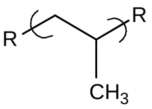
Poly(1,4-phenylene adipate)



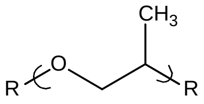
Poly(phenylene oxide)
(PPO) Poly(2,6-dimethyl-p-
phenylene ether)



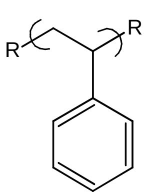
Poly(phenylene sulfide)
(PPS)



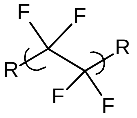
Polypropylene
(PP)



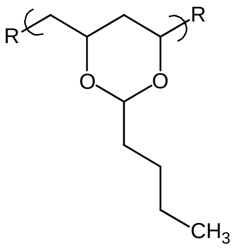
Poly(propylene
glycol) (PPG)



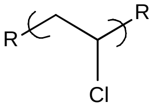
Polystyrene



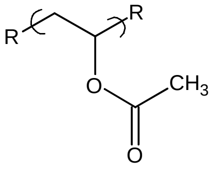
Polytetrafluoroethylene
(PTFE)



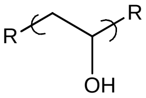
Poly(vinyl butyral)



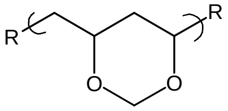
Poly(vinyl chloride)
(PVC)



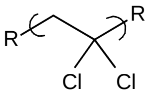
Poly(vinyl acetate)
(PVAc)



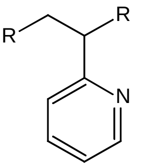
Poly(vinyl alcohol)
(PVA)



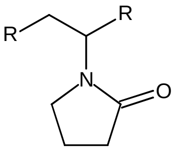
Poly(vinyl formal)
(PVF)



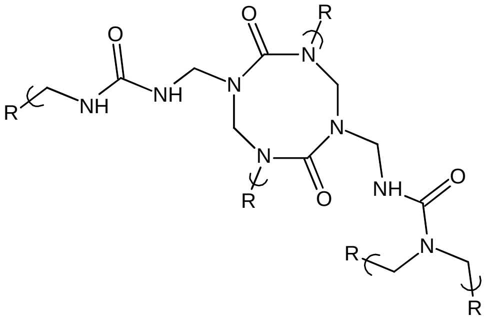
Poly(vinylidene
chloride)



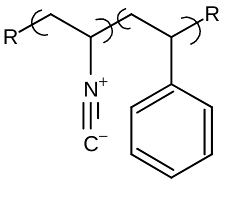
Poly(vinyl pyridine)



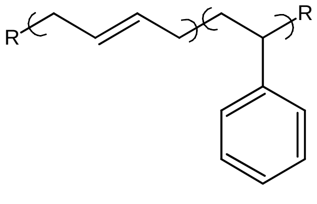
Poly(vinyl pyrrolidone)



Urea–formaldehyde resin (UF)



Styrene–acrylonitrile (SAN)



Styrene–butadiene rubber (SBR)

Appendix F
Mathematical Values and Units

Prefixes for Multiples and Submultiples

Multiple/ Submultiple	Prefix	SI Symbol
10^{12}	tetra	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k, K
10^{2}	hecto	h
10^{1}	deka	da
10^{0}		
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-15}	femto	f
10^{-18}	atto	a

Units of Measure

Quality	Unit	SI Symbol	Formula
Acceleration			m/s^2
Amount of substance	mole	mol	
Bulk modulus	N/m^2		
Chemical potential	joule	J	N m
Compressibility			1/Pa
Density			kg/m^3
Electrical charge	coulomb	C	A s
Electrical capacitance	farad	F	A s/V
Electrical conductivity	siemens	S	A/V
Electrical current	ampere	A	
Electrical field strength			V/m
Electrical inductance	henry	H	V s/A
Electrical resistance	ohm	Ω	V/A
Electromotive force	volt	V	W/A
Energy	joule	J	N m
Enthalpy	joule	J	N m
Entropy			J/K
Force	newton	n	$kg\ m/s^2$
Frequency	hertz	Hz	$cycles/s^2$
Gibbs free energy	joule	J	N m
Heat capacity			J/K

(continued)

Units of Measure (continued)

Quality	Unit	SI Symbol	Formula
Heat flow			J/s m^2
Length	meter	m	
Illuminance	lux	lx	l m/m^2
Luminance			cd/m^2
Luminous flux	lumen	lm	cd sr
Luminous intensity	candela	cd	
Magnetic field strength			A/m
Magnetic flux	weber	Wb	V s
Magnetic flux density	tesla	T	Wb/m^2
Magnetic permeability			H/m
Magnetic permittivity			F/m
Mass	kilogram	kg	
Power	watt	W	J/s
Pressure	pascal	Pa	N/m^2
Resistivity			Ω m
Shear modulus			N/m^2
Surface tension			N/m
Temperature	kelvin	K	
Thermal conductivity			W/mk
Thermal expansion			1/K
Time	second	s	
Velocity			m/s
Viscosity (dynamic)			Ns/m^2
Viscosity (kinematic)			m^2/s
Voltage	volt	V	W/A
Volume			m^3
Wavelength			1/m
Work			N/m
Young's modulus			N/m^2

