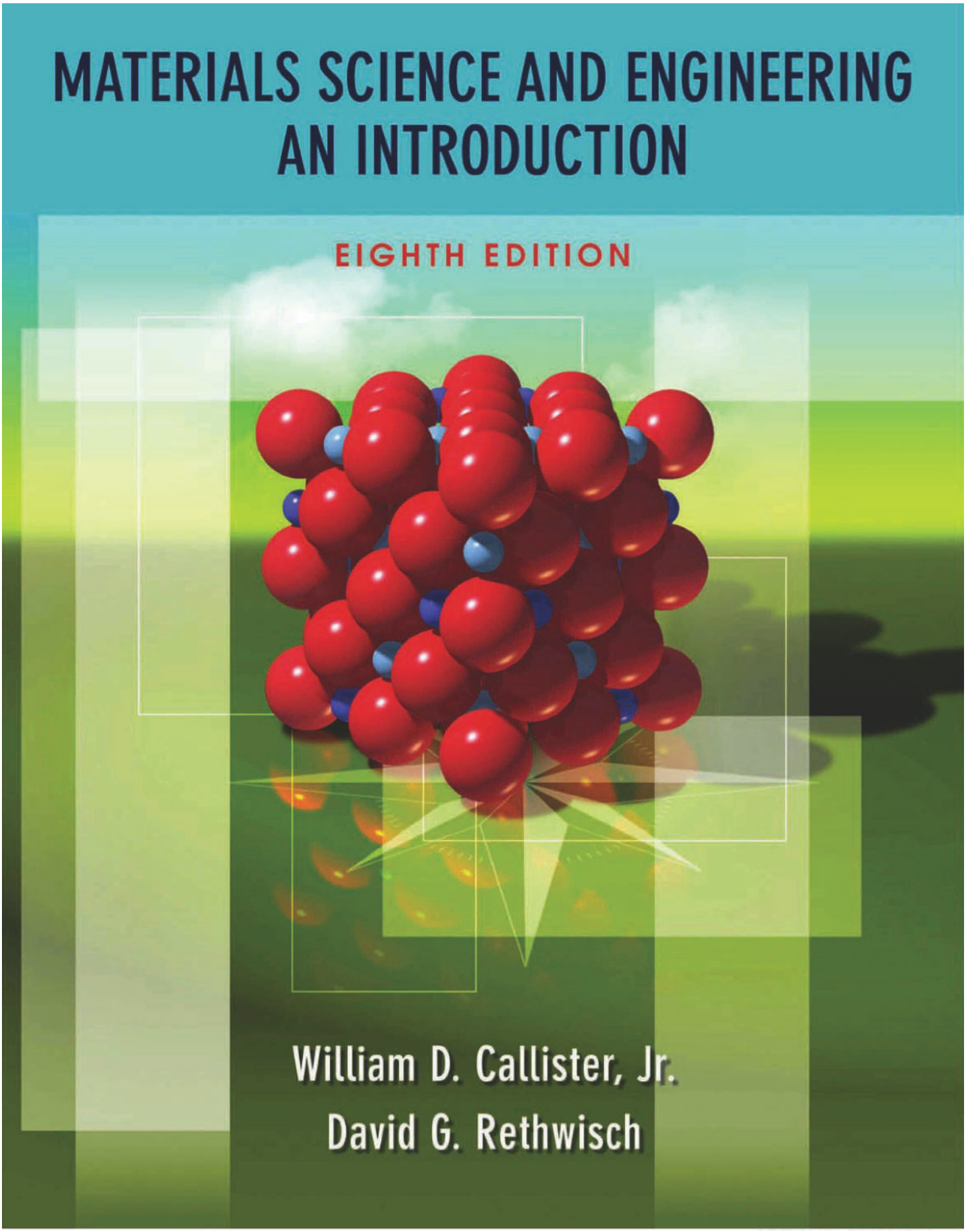
MATERIALS SCIENCE AND ENGINEERING
AN INTRODUCTION

EIGHTH EDITION



William D. Callister, Jr.
David G. Rethwisch

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Characteristics of Selected Elements

Element	*Symbol*	*Atomic Number*	*Atomic Weight (amu)*	*Density of Solid, 20°C (g/cm^3)*	*Crystal Structure, 20°C*	*Atomic Radius (nm)*	*Ionic Radius (nm)*	*Most Common Valence*	*Melting Point (°C)*
Aluminum	Al	13	26.98	2.71	FCC	0.143	0.053	3+	660.4
Argon	Ar	18	39.95	—	—	—	—	Inert	−189.2
Barium	Ba	56	137.33	3.5	BCC	0.217	0.136	2+	725
Beryllium	Be	4	9.012	1.85	HCP	0.114	0.035	2+	1278
Boron	B	5	10.81	2.34	Rhomb.	—	0.023	3+	2300
Bromine	Br	35	79.90	—	—	—	0.196	1−	−7.2
Cadmium	Cd	48	112.41	8.65	HCP	0.149	0.095	2+	321
Calcium	Ca	20	40.08	1.55	FCC	0.197	0.100	2+	839
Carbon	C	6	12.011	2.25	Hex.	0.071	~0.016	4+	(sublimes at 3367)
Cesium	Cs	55	132.91	1.87	BCC	0.265	0.170	1+	28.4
Chlorine	Cl	17	35.45	—	—	—	0.181	1−	−101
Chromium	Cr	24	52.00	7.19	BCC	0.125	0.063	3+	1875
Cobalt	Co	27	58.93	8.9	HCP	0.125	0.072	2+	1495
Copper	Cu	29	63.55	8.94	FCC	0.128	0.096	1+	1085
Fluorine	F	9	19.00	—	—	—	0.133	1−	−220
Gallium	Ga	31	69.72	5.90	Ortho.	0.122	0.062	3+	29.8
Germanium	Ge	32	72.64	5.32	Dia. cubic	0.122	0.053	4+	937
Gold	Au	79	196.97	19.32	FCC	0.144	0.137	1+	1064
Helium	He	2	4.003	—	—	—	—	Inert	−272 (at 26 atm)
Hydrogen	H	1	1.008	—	—	—	0.154	1+	−259
Iodine	I	53	126.91	4.93	Ortho.	0.136	0.220	1−	114
Iron	Fe	26	55.85	7.87	BCC	0.124	0.077	2+	1538
Lead	Pb	82	207.2	11.35	FCC	0.175	0.120	2+	327
Lithium	Li	3	6.94	0.534	BCC	0.152	0.068	1+	181
Magnesium	Mg	12	24.31	1.74	HCP	0.160	0.072	2+	649
Manganese	Mn	25	54.94	7.44	Cubic	0.112	0.067	2+	1244
Mercury	Hg	80	200.59	—	—	—	0.110	2+	−38.8
Molybdenum	Mo	42	95.94	10.22	BCC	0.136	0.070	4+	2617
Neon	Ne	10	20.18	—	—	—	—	Inert	−248.7
Nickel	Ni	28	58.69	8.90	FCC	0.125	0.069	2+	1455
Niobium	Nb	41	92.91	8.57	BCC	0.143	0.069	5+	2468
Nitrogen	N	7	14.007	—	—	—	0.01–0.02	5+	−209.9
Oxygen	O	8	16.00	—	—	—	0.140	2−	−218.4
Phosphorus	P	15	30.97	1.82	Ortho.	0.109	0.035	5+	44.1
Platinum	Pt	78	195.08	21.45	FCC	0.139	0.080	2+	1772
Potassium	K	19	39.10	0.862	BCC	0.231	0.138	1+	63
Silicon	Si	14	28.09	2.33	Dia. cubic	0.118	0.040	4+	1410
Silver	Ag	47	107.87	10.49	FCC	0.144	0.126	1+	962
Sodium	Na	11	22.99	0.971	BCC	0.186	0.102	1+	98
Sulfur	S	16	32.06	2.07	Ortho.	0.106	0.184	2−	113
Tin	Sn	50	118.71	7.27	Tetra.	0.151	0.071	4+	232
Titanium	Ti	22	47.87	4.51	HCP	0.145	0.068	4+	1668
Tungsten	W	74	183.84	19.3	BCC	0.137	0.070	4+	3410
Vanadium	V	23	50.94	6.1	BCC	0.132	0.059	5+	1890
Zinc	Zn	30	65.41	7.13	HCP	0.133	0.074	2+	420
Zirconium	Zr	40	91.22	6.51	HCP	0.159	0.079	4+	1852