Physical Constants

Quantity	Symbol	SI	CGS
Acceleration (due to gravity at earth's surface at Equator)	g	9.7805 m/s^2	9.7805×10^2 cm/s^2
Avogadro's constant	N_a	6.02252×10^{23}/mol	6.02252×10^{23}/mol
Boltzmann's constant	k	1.3806×10^{-23} J/K	1.3806×10^{-16} erg/K
Electron charge		1.602×10^{-19} C	!.602 $\times 10^{-20}$ emu
Faraday's constant	F	9.6487×10^4 1/mol	9.6487×10^3 emu/mol
Gas constant	R	8.314 J/mol K	1.987 cal/mol K
Gradational constant	G	6.67×10^{-11} N m^2/kg^2	6.67×10^{-8} dyne cm^2/g^2
Permittivity of a vacuum	ε_o	8.84×10^{-12} F/m^2	1.0 dyne cm^2/$statcoul^{-2}$
Permeability of a vacuum	μ	1.25×10^{-6} H/m	
Planck's constant	h	6.626×10^{-34} J s	6.626×10^{-27} erg s
Velocity of light in a vacuum	c	2.9979×10^8 m/s	2.9979×10^{10} cm/s

Appendix G
Comments on Health

Most polymers are nontoxic under the normal and intended use. (Some biopolymers, such as snake venom, should not be dealt with except under very controlled conditions.) Most of the additives employed are also relatively nontoxic. Even so, care should be exercised when dealing with many of the monomers of synthetic polymers and when dealing with polymeric materials under extreme conditions such as in commercial and domestic fires.

FIRE

Fire hazards involve not only burning, but most deaths occur from the ingestion of volatiles produced by the fire. Carbon monoxide, the major cause of death, causes unconsciousness in less than 3 min due to its preferential attack on hemoglobin.

Interestingly, one important observation concerning burning in general is where colored smoke is produced. Some materials burn, producing lots of dark-colored smoke. Some of this smoke may be due to the production of aromatic systems including fused ring systems, which may contain harmful chemicals including respiratory toxins and carcinogenic agents.

MEASURES OF TOXICITY

Toxicity involves the effect of various materials on living objects including bacteria, plants, mice, fish, and humans. Tests to determine the toxicity of materials are typically done in a number of ways including inhalation, simple skin contact, and subcutaneous injection.

While mainly concerned with the effects of various agents on humans, most standard tests are carried out on animals, often a suitable test animal that is believed to be a good model for transferring results from the animal tests to humans. Table 1 contains some of the toxicity values found in today's literature.

While commercially available synthetic polymers are relatively nontoxic, the monomers vary greatly in toxicity. This points out the need for monomers and other potentially toxic chemicals to be removed from the polymers. Table 2 contains the time–weight average (TWA) for some monomers as cited by the United States Occupational Standards. For comparison, entries for some well-known toxic materials have been added.

CUMULATIVE EFFECTS

While exposure of the general public to toxins is to be avoided, exposure to people who deal with commercial chemicals on a daily basis is even more important. Such people must take special care to avoid exposure since the toxicity of many of these chemicals accumulate in our bodies, slowly building to levels that may be unhealthy.

Most of the toxic and environmentally unwanted chemicals a decade ago have been eliminated from the common workplace. This includes halogenated hydrocarbons, such as

TABLE 1
Description of Toxic Measures

TDLo/Toxic Dose Low—The lowest dose introduced by any route other than inhalation over any period of time that produces any toxic effect in humans or that produces carcinogenic, teratogenic, mutagenic, or neoplastic effects in humans and animals.
TCLo/Toxic Concentration Low—Any concentration in air that causes any toxic effect in humans or produces a carcinogenic, teratogenic, mutagenic, or neoplastigenic toxic effect in humans or animals.
LDLo/Lethal Dose Low—The lowest dose introduced by any route other than inhalation over a period of time to have caused death in humans or the lowest single dose to have caused death in animals.
LD_{50}/Lethal Dose Fifty—A calculated dose expected to cause the death of 50% of a tested population from exposure by any route other than inhalation.
LCLo/Lethal Concentration Low—The lowest concentration in air to have caused death in a human or animal when exposed for 24 h or less.
LC_{50}/Lethal Concentration Fifty—A calculated concentration of a substance in air that would cause death in 50% of a test population from exposure for 24 h or less.
EEGL/Emergency Exposure Guideline Level—Exposure limits for very short exposure.
WEEL/Workplace Environmental Exposure Level–Exposure limits for healthy workers exposed repeatedly without adverse health effects.
OEL/Occupational Exposure Limits—Worker exposure guide.
PREL/Permissible Exposure Limits—Worker exposure limits for no ill effect.
NOAEL/No Observable Adverse Effect Level—Safe usage level.
LOAEL/Lowest Observable Adverse Effect Level—Safe usage level.

carbon tetrachloride, and aromatic hydrocarbons, such as benzene and toluene. Further, chemicals that are known to be potentially toxic, such as some monomers, are being eliminated from the polymeric materials to within the limits of detection.

Industrial recognition of customer and employee safety is a major factor and is included in international programs such as ISO 9000 and ISO 14000. Further, a number of national and state agencies and associations deal with aspects of the environmental and personal safety issues on an ongoing basis.

ENVIRONMENT

Today, industry and business recognize that part of doing business is taking care of the environment. Along with various agencies, business and industry are finding that good environmental practices mean good business. Advances continue with respect to lowering potentially harmful emissions into water and air shared by all of us. Chemical industries are taking the lead in this cleanup process. A combination of vigilance and trust is needed to continue this effort.

TABLE 2
TWA Values for Selected Monomers and Additional Recognized Toxins

Chemical	TWA (ppm)	Chemical	TWA (ppm)
Acetic anhydride	5	Ethylene oxide	50
Acrylonitrile	20	Formaldehyde	3
Benzene	10	Hydrazine	1
1,3-Butadiene	1000	Hydrogen cyanide	10
Carbon monoxide	50	Phenol	5
Chloroprene	25	Styrene	100
1,2-Ethylenediamine	10	Vinyl chloride	500

Appendix H

ISO 9000 and 14000

The International Organization for Standardization (ISO) has members in about 100 countries, working to develop common global standards.

The ISO 9000 series encompasses the product development sequence from strategic planning to customer service. Currently, it is a series of five quality system standards, with two of the standards focusing on guidance and three that are contractual standards.

ISO 9000 certification is often obtained to promote a company's perceived quality level, for supplier control, and to promote certain management practices, often Total Quality Management (TQM) management practices. It acts as a global standardizing "tool" with respect to business and industry in its broadest sense including banking, volunteer organizations, and most aspects of the chemical (including the polymer) industry.

ISO 9000 requires what is called a "third party" assessment but involves developing "first" and "second" party strategies. "First party" refers to the supplier company that requests ISO 9000 certification. "Second party" refers to the customer whose "needs" have been met by the "first party" through the use of quality management procedures achieved by ISO 9000 compliance. "Third party" refers to an outside reviewer who "certifies" that the "first party" has satisfied ISO 9000 procedures.

While ISO 9000 is a management tool, it affects the way "industry does business" and deals with quality control issues such as how machinery and parts manufactured by a company are monitored for quality. It focuses on satisfying the "customer," the "purchaser" of the raw materials, manufactured parts, or assembled items, and includes the eventual "end-customer"—the general public. It is an attempt to assure quality goods.

ISO 14000 is a series of standards intended to assist in managing the impact of manufactured materials including finished products and original "feedstocks." It addresses the need to have one internationally accepted environmental management system that involves "cradle to grave" responsibility for manufactured materials emphasizing the impact of products, operations, and services on the environment.

Appendix I
Electronic Education Web Sites

The information concerning polymers on the World Wide Web is rapidly expanding. This is a valuable source of information giving both applied and fundamental data on a wide range of polymer-related topics. As you search, please be aware that there exist specific pooled information sites on many topics including those considered "hot" topics such as the human genome. There are also web clusters that deal with special topics such as nanomaterials and electrically conductive materials. Have fun "surfing the web." It is an important source of information about polymers.

Sites that you should consider visiting and that are not obvious because of their names are:

- www.polyed.org—a general site for PolyEd, the joint polymer education committee of the American Chemical Society divisions of Polymer Chemistry and Polymeric Materials: Science and Engineering. It contains many connections to other important web sites dealing with polymers.
- www.uwsp.edu/chemistry/ipec—a general site for the Intersociety Polymer Educational Council, which is a joint society venture that focuses on K-12 science education employing polymers as the connective vehicle. The Polymer Ambassadors have their own sites at www.polymerambassadors.org and http://www.polymerambassadors.org/WWWsites2.html.
- www.pslc.ws/macrog/index.htm or simply type in "macrogalleria" and you will be taken to a fun and educational web site that focuses on the relationship between everyday items and their polymeric nature, and the fundamentals that underlie their use in these materials.

Following are other web sites where valuable information may be available:

- Case-Western Reserve University, http://abalone.cwru.edu/tutorial/enhanses/main.htm
- History of polymers, http://www.chemheritage.org/educationalservices/faces/poly/home.htm
- Recycling of Plastics, http://www.plasticbag.com/environmental/pop.html
- Teaching plastics, http://teachingplastics.org
- National Plastics Center and Museum, http://www.plasticsmuseum.org
- Society of Plastics Engineers, http://www.4spe.org
- Society of Plastics Industry, http://www.plasticsindustry.org/outreach/environment/index.htm

Appendix J
Stereogeometry of Polymers

The precise stereogeometry of molecules is important in determining the physical properties of a material and is critical in determining the biological properties of materials. Most synthetic and nonspecific natural polymers are a mix of stereoshapes with numerous stereocenters along the polymer chain. For polypropylene, every other backbone carbon is most likely a stereocenter. Even polyethylene has stereochemical sites wherever there is branching. The imprecise structures of most natural nonspecific polymers such as the polyisoprenes and polysaccharides have stereocenters at each branch.

For stereospecific natural polymers, the entire geometry is critical to the proper behavior and activity of the material. Thus, stereogeometry is important and a brief review is in order.

We have two general types of isomers—constitutional isomers that have the same number and kind of atoms but connected in a different order, such as *cis* and *trans* arrangements, and stereoiosomers. We have two types of steroisomers—diastereomers that are not mirrior images of one another and enantioimers that are mirror-image stereoisomers. Just as our hands cannot be superimposed on their mirror image, enantiomers are nonsuperimposible on one another. Chiral objects or sites are enantiomeric. In fact, the term "chiral" comes from the Greek word for hand, *kheir*.

By comparison, achiral objects, such as a simple nail, ball, basket, white pocketless T-shirt, are all superimposible on their mirror image.

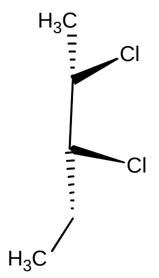
A collection containing only one enantiomeric form of a chiral molecule is referred to by several names including enantiopure, enantiomerically pure, or optically pure. A sample containing predominantly one enantiomer is called enantiomerically enriched or enantioenriched. A collection containing equal amounts of two enantiomeric forms of a chiral molecule is called a racemic mixture or racemate.

Unlike other stereoisomers, enantiomers have identical physical properties and, consequently, are difficult to separate. A process by which enantiomers can be separated is called resolution.

Diastereomers are nonenantiomeric isomers that result when more than one stereocenter is present in a molecule. The distinction between diastereomers and enantiomers is not always clear but, in general, enantiomers have mirror images, whereas diastereomers are not mirror images of one another. As such diastereomers have different physical properties such as boiling and melting points, solubilities, etc.

The total number of stereoisomers due to tetrahedral stereocenters does not exceed 2^n where n is the number of tetrahedral stereocenters. For a compound with two stereocenters $n = 2$ giving a total of 4 (maximum) stereoisomers.

Following are four formula isomers first drawn in the more conventional straight-chain manner and below in more conformationally correct forms drawn for a compound, 2,3-dichlorohexane, with two stereocenters.