Values of Selected Physical Constants

Quantity	*Symbol*	*SI Units*	*cgs Units*
Avogadro's number	N_A	6.022×10^{23} molecules/mol	6.022×10^{23} molecules/mol
Boltzmann's constant	k	1.38×10^{-23} J/atom · K	1.38×10^{-16} erg/atom · K 8.62×10^{-5} eV/atom · K
Bohr magneton	μ_B	9.27×10^{-24} A · m^2	9.27×10^{-21} erg/gauss[a]
Electron charge	e	1.602×10^{-19} C	4.8×10^{-10} statcoul[b]
Electron mass	—	9.11×10^{-31} kg	9.11×10^{-28} g
Gas constant	R	8.31 J/mol · K	1.987 cal/mol · K
Permeability of a vacuum	μ_0	1.257×10^{-6} henry/m	unity[a]
Permittivity of a vacuum	ϵ_0	8.85×10^{-12} farad/m	unity[b]
Planck's constant	h	6.63×10^{-34} J · s	6.63×10^{-27} erg · s 4.13×10^{-15} eV · s
Velocity of light in a vacuum	c	3×10^8 m/s	3×10^{10} cm/s

[a] In cgs-emu units.
[b] In cgs-esu units.

Unit Abbreviations

A = ampere	in. = inch	N = newton
Å = angstrom	J = joule	nm = nanometer
Btu = British thermal unit	K = degrees Kelvin	P = poise
C = Coulomb	kg = kilogram	Pa = Pascal
°C = degrees Celsius	lb_f = pound force	s = second
cal = calorie (gram)	lb_m = pound mass	T = temperature
cm = centimeter	m = meter	μm = micrometer (micron)
eV = electron volt	Mg = megagram	W = watt
°F = degrees Fahrenheit	mm = millimeter	psi = pounds per square inch
ft = foot	mol = mole	
g = gram	MPa = megapascal	

SI Multiple and Submultiple Prefixes

Factor by Which Multiplied	*Prefix*	*Symbol*
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^{-2}	centi[a]	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

[a] Avoided when possible.

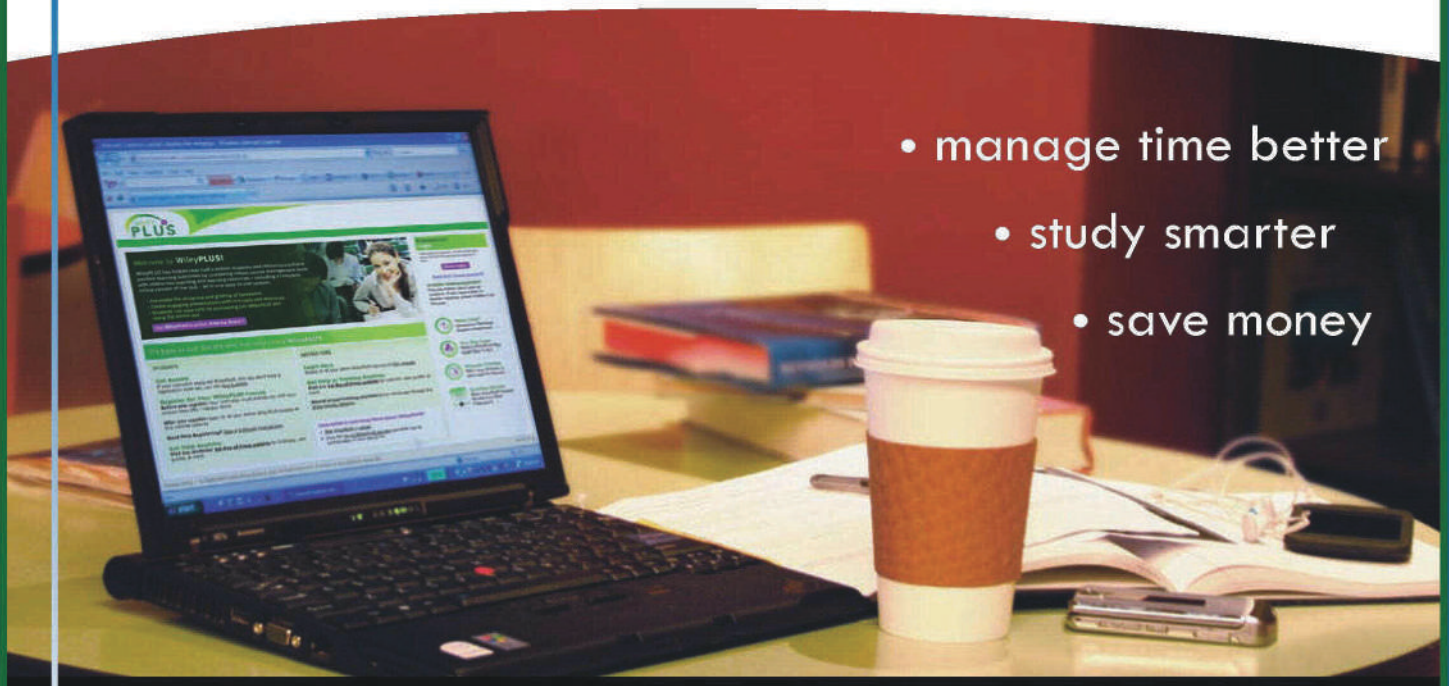
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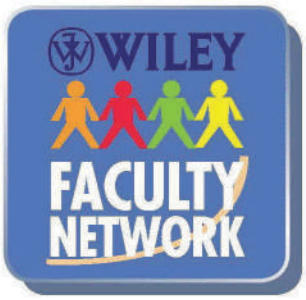
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MAKE IT YOURS!

EIGHTH EDITION

Materials Science and Engineering

An Introduction

William D. Callister, Jr.

Department of Metallurgical Engineering
The University of Utah

David G. Rethwisch

Department of Chemical and Biochemical Engineering
The University of Iowa



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Front Cover: Depiction of a unit cell for the inverse spinel crystal structure. Red spheres represent O^{2-} oxygen ions; dark blue and light blue spheres denote Fe^{2+} and Fe^{3+} iron ions, respectively. (As discussed in Chapter 20, some of the magnetic ceramic materials have this inverse spinel crystal structure.)
Back Cover: The image on the right shows the ionic packing of a close-packed plane for the inverse spinel crystal structure. The relationship between this close-packed plane and the unit cell is represented by the image on the left; a section has been taken through the unit cell, which exposes this close-packed plane.

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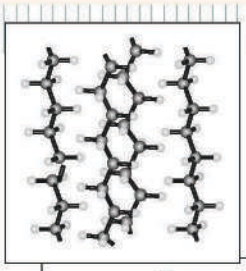
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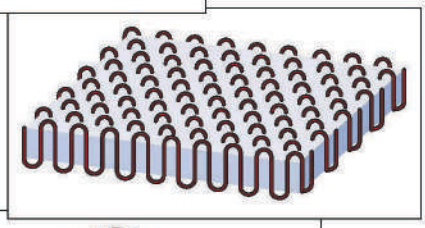
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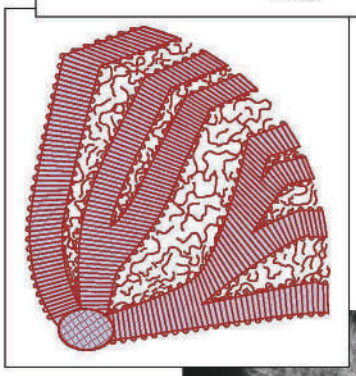
Chapter 14 Polymer Structures



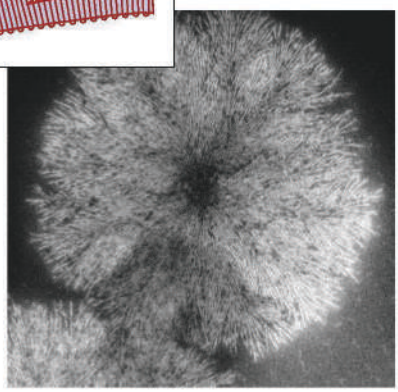
(a)



(b)



(c)



(d)



(e)

(a) Schematic representation of the arrangement of molecular chains for a crystalline region of polyethylene. Black and gray balls represent, respectively, carbon and hydrogen atoms. (b) Schematic diagram of a polymer chain-folded crystallite—a plate-shaped crystalline region in which the molecular chains (red lines/curves) fold back and forth on themselves; these folds occur at the crystallite faces. (c) Structure of a spherulite found in some semicrystalline polymers (schematic). Chain-folded crystallites radiate outward from a common center. Separating and connecting these crystallites are regions of amorphous material, wherein the molecular chains (red curves) assume misaligned and disordered configurations. (d) Transmission electron micrograph showing the spherulite structure. Chain-folded lamellar crystallites (white lines) approximately 10 nm thick extend in radial directions from the center. 12,000×. (e) A polyethylene produce bag containing some fruit. [Photograph of Figure (d) supplied by P. J. Phillips. First published in R. Bartnikas and R. M. Eichhorn, *Engineering Dielectrics*, Vol. IIA, *Electrical Properties of Solid Insulating Materials: Molecular Structure and Electrical Behavior*, 1983. Copyright ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission. Figure (e) from Glow Images.]

A relatively large number of chemical and structural characteristics affect the properties and behaviors of polymeric materials. Some of these influences are as follows:

1. Degree of crystallinity of semicrystalline polymers—on density, stiffness, strength, and ductility (Sections 14.11 and 15.8).
2. Degree of crosslinking—on the stiffness of rubberlike materials (Section 15.9).
3. Polymer chemistry—on melting and glass-transition temperatures (Section 15.14).

In the processing/structure/properties/performance scheme for polymer fibers, the reason for studying polymer structures is as follows:

- In this chapter we explore the various structural elements of polymers, the concepts of crystallinity and crystals in polymers, and how degree of crystallinity is influenced by these structural elements. The manner in which the structural elements affect the properties of polymer fibers is discussed in Chapter 15.

Learning Objectives

After studying this chapter you should be able to do the following:

1. **Describe a typical polymer molecule in terms of its chain structure and, in addition, how the molecule may be generated from repeat units.**
2. **Draw repeat units for polyethylene, poly(vinyl chloride), polytetrafluoroethylene, polypropylene, and polystyrene.**
3. **Calculate number-average and weight-average molecular weights and degree of polymerization for a specified polymer.**
4. **Name and briefly describe:**
   (a) the four general types of polymer molecular structures,
   (b) the three types of stereoisomers,
   (c) the two kinds of geometrical isomers, and
   (d) the four types of copolymers.
5. **Cite the differences in behavior and molecular structure for thermoplastic and thermosetting polymers.**
6. **Briefly describe the crystalline state in polymeric materials.**
7. **Briefly describe/diagram the spherulitic structure for a semicrystalline polymer.**

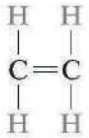
14.1 INTRODUCTION

Naturally occurring polymers—those derived from plants and animals—have been used for many centuries; these materials include wood, rubber, cotton, wool, leather, and silk. Other natural polymers such as proteins, enzymes, starches, and cellulose are important in biological and physiological processes in plants and animals. Modern scientific research tools have made possible the determination of the molecular structures of this group of materials, and the development of numerous polymers, which are synthesized from small organic molecules. Many of our useful plastics, rubbers, and fiber materials are synthetic polymers. In fact, since the conclusion of World War II, the field of materials has been virtually revolutionized by the advent of synthetic polymers. The synthetics can be produced inexpensively, and their properties may be managed to the degree that many are superior to their natural counterparts. In some applications metal and wood parts have been replaced by plastics, which have satisfactory properties and may be produced at a lower cost.

As with metals and ceramics, the properties of polymers are intricately related to the structural elements of the material. This chapter explores molecular and crystal structures of polymers; Chapter 15 discusses the relationships between structure and some of the physical and chemical properties, along with typical applications and forming methods.

14.2 HYDROCARBON MOLECULES

Because most polymers are organic in origin, we briefly review some of the basic concepts relating to the structure of their molecules. First, many organic materials are *hydrocarbons;* that is, they are composed of hydrogen and carbon. Furthermore, the intramolecular bonds are covalent. Each carbon atom has four electrons that may participate in covalent bonding, whereas every hydrogen atom has only one bonding electron. A single covalent bond exists when each of the two bonding atoms contributes one electron, as represented schematically in Figure 2.10 for a molecule of methane (CH_4). Double and triple bonds between two carbon atoms involve the sharing of two and three pairs of electrons, respectively. For example, in ethylene, which has the chemical formula C_2H_4, the two carbon atoms are doubly bonded together, and each is also singly bonded to two hydrogen atoms, as represented by the structural formula



where — and = denote single and double covalent bonds, respectively. An example of a triple bond is found in acetylene, C_2H_2:



unsaturated

Molecules that have double and triple covalent bonds are termed **unsaturated.** That is, each carbon atom is not bonded to the maximum (four) other atoms; therefore, it is possible for another atom or group of atoms to become attached to the original molecule. Furthermore, for a **saturated** hydrocarbon, all bonds are single ones, and no new atoms may be joined without the removal of others that are already bonded.

saturated

Some of the simple hydrocarbons belong to the paraffin family; the chainlike paraffin molecules include methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). Compositions and molecular structures for paraffin molecules are contained in Table 14.1. The covalent bonds in each molecule are strong, but only weak hydrogen and van der Waals bonds exist between molecules, and thus these hydrocarbons have relatively low melting and boiling points. However, boiling temperatures rise with increasing molecular weight (Table 14.1).

isomerism

Hydrocarbon compounds with the same composition may have different atomic arrangements, a phenomenon termed **isomerism.** For example, there are two isomers for butane; normal butane has the structure

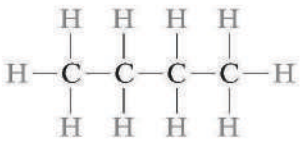
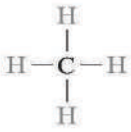
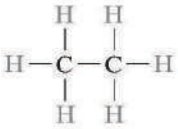
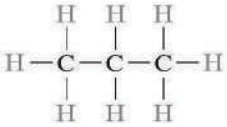
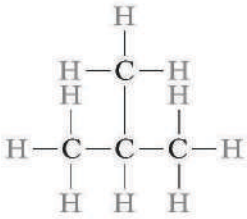


Table 14.1 Compositions and Molecular Structures for Some of the Paraffin Compounds: C_nH_{2n+2}

Name	*Composition*	*Structure*	*Boiling Point (°C)*
Methane	CH_4		−164
Ethane	C_2H_6		−88.6
Propane	C_3H_8		−42.1
Butane	C_4H_{10}		−0.5
Pentane	C_5H_{12}		36.1
Hexane	C_6H_{14}		69.0

whereas a molecule of isobutane is represented as follows:



Some of the physical properties of hydrocarbons will depend on the isomeric state; for example, the boiling temperatures for normal butane and isobutane are −0.5 and −12.3°C (31.1 and 9.9°F), respectively.