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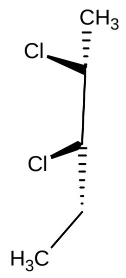

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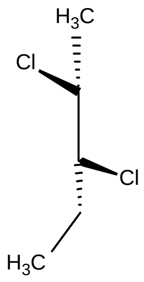

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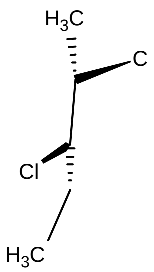

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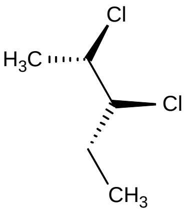
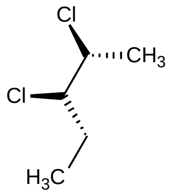


1.



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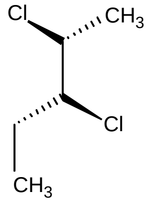

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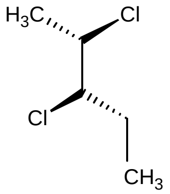


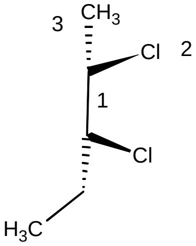
4.

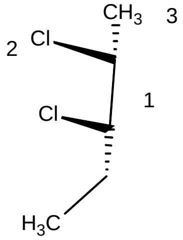
Structures 1 and 3, as well as 2 and 4 and structures 1 and 4, etc. are stereoisomers but they are not mirror images of one another; thus, they are diastereomers. Structures 1 and 2, as well as 3 and 4, are mirror images of one another, and so we have a pair of compounds that are not superimposable and they are enantiomers to one another; i.e., 1 and 2 are enantiomers and 3 and 4 are enantiomers.

Enantiomers can rotate the plane of polarized light. If the rotation is positive, the enantiomer is given the symbol "+" or "d" and is referred to as the dextrorotary enantiomer. On the contrary, if the compound causes the light to be rotated in the negative direction, the compound is given the symbol "−"or "l" and is referred to as the levorotatory enantiomer. An equal mixture of two enantiomers, racemates, does not rotate plane-polarized light because the rotation due to one enantiomer is canceled by that of the other. There is no relationship between the absolute configuration, S or R, and the direction of rotation of plane-polarized light (+ or −).

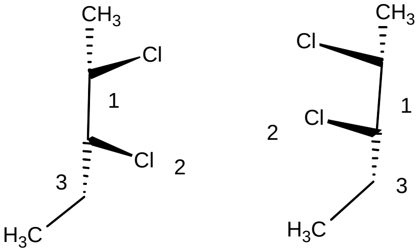
The absolute configuration around each stereogeometrical site is most often determined using the Cahn–Ingold–Prelog sequence rules. (These rules are found in most organic texts.) For tetrahedral carbons containing four different groups we determine the group with the highest priority and assign it the number 1 and the group with the lowest priority the number 4. We then view the molecule having at its center the particular stereocarbon in question and arrange at the top the number 1 group. In doing so, we can see if the direction going from 1 — > 2 — > 3 is clockwise, R, or counterclockwise, S.

For structure 1 given above, looking only at the top stereocarbon, the arrangement is counterclockwise and so this particular site is designated as S. For structure 2 above, again looking only at the top stereocarbon, the arrangement is clockwise and so that carbon is designated as R.



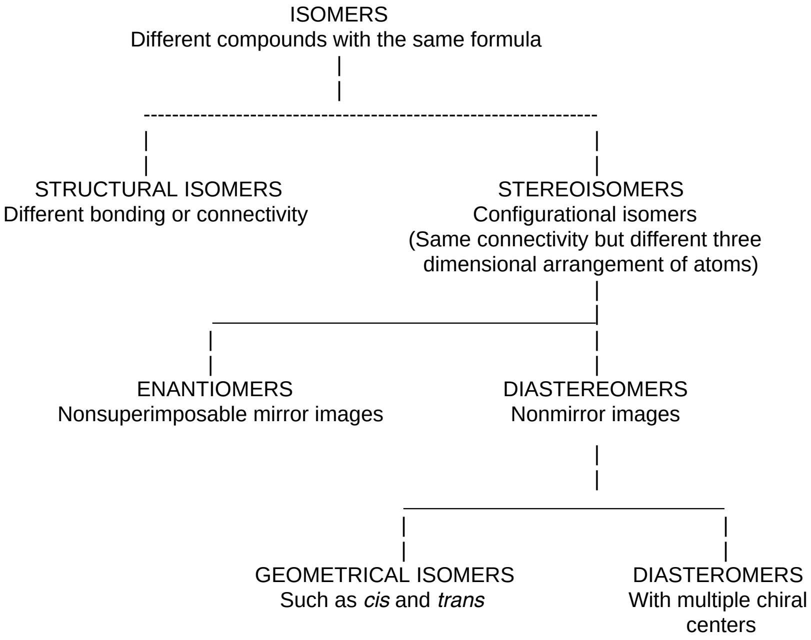


Now looking at only the second carbon, we have for the first compound a clockwise arrangement, meaning it is R, and for the second compound the arrangement is clockwise, so it is designated as S.

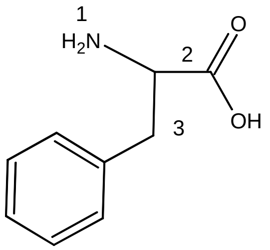


Thus, the two stereocarbons in the first compound would be designated as S, R or 2S, 3R, and in the second compound as R, S or 2R, 3S, with the numbers indicating the position of the carbon atoms. Often you will find that both the stereogeometry and rotation of light are given.

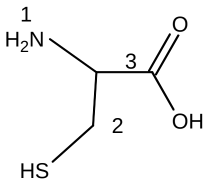
We can develop a concept map that describes the possible geometrical isomers as follows.