There are numerous other organic groups, many of which are involved in polymer structures. Several of the more common groups are presented in Table 14.2, where R and R′ represent organic groups such as CH_3, C_2H_5, and C_6H_5 (methyl, ethyl, and phenyl).



Concept Check 14.1

Differentiate between polymorphism (see Chapter 3) and isomerism.

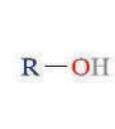
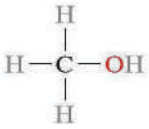
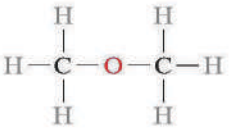
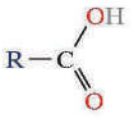
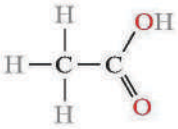
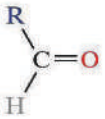
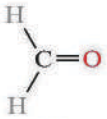
[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

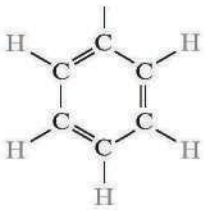
14.3 POLYMER MOLECULES

macromolecule

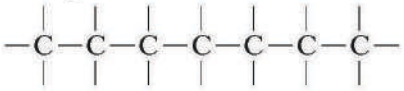
The molecules in polymers are gigantic in comparison to the hydrocarbon molecules already discussed; because of their size they are often referred to as **macromolecules.** Within each molecule, the atoms are bound together by covalent interatomic bonds.

Table 14.2 Some Common Hydrocarbon Groups

Family	*Characteristic Unit*		*Representative Compound*
Alcohols			Methyl alcohol
Ethers			Dimethyl ether
Acids			Acetic acid
Aldehydes			Formaldehyde
Aromatic hydrocarbons			Phenol

[a] The simplified structure  denotes a phenyl group, 

For carbon chain polymers, the backbone of each chain is a string of carbon atoms. Many times each carbon atom singly bonds to two adjacent carbon atoms on either side, represented schematically in two dimensions as follows:



Each of the two remaining valence electrons for every carbon atom may be involved in side bonding with atoms or radicals that are positioned adjacent to the chain. Of course, both chain and side double bonds are also possible.

repeat unit

monomer

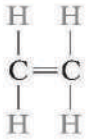
These long molecules are composed of structural entities called **repeat units,** which are successively repeated along the chain.[1] The term **monomer** refers to the small molecule from which a polymer is synthesized. Hence, *monomer* and *repeat unit* mean different things, but sometimes the term *monomer* or *monomer unit* is used instead of the more proper term *repeat unit.*

polymer

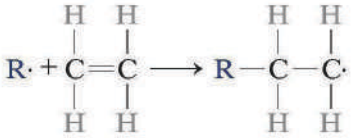
[1] A repeat unit is also sometimes called a mer. *Mer* originates from the Greek word *meros,* which means "part"; the term **polymer** was coined to mean "many mers."

14.4 THE CHEMISTRY OF POLYMER MOLECULES

Consider again the hydrocarbon ethylene (C_2H_4), which is a gas at ambient temperature and pressure and has the following molecular structure:

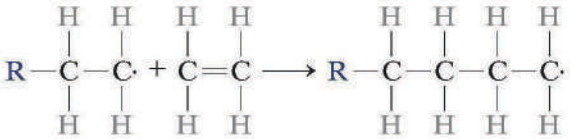


If the ethylene gas is reacted under appropriate conditions, it will transform to polyethylene (PE), which is a solid polymeric material. This process begins when an active center is formed by the reaction between an initiator or catalyst species (R·) and the ethylene monomer, as follows:



(14.1)

The polymer chain then forms by the sequential addition of monomer units to this active growing chain molecule. The active site, or unpaired electron (denoted by ·), is transferred to each successive end monomer as it is linked to the chain. This may be represented schematically as follows:



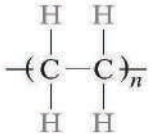
(14.2)

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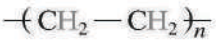


Repeat Unit Structures

The final result, after the addition of many ethylene monomer units, is the polyethylene molecule;[2] a portion of one such molecule and the polyethylene repeat unit are shown in Figure 14.1*a*. This polyethylene chain structure can also be represented as



or alternatively as



Here the repeat units are enclosed in parentheses, and the subscript n indicates the number of times it repeats.[3]

The representation in Figure 14.1*a* is not strictly correct in that the angle between the singly bonded carbon atoms is not 180° as shown, but rather close to 109°. A more accurate three-dimensional model is one in which the carbon atoms form a zigzag pattern (Figure 14.1*b*), the C—C bond length being 0.154 nm. In this

[2] A more detailed discussion of polymerization reactions, including both addition and condensation mechanisms, is given in Section 15.20.

[3] Chain ends/end groups (i.e., the Rs in Equation 14.2) are not normally represented in chain structures.

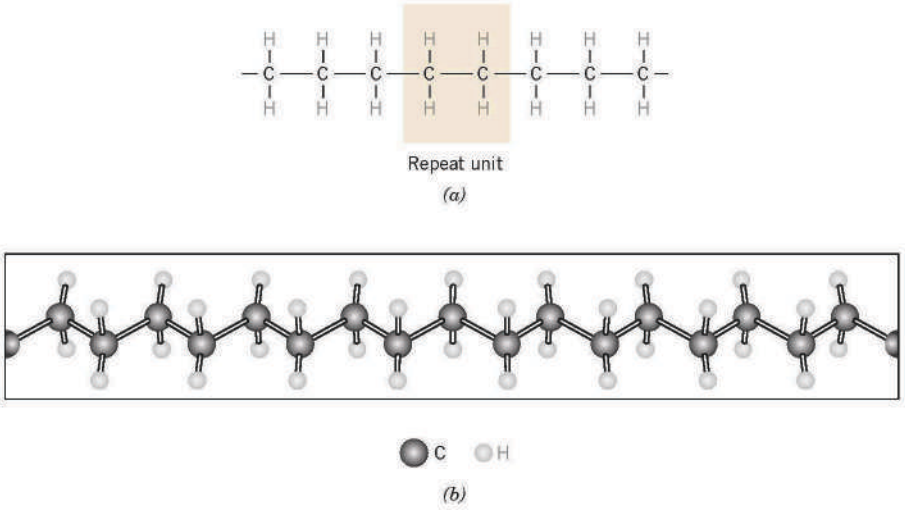


Figure 14.1 For polyethylene, (*a*) a schematic representation of repeat unit and chain structures, and (*b*) a perspective of the molecule, indicating the zigzag backbone structure.

discussion, depiction of polymer molecules is frequently simplified using the linear chain model shown in Figure 14.1*a*.