With the exception of alanine, all of the naturally occurring amino acids contain a chiral carbon adjacent to the amino acid grouping. All of these amino acids are of the l or L form, meaning they rotate light in a negative direction. The rules governing the specification of the absolute configuration are such that you can get both S and R forms of the amino acids. Thus L-phenylalanine is an S enantiomer while L-cysteine is an R enantiomer.



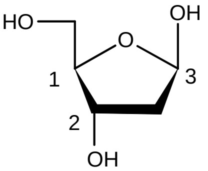
L-phenylalanine or
S-phenylalanine

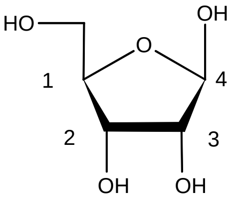


L-cysteine or
R-cysteine

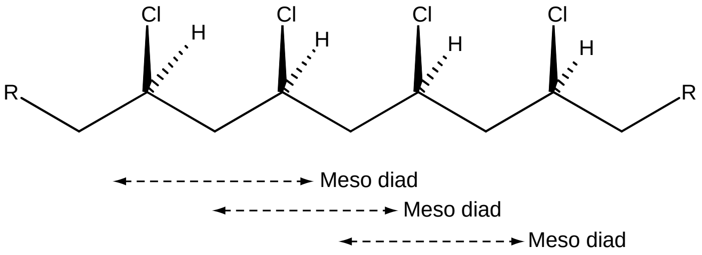
As noted above, with the exception of alanine, the addition of amino acids to form polypeptides allows for a large number of stereochemical isomers to be formed, even considering that all are of the L form. But nature does not allow for this diversity and rather selects only one configuration for a sequence to occur in its synthesis of structure-specific proteins such as those employed as enzymes. Even those employed for other activities such as muscle have a specific geochemistry. In fact, the cell produces only geometry-specific polypeptides.

Nature is also selective in the geometry involved in nucleic acid synthesis. This specificity involves both the base order and the particular sugar employed. For DNA the employed sugar is β-2-deoxy-D-ribose, deoxyribose (below left). Deoxyribose has three chiral centers but only one of them is employed in the synthesis of nucleic acids. Ribose, the sugar employed in the synthesis of RNA, has four geometric sites (below right).



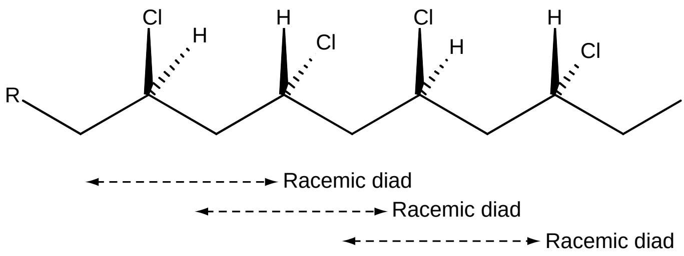


Now let us examine simple vinyl polymers, with only one site of substitution per repeat unit. When we look at a polymer chain, we focus only on combinations of diads or couples. For our discussion, we will use segments of poly(vinyl chloride). The geometries can be divided into three general groups. The first group, in which the substitutes, or here the chloride atoms, are all identical with adjoining neighbors, comprise meso diads. Polymers or sections of polymers that contain meso diads are referred to as isotactic.



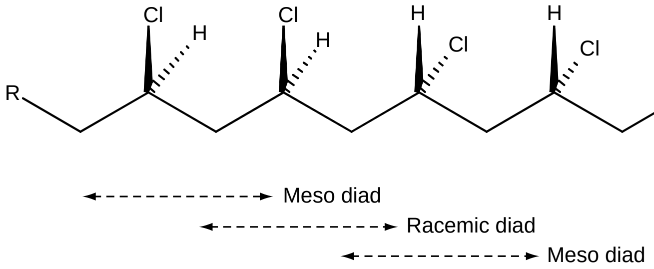
Isotactic poly(vinyl chloride) segment

In the second grouping, the geometry of the substitutes alternates on the chiral carbons that contain the chloride atoms. Here each diad is racemic. Such segments are referred to as syndiotactic.



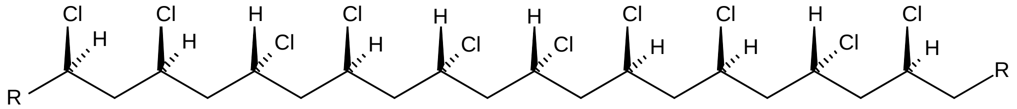
Syndiotactic poly(vinyl chloride) segment

The third group consists of mixtures of racemic and meso diads. These sequences are given the name atactic or "having nothing to do with tacticity or orderly arrangement."



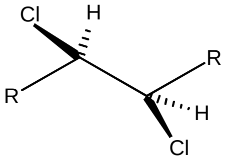
Atactic poly(vinyl chloride) segment

Stereoregular polymers are those that contain large ordered segments. In truth, even stereoregular polymers contain some atactic regions. Even so, polymers that contain large fractions of ordered segments exhibit a greater tendency to form crystalline regions and to exhibit, relative to those containing large amounts of atactic regions, greater stress/strain values, greater resistance to gas flow, greater resistance to chemical degradation, lower solubilities, etc.

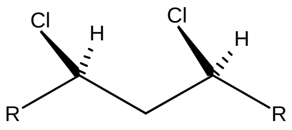


Atactic poly(vinyl chloride) segment

While the situation with respect to simple vinyl polymers is straightforward, the tacticity and geometrical arguments are more complicated for more complex polymers. Here we will only briefly consider this situation. Before we move to an illustration of this let us view two related chloride-containing materials pictured below. We notice that by inserting a methylene between the two chlorine-containing carbons the description of the structure changes from racemic to meso. Thus, there exists difficulty between the historical connection of meso with isotactic and racemic with syndiotactic.

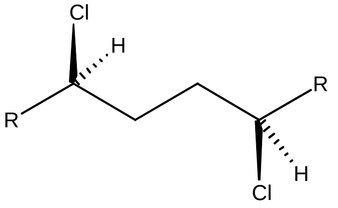


2R,3R-dichloro diad
Racemic

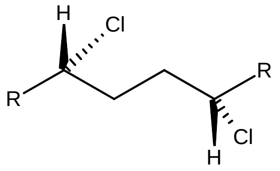


2R,4S-dichloro diad plus inserted methylene
Meso

Let us now move to the insertion of another methylene, forming the following segments. The first set contains racemic pairs.

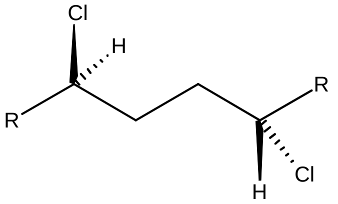


2R,5R-dichloro segment
Racemic pairs

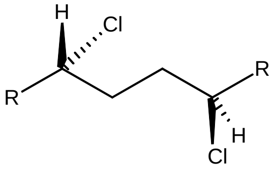


2S,5S-dichloro segment

The second contains a meso pairing.



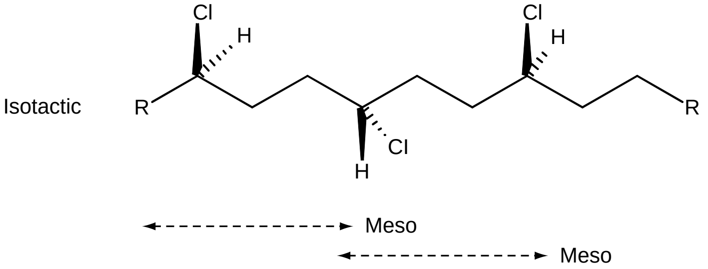
2R,5S-dichloro segment



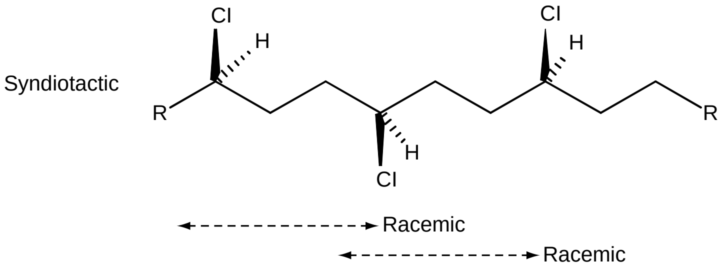
2S,5R-dichloro segment

Meso pair

Now let us look at triad segments of our poly(vinyl chloride). The first one had meso adjacent units and is isotactic by definition of the meso, racemic argument but the adjacent chlorides are not on one side of the plane.

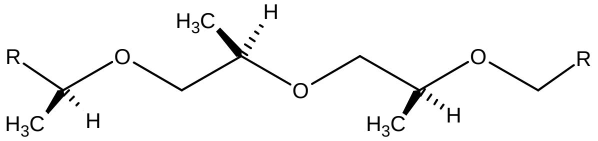


The second pair contains racemic diads and is syndiotactic by the meso, racemic argument but with the chloride atoms on the same side.

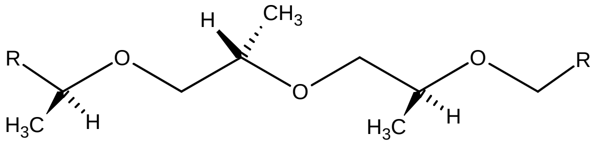


We will now consider segments of a polymer derived from the polymerization of propylene oxide. Here the simplest approach is to simply consider this an extension of the case immediately above except where the chloride atoms are substituted by methyl radicals and the next methylene is now an oxygen atom. Thus, we can make the same assignments based on the meso, racemic considerations.

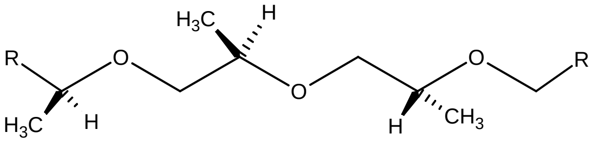
Syndiotactic



Isotactic

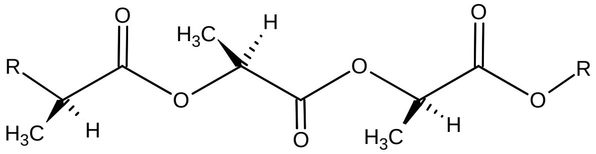


Atactic

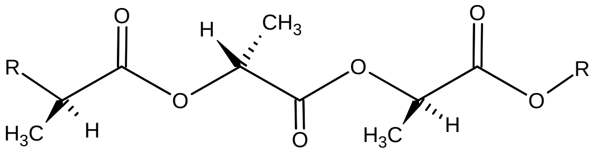


Similarly, we can make assignments for poly(lactic acid) except considering that the carbon next to the chloride-containing carbon has a methyl group, the next following methylene is now a carbonyl, and the next following methylene is an oxygen.

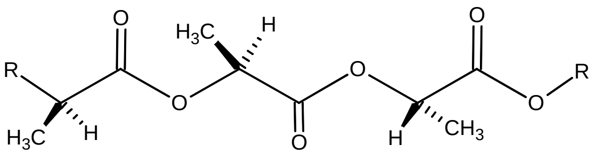
Syndiotactic



Isotactic



Atactic



Appendix K
Statistical Treatment of Measurements

In research and product development and control, there exists variability in the particular value measured such as percentage yield, melting point, tensile strength, and electrical conductivity as you repeat the measurement. Accuracy concerns how close to the true value your measured value is. Unless there is an established value for a particular material, the values you obtain may well contribute to the "true" value. Precision deals with the closeness of a group of measurements to one another. Today, most modern instruments making spectral measurements collect many spectra in a short time and those measurements undergo some type of statistical treatment, such as FT-IR, so that the statistical treatment of these results has already been completed. In comparison, many measurements are done more or less singularly. This is true for most physical testing measurements. Thus, to evaluate the tensile strength of a polycarbonate plastic sheeting, sample "dog-bones" of the shape given in Figure 14.11 are cut from several sheets picked at random and tested under an appropriate set of conditions. These results are then statistically treated and the reported value given along with the variability. Following is a brief summary of one of the more common statistical treatments for such measurements.