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Repeat Unit Structures

Of course, polymer structures having other chemistries are possible. For example, the tetrafluoroethylene monomer, $CF_2{=}CF_2$ can polymerize to form *polytetrafluoroethylene* (PTFE) as follows:

$$n\left[\begin{array}{cc} F & F \\ | & | \\ C{=}C & \\ | & | \\ F & F \end{array}\right] \longrightarrow \begin{array}{cc} F & F \\ | & | \\ {+}C{-}C{+}_n & \\ | & | \\ F & F \end{array} \tag{14.3}$$

Polytetrafluoroethylene (having the trade name Teflon) belongs to a family of polymers called the fluorocarbons.

VMSE

Repeat Unit Structures

The vinyl chloride monomer ($CH_2{=}CHCl$) is a slight variant of that for ethylene, in which one of the four H atoms is replaced with a Cl atom. Its polymerization is represented as

$$n\left[\begin{array}{cc} H & H \\ | & | \\ C{=}C & \\ | & | \\ H & Cl \end{array}\right] \longrightarrow \begin{array}{cc} H & H \\ | & | \\ {+}C{-}C{+}_n & \\ | & | \\ H & Cl \end{array} \tag{14.4}$$

and leads to *poly(vinyl chloride)* (PVC), another common polymer.

Some polymers may be represented using the following generalized form:

$$\begin{array}{cc} H & H \\ | & | \\ {+}C{-}C{+}_n & \\ | & | \\ H & R \end{array}$$

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Repeat Unit Structures

where the R depicts either an atom [i.e., H or Cl, for polyethylene or poly(vinyl chloride), respectively], or an organic group such as CH_3, C_2H_5, and C_6H_5 (methyl, ethyl, and phenyl). For example, when R represents a CH_3 group, the polymer is *polypropylene* (PP). Poly(vinyl chloride) and polypropylene chain structures are also represented in Figure 14.2. Table 14.3 lists repeat units for some of the more common polymers; as may be noted, some of them—for example, nylon, polyester,

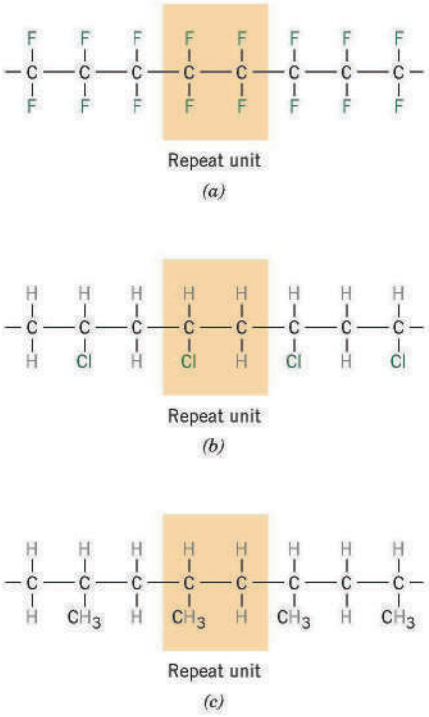
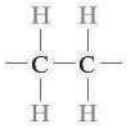
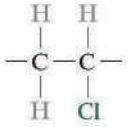
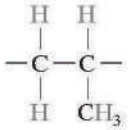
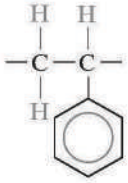


Figure 14.2 Repeat unit and chain structures for (*a*) polytetrafluoroethylene, (*b*) poly(vinyl chloride), and (*c*) polypropylene.

Table 14.3 A Listing of Repeat Units for 10 of the More Common Polymeric Materials

Polymer	*Repeat Unit*
Polyethylene (PE)	
Poly(vinyl chloride) (PVC)	
Polytetrafluoroethylene (PTFE)	
Polypropylene (PP)	
Polystyrene (PS)	

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Repeat Unit Structures



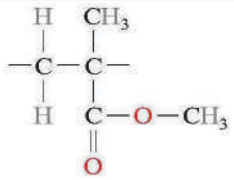
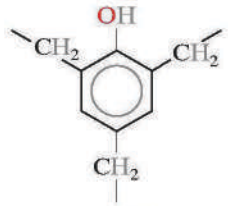
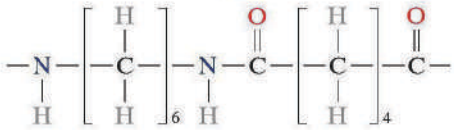
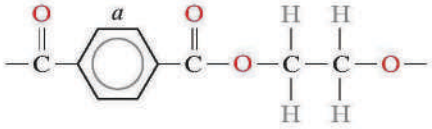
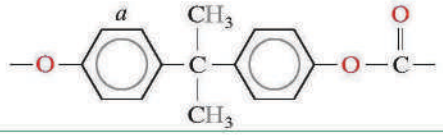


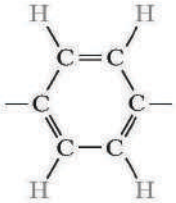




(*Continued*)

Table 14.3 (Continued)

Polymer	*Repeat Unit*
Poly(methyl methacrylate) (PMMA)	
Phenol-formaldehyde (Bakelite)	
Poly(hexamethylene adipamide) (nylon 6,6)	
Poly(ethylene terephthalate) (PET, a polyester)	
Polycarbonate (PC)	

[a] The  symbol in the backbone chain denotes an aromatic ring as 

and polycarbonate—are relatively complex. Repeat units for a large number of relatively common polymers are given in Appendix D.

homopolymer

copolymer

When all of the repeating units along a chain are of the same type, the resulting polymer is called a **homopolymer.** Chains may be composed of two or more different repeat units, in what are termed **copolymers** (see Section 14.10).

bifunctional

functionality

trifunctional

The monomers discussed thus far have an active bond that may react to form two covalent bonds with other monomers forming a two-dimensional chainlike molecular structure, as indicated earlier for ethylene. Such a monomer is termed **bifunctional.** In general, the **functionality** is the number of bonds that a given monomer can form. For example, monomers such as phenol–formaldehyde (Table 14.3) are **trifunctional;** they have three active bonds, from which a three-dimensional molecular network structure results.

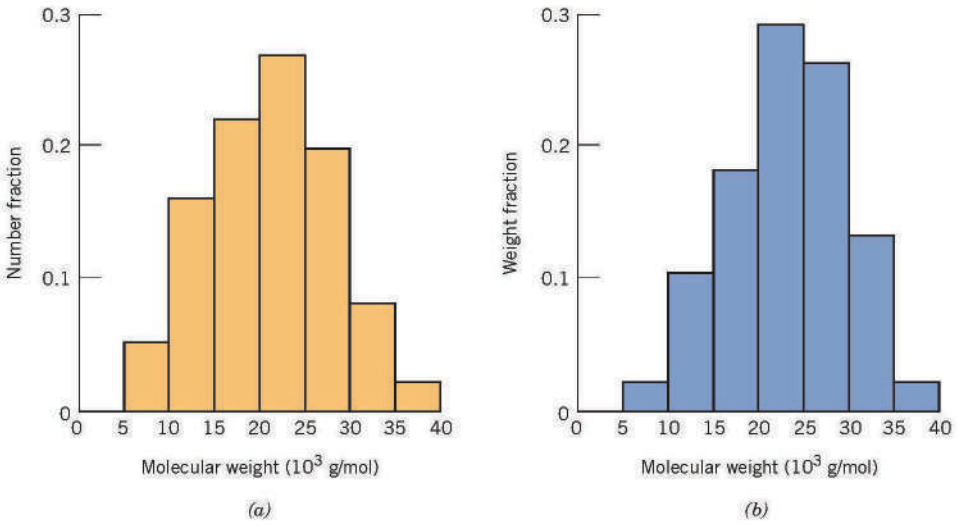


Figure 14.3 Hypothetical polymer molecule size distributions on the basis of (*a*) number and (*b*) weight fractions of molecules.

Concept Check 14.2

On the basis of the structures presented in the previous section, sketch the repeat unit structure for poly(vinyl fluoride).

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

14.5 MOLECULAR WEIGHT

Extremely large molecular weights[4] are observed in polymers with very long chains. During the polymerization process, not all polymer chains will grow to the same length; this results in a distribution of chain lengths or molecular weights. Ordinarily, an average molecular weight is specified, which may be determined by the measurement of various physical properties such as viscosity and osmotic pressure.

There are several ways of defining average molecular weight. The number-average molecular weight $\overline{M}_n$ is obtained by dividing the chains into a series of size ranges and then determining the number fraction of chains within each size range (Figure 14.3*a*). The number-average molecular weight is expressed as

Number-average molecular weight

$$\overline{M}_n = \Sigma x_i M_i \tag{14.5a}$$

where M_i represents the mean (middle) molecular weight of size range i, and x_i is the fraction of the total number of chains within the corresponding size range.

[4] *Molecular mass, molar mass,* and *relative molecular mass* are sometimes used and are really more appropriate terms than *molecular weight* in the context of the present discussion—in actual fact, we are dealing with masses and not weights. However, molecular weight is most commonly found in the polymer literature and thus will be used throughout this book.

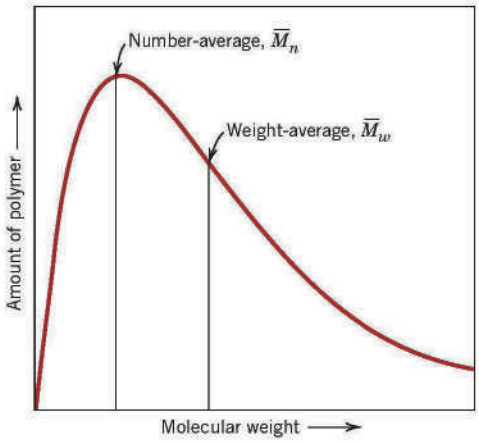


Figure 14.4 Distribution of molecular weights for a typical polymer.

A weight-average molecular weight $\overline{M}_w$ is based on the weight fraction of molecules within the various size ranges (Figure 14.3*b*). It is calculated according to

Weight-average molecular weight

$$\overline{M}_w = \Sigma w_i M_i \tag{14.5b}$$

where, again, M_i is the mean molecular weight within a size range, whereas w_i denotes the weight fraction of molecules within the same size interval. Computations for both number-average and weight-average molecular weights are carried out in Example Problem 14.1. A typical molecular weight distribution along with these molecular weight averages is shown in Figure 14.4.

degree of polymerization

An alternate way of expressing average chain size of a polymer is as the **degree of polymerization,** DP, which represents the average number of repeat units in a chain. DP is related to the number-average molecular weight $\overline{M}_n$ by the equation

Degree of polymerization—dependence on number-average and repeat unit molecular weights

$$DP = \frac{\overline{M}_n}{m} \tag{14.6}$$

where m is the repeat unit molecular weight.

EXAMPLE PROBLEM 14.1

Computations of Average Molecular Weights and Degree of Polymerization

Assume that the molecular weight distributions shown in Figure 14.3 are for poly(vinyl chloride). For this material, compute **(a)** the number-average molecular weight, **(b)** the degree of polymerization, and **(c)** the weight-average molecular weight.

Solution

(a) The data necessary for this computation, as taken from Figure 14.3*a*, are presented in Table 14.4a. According to Equation 14.5a, summation of all the $x_i M_i$ products (from the right-hand column) yields the number-average molecular weight, which in this case is 21,150 g/mol.

Table 14.4a **Data Used for Number-Average Molecular Weight Computations in Example Problem 14.1**

Molecular Weight Range (g/mol)	*Mean M_i (g/mol)*	x_i	x_iM_i
5,000–10,000	7,500	0.05	375
10,000–15,000	12,500	0.16	2000
15,000–20,000	17,500	0.22	3850
20,000–25,000	22,500	0.27	6075
25,000–30,000	27,500	0.20	5500
30,000–35,000	32,500	0.08	2600
35,000–40,000	37,500	0.02	750
			$\overline{M}_n = 21{,}150$

(b) To determine the degree of polymerization (Equation 14.6), it is first necessary to compute the repeat unit molecular weight. For PVC, each repeat unit consists of two carbon atoms, three hydrogen atoms, and a single chlorine atom (Table 14.3). Furthermore, the atomic weights of C, H, and Cl are, respectively, 12.01, 1.01, and 35.45 g/mol. Thus, for PVC

$$\begin{aligned} m &= 2(12.01\ \text{g/mol}) + 3(1.01\ \text{g/mol}) + 35.45\ \text{g/mol} \\ &= 62.50\ \text{g/mol} \end{aligned}$$

and

$$DP = \frac{\overline{M}_n}{m} = \frac{21{,}150\ \text{g/mol}}{62.50\ \text{g/mol}} = 338$$

(c) Table 14.4b shows the data for the weight-average molecular weight, as taken from Figure 14.3*b*. The w_iM_i products for the size intervals are tabulated in the right-hand column. The sum of these products (Equation 14.5b) yields a value of 23,200 g/mol for $\overline{M}_w$.

Table 14.4b **Data Used for Weight-Average Molecular Weight Computations in Example Problem 14.1**

Molecular Weight Range (g/mol)	*Mean M_i (g/mol)*	w_i	w_iM_i
5,000–10,000	7,500	0.02	150
10,000–15,000	12,500	0.10	1250
15,000–20,000	17,500	0.18	3150
20,000–25,000	22,500	0.29	6525
25,000–30,000	27,500	0.26	7150
30,000–35,000	32,500	0.13	4225
35,000–40,000	37,500	0.02	750
			$\overline{M}_w = 23{,}200$

Many polymer properties are affected by the length of the polymer chains. For example, the melting or softening temperature increases with increasing molecular weight (for $\overline{M}$ up to about 100,000 g/mol). At room temperature, polymers with very short chains (having molecular weights on the order of 100 g/mol) will generally exist as liquids. Those with molecular weights of approximately 1000 g/mol are waxy solids (such as paraffin wax) and soft resins. Solid polymers (sometimes termed *high polymers*), which are of prime interest here, commonly have molecular weights ranging between 10,000 and several million g/mol. Thus, the same polymer material can have quite different properties if it is produced with a different molecular weight. Other properties that depend on molecular weight include elastic modulus and strength (see Chapter 15).

14.6 MOLECULAR SHAPE

Previously, polymer molecules have been shown as linear chains, neglecting the zigzag arrangement of the backbone atoms (Figure 14.1*b*). Single chain bonds are capable of rotating and bending in three dimensions. Consider the chain atoms in Figure 14.5*a*; a third carbon atom may lie at any point on the cone of revolution and still subtend about a 109° angle with the bond between the other two atoms. A straight chain segment results when successive chain atoms are positioned as in Figure 14.5*b*. On the other hand, chain bending and twisting are possible when there is a rotation of the chain atoms into other positions, as illustrated in Figure 14.5*c*.[5] Thus, a single chain molecule composed of many chain atoms might assume a shape similar to that represented schematically in Figure 14.6, having a multitude of bends, twists, and kinks.[6] Also indicated in this figure is the end-to-end distance of the polymer chain r; this distance is much smaller than the total chain length.