The first step involves calculation of the average value (A), which is simply the summation of the individual values (A_i), divided by the number of measurements or observations (n). This is described mathematically as:

$A = (\Sigma A_i)/n$ where the summation is for all of the n values.

The most common statistical measure of the variability, dispersion, or scatter is the standard deviation (s) defined as:

$$s = \left[\left(\sum (A_i - A)^2\right)/n - 1\right]^{1/2}$$

The smaller the value of s, the greater is the precision of the measurements. Some testing calls for the precision to be within some s value such as one s, two s, three s, etc.

Appendix L
Combinatorial Chemistry

Langer and coworkers synthesized a series of copolymers containing various amounts of diacrylate and amine monomers, investigating copolymer composition with the ability to act as transport DNA into cells. They screened 140 copolymers as synthetic gene-delivery vectors. Of these, 56 were able to bind DNA. These polymers were then screened for their ability to facilitate the transfer of plasmid DNA into a common monkey cancer cell line. Two of the copolymers with quite varied compositions showed good activity—one expected and the other unexpected. The expected copolymer composition would have been a selected composition in a typical search and the other would have been omitted. Thus, combinatorial-like approaches can offer unexpected results to problems.

Appendix M
Polymerization Reactors

Polymerization can occur within glass ampules, large-scale batch reactors, laboratory beakers, flow-through systems, etc. The processes used for small preparation in the research laboratory can be similar or dissimilar to those employed for the industrial-scale preparation of pound and larger quantities. While the kind or polymerization influences molecular weight and molecular-weight distribution, polymer structure, and composition as well as some of the physical characteristics, the kind of reactor also influences these factors. The reactor must allow adequate temperature control, mix of reactants, and, if needed, catalysts (and at times a number of additives), reactant homogeneity, blending/mixing, etc. It must also allow for the economical "mass production" of the material. While there exists a wide variety of commercial reactors, we will look at only three of the most used styles—batch, plug flow, and continuous stirred tank reactors.

Batch

In batch reactions, the reactants are added (charged) to the reactor, mixed for a specific time and temperature, and then removed (discharged). Batch reactors are generally simple and can vary from relatively small (such as a gallon) to large (several hundred gallons) with the reaction occurring under varying conditions throughout the reaction vessel with time, giving products that vary with time and, secondarily, location within the vessel. This second condition is referred to as the polymerization occurring under nonsteady state or unsteady state conditions.

The general material balance can be described as follows:

$$\begin{array}{lclclcl} \text{Rate of} & & \text{Rate of} & & \text{Rate of} & & \text{Rate of polymer} \\ \text{monomer flow} & = & \text{monomer flow} & + & \text{monomer loss} & + & \text{accumulation in} \\ \text{into reactor} & & \text{from reactor} & & \text{through reaction} & & \text{reactor} \end{array}$$

In a batch system the first two terms are zero since monomer is only added once and leaves only once, after the reaction is completed.

Thus, $0 =$ Rate of monomer loss through reaction + Rate of polymer accumulation

$$0 = \mathrm{d}[M]/\mathrm{d}t + R_\mathrm{p} \quad \text{or}$$
$$-\mathrm{d}[M]/\mathrm{d}t = R_\mathrm{p}$$

For free radical polymerization we have:

$$R_\mathrm{p} = k'[M][I]^{1/2} = k''[M] \quad \text{or}$$
$$\mathrm{d}t = \mathrm{d}[M]/k''[M]$$

Integration gives:

$$\log([M]/[M_0]) = -k''t \text{ and}$$

$$[M] = [M_0]\mathrm{e}^{-k''t} \text{ and}$$

$$\% \text{ Conversion} = 100\ ([M_0] - [M]/[M_0]) = 100\ (1 - \mathrm{e}^{-k''t})$$

This was derived assuming uniform concentration because good mixing is important for this relationship to hold. It also assumes a constant temperature. Both these assumptions are only approached in most batch systems. Further, stirring becomes more difficult as conversion increases so that both control of localized temperature and concentration become more difficult. In reality, this relationship holds for only a few percentage points of conversion. Overall, temperature is a major concern for vinyl polymerizations because they are relatively quite exothermic. This is particularly important for bulk polymerizations. This, coupled with the general rapid increase in viscosity, leads to the Trommsdorff-like effects.

Plug Flow (Tubular)

A plug flow or tubular flow reactor is tubular in shape with a high length/diameter (l/d) ratio. In an ideal case (as in the case of an ideal gas, this only approached reality) flow is orderly with no axial diffusion and no difference in velocity of any members in the tube. Thus, the time a particular material remains within the tube is the same as that for any other material. We can derive relationships for such an ideal situation for a first-order reaction. One that relates extent of conversion with mean residence time, *t*, for free radical polymerizations is:

$$[M] = [M_0]\ \mathrm{e}^{-k''t} \text{ and}$$

$$k'' = -(1/\tau)\ln([M]/[M_0])$$

Again, while such relationships are important, they are approximate at best. For vinyl polymerizations temperature control is again difficult, with temperature increasing from the cooling reactor wall to the center of the tube, and along with high and different viscosities leads to broad molecular weight distributions. Further, these factors contribute to differences in initiator and monomer concentrations again leading to even greater molecular weight distributions.