Polymers consist of large numbers of molecular chains, each of which may bend, coil, and kink in the manner of Figure 14.6. This leads to extensive intertwining and entanglement of neighboring chain molecules, a situation similar to a heavily tangled

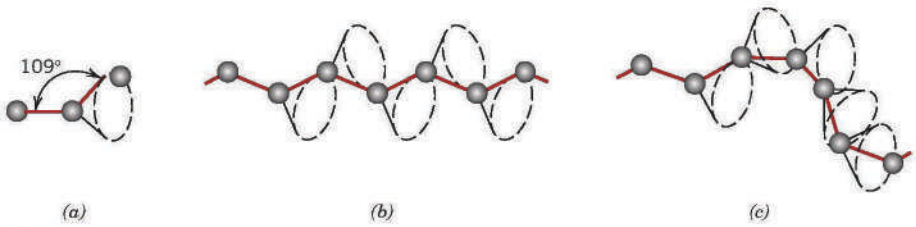


Figure 14.5 Schematic representations of how polymer chain shape is influenced by the positioning of backbone carbon atoms (gray circles). For (*a*), the rightmost atom may lie anywhere on the dashed circle and still subtend a 109° angle with the bond between the other two atoms. Straight and twisted chain segments are generated when the backbone atoms are situated as in (*b*) and (*c*), respectively. (From Askeland, *Science and Engineering of Materials*, 3E. © 1994 Cengage Learning, a part of Cengage Learning, Inc. Reproduced by permission. www.cengage.com/permissions)

[5] For some polymers, rotation of carbon backbone atoms within the cone may be hindered by bulky side group elements on neighboring chain atoms.

[6] The term *conformation* is often used in reference to the physical outline of a molecule, or molecular shape, that can be altered only by rotation of chain atoms about single bonds.

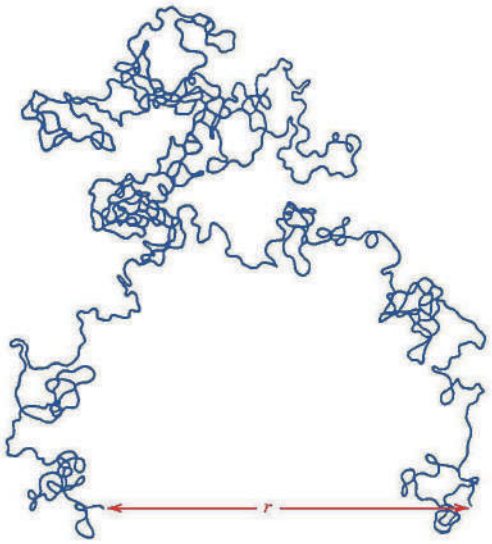


Figure 14.6 Schematic representation of a single polymer chain molecule that has numerous random kinks and coils produced by chain bond rotations. (From L. R. G. Treloar, *The Physics of Rubber Elasticity*, 2nd edition, Oxford University Press, Oxford, 1958, p. 47.)

fishing line. These random coils and molecular entanglements are responsible for a number of important characteristics of polymers, to include the large elastic extensions displayed by the rubber materials.

Some of the mechanical and thermal characteristics of polymers are a function of the ability of chain segments to experience rotation in response to applied stresses or thermal vibrations. Rotational flexibility is dependent on repeat unit structure and chemistry. For example, the region of a chain segment that has a double bond (C=C) is rotationally rigid. Also, introduction of a bulky or large side group of atoms restricts rotational movement. For example, polystyrene molecules, which have a phenyl side group (Table 14.3), are more resistant to rotational motion than are polyethylene chains.

14.7 MOLECULAR STRUCTURE

The physical characteristics of a polymer depend not only on its molecular weight and shape but also on differences in the structure of the molecular chains. Modern polymer synthesis techniques permit considerable control over various structural possibilities. This section discusses several molecular structures including linear, branched, crosslinked, and network, in addition to various isomeric configurations.

Linear Polymers

linear polymer

Linear polymers are those in which the repeat units are joined together end to end in single chains. These long chains are flexible and may be thought of as a mass of spaghetti, as represented schematically in Figure 14.7*a*, where each circle represents a repeat unit. For linear polymers, there may be extensive van der Waals and hydrogen bonding between the chains. Some of the common polymers that form with linear structures are polyethylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate), nylon, and the fluorocarbons.

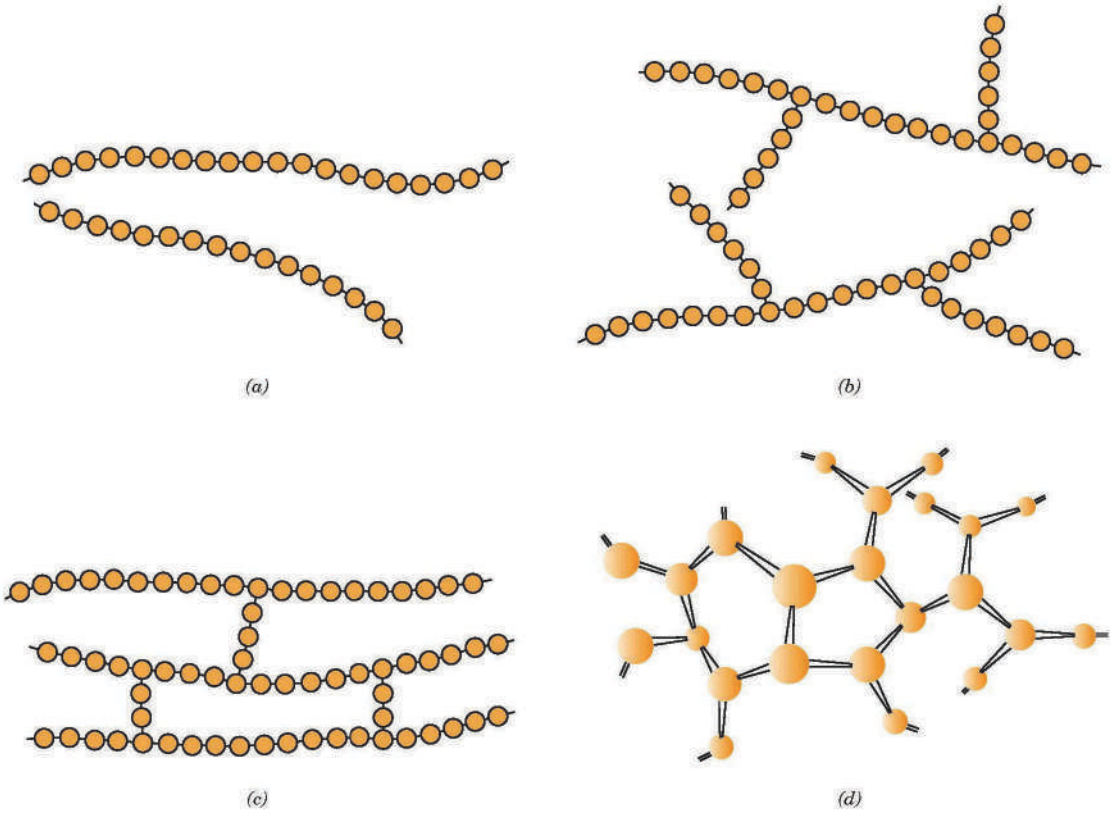


Figure 14.7 Schematic representations of (*a*) linear, (*b*) branched, (*c*) crosslinked, and (*d*) network (three-dimensional) molecular structures. Circles designate individual repeat units.

Branched Polymers

branched polymer

Polymers may be synthesized in which side-branch chains are connected to the main ones, as indicated schematically in Figure 14.7*b*; these are fittingly called **branched polymers.** The branches, considered to be part of the main-chain molecule, may result from side reactions that occur during the synthesis of the polymer. The chain packing efficiency is reduced with the formation of side branches, which results in a lowering of the polymer density. Polymers that form linear structures may also be branched. For example, high-density polyethylene (HDPE) is primarily a linear polymer, whereas low-density polyethylene (LDPE) contains short chain branches.

Crosslinked Polymers

crosslinked polymer

In **crosslinked polymers,** adjacent linear chains are joined one to another at various positions by covalent bonds, as represented in Figure 14.7*c*. The process of crosslinking is achieved either during synthesis or by a nonreversible chemical reaction. Often, this crosslinking is accomplished by additive atoms or molecules that are covalently bonded to the chains. Many of the rubber elastic materials are crosslinked; in rubbers, this is called vulcanization, a process described in Section 15.9.

Network Polymers

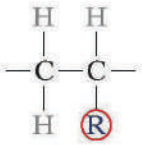
network polymer

Multifunctional monomers forming three or more active covalent bonds make three-dimensional networks (Figure 14.7*d*) and are termed **network polymers.** Actually, a polymer that is highly crosslinked may also be classified as a network polymer. These materials have distinctive mechanical and thermal properties; the epoxies, polyurethanes, and phenol-formaldehyde belong to this group.

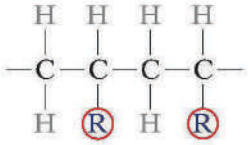
Polymers are not usually of only one distinctive structural type. For example, a predominantly linear polymer may have limited branching and crosslinking.

14.8 MOLECULAR CONFIGURATIONS

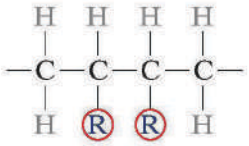
For polymers having more than one side atom or group of atoms bonded to the main chain, the regularity and symmetry of the side group arrangement can significantly influence the properties. Consider the repeat unit



in which R represents an atom or side group other than hydrogen (e.g., Cl, CH_3). One arrangement is possible when the R side groups of successive repeat units are bound to alternate carbon atoms as follows:



This is designated as a head-to-tail configuration.[7] Its complement, the head-to-head configuration, occurs when R groups are bound to adjacent chain atoms:



In most polymers, the head-to-tail configuration predominates; often a polar repulsion occurs between R groups for the head-to-head configuration.

Isomerism (Section 14.2) is also found in polymer molecules, wherein different atomic configurations are possible for the same composition. Two isomeric subclasses, stereoisomerism and geometrical isomerism, are topics of discussion in the succeeding sections.

[7] The term *configuration* is used in reference to arrangements of units along the axis of the chain, or atom positions that are not alterable except by the breaking and then re-forming of primary bonds.

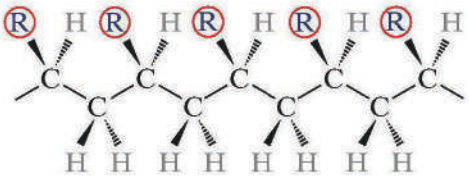
Stereoisomerism

stereoisomerism

Stereoisomerism denotes the situation in which atoms are linked together in the same order (head-to-tail) but differ in their spatial arrangement. For one stereoisomer, all of the R groups are situated on the same side of the chain as follows:

VMSE

Stereo and Geometrical Isomers



isotactic configuration

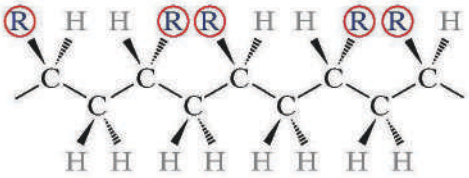
This is called an **isotactic configuration.** This diagram shows the zigzag pattern of the carbon chain atoms. Furthermore, representation of the structural geometry in three dimensions is important, as indicated by the wedge-shaped bonds; solid wedges represent bonds that project out of the plane of the page, and dashed ones represent bonds that project into the page.[8]

syndiotactic configuration

In a **syndiotactic configuration,** the R groups alternate sides of the chain:[9]

VMSE

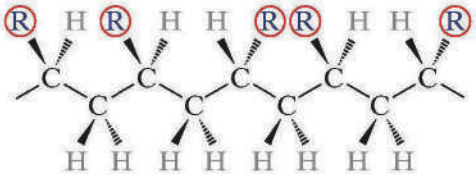
Stereo and Geometrical Isomers



and for random positioning.

VMSE

Stereo and Geometrical Isomers

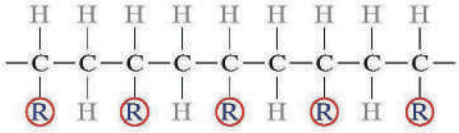


atactic configuration

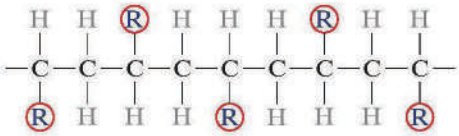
the term **atactic configuration** is used.[10]

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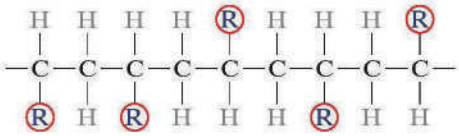
[8] The isotactic configuration is sometimes represented using the following linear (i.e., nonzigzag) and two-dimensional schematic:



[9] The linear and two-dimensional schematic for syndiotactic is represented as



[10] For atactic the linear and two-dimensional schematic is



Conversion from one stereoisomer to another (e.g., isotactic to syndiotactic) is not possible by a simple rotation about single chain bonds; these bonds must first be severed, and then, after the appropriate rotation, they are re-formed.

In reality, a specific polymer does not exhibit just one of these configurations; the predominant form depends on the method of synthesis.

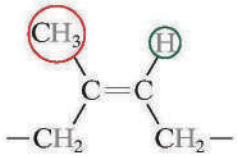
Geometrical Isomerism

Other important chain configurations, or geometrical isomers, are possible within repeat units having a double bond between chain carbon atoms. Bonded to each of the carbon atoms participating in the double bond is a side group, which may be situated on one side of the chain or its opposite. Consider the isoprene repeat unit having the structure

VMSE



Stereo and Geometrical Isomers



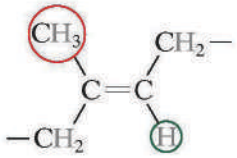
in which the CH_3 group and the H atom are positioned on the same side of the double bond. This is termed a **cis** structure, and the resulting polymer, *cis*-polyisoprene, is natural rubber. For the alternative isomer

cis (structure)

VMSE



Stereo and Geometrical Isomers



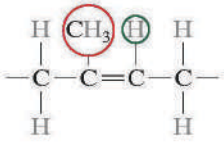
the **trans** structure, the CH_3 and H reside on opposite sides of the double bond.[11] *Trans*-polyisoprene, sometimes called gutta percha, has properties that are distinctly different from natural rubber as a result of this configurational alteration. Conversion of trans to cis, or vice versa, is not possible by a simple chain bond rotation because the chain double bond is extremely rigid.

trans (structure)

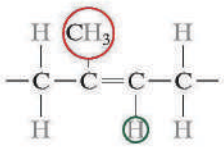
Summarizing the preceding