Continuous Stirred Tank Reactor

In the continuous stirred tank reactor (CSTR) instant mixing to achieve a homogeneous reaction mixture is assumed so that the composition throughout the reactor is uniform. During the reaction, monomer is fed into the system at the same rate as polymer is withdrawn. The "heat" problem is somewhat diminished because of the constant removal of heated products and the addition of nonheated reactants.

In a CSTR, each reaction mixture component has an equal chance of being removed at any time regardless of the time it has been in the reactor. Thus, in a CSTR, unlike the tubular and bach systems, the residence time is variable and can take the exponential form

$$R(t) = \mathrm{e}^{-t/\tau}$$

where R(t) is the residence time distribution, t the time, and τ the mean residence time, which is a ratio of the reactor volume to the volumetric flow rate. The residence time distribution

TABLE 1
Listing of Selected Polymerization Processes and the Most Industrially Employed Reactor Types

Polymerization Reaction	Polymerization Process	Batch	Plug Flow	CSTR
Stepwise	Solution	X	X	
Chain-free radical	Bulk	X		X
	Solution	X	X	X
	Suspension	X		
	Emulsion	X		X
	Precipitation	X		X
Chain-ionic	Solution	X		
	Precipitation	X	X	X

influences the mixing effectiveness, which in turn determines the uniformity of the composition and temperature of the reactants in the reactor and ultimately the primary and secondary polymer structure.

Table 1 contains a listing of selected polymerization processes and the most industrially employed reactor types.

Appendix N
Material Selection Charts

In the selection of a material for a specific application many considerations are involved. Today, for the most part, charts and other relationships are computerized. Here we will look at their use by employing a graphical chart for illustration only. Let us consider making a shaft for a blade that mixes salt water with freshwater for controlled saline irrigation. The shaft material must be strong and lightweight and able to absorb twisting shear. As strength and weight are two important considerations, we will focus on these. A mathematical relationship between weight or mass and strength for a cylindrical shaft can be made such that:

$$\text{Mass is proportional to [density/(shear stress)}^{2/3}\text{] times some safety factors.}$$

This tells us that the best lightweight material to make our shaft is a material with a low density/(shear stress)$^{2/3}$ ratio.

Often, the inverse of this ratio is employed and given the name performance index, P. (There are performance indexes for many different relationships between various physical behaviors.) Here then:

$$P = (\text{shear stress})^{2/3}/\text{density}.$$

Taking the log of both sides gives:

$$\log P = 2/3\ \log\ \text{shear stress} - \text{density}.$$

Rearrangement gives:

$$\log \text{shear strength} = 3/2\ \log + 3/2\ \log P.$$

This expression tells us that a plot of the log of the shear strength versus log density will give a family of straight and parallel lines, each with a slope of 3/2 and each straight line corresponding to a different performance index, P. These lines are called design guidelines. Figure 1 contains a general plot of log shear strength versus density for a number of materials grouped together under a common heading. Within each circle are particular materials with appropriate strength and density values. For instance, polytetrafluoroethylene exists in the midrange, extreme right on the “Polymers” circle and so has a relatively high density and strength, while polypropylene exists in the upper left corner of the “Polymers” circle and has a relatively low density and good strength. Such charts allow the quick focusing in on the general type of material that exhibits needed characteristics.

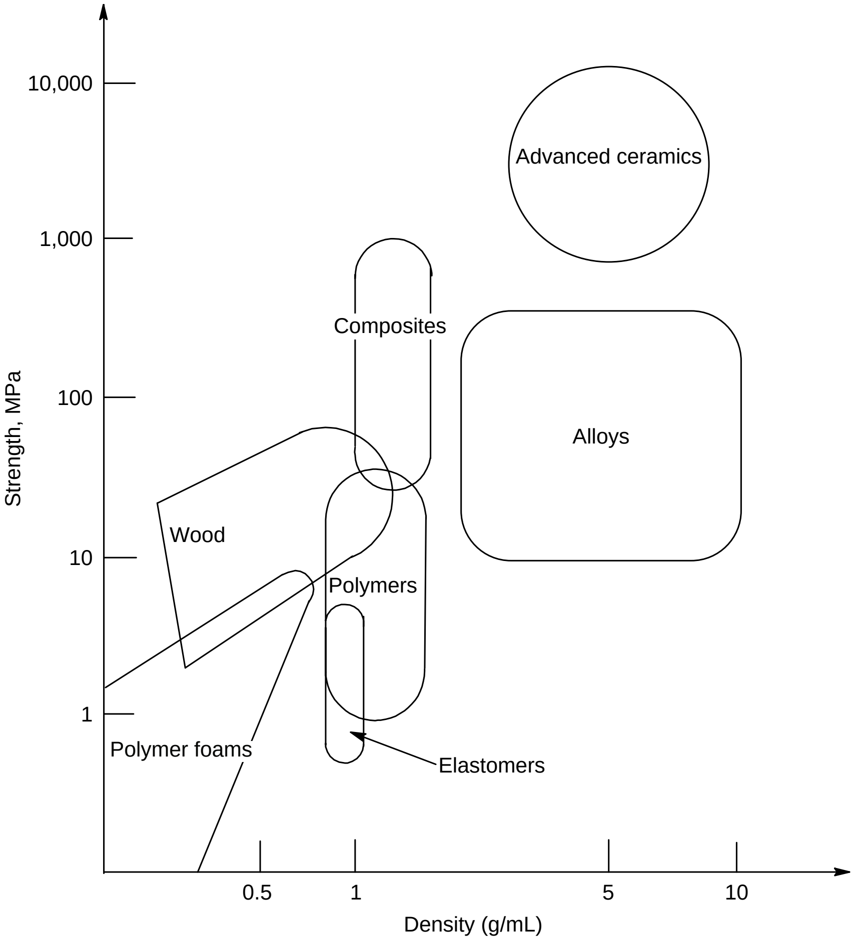


FIGURE 1 Materials selection chart for a material's strength as a function of density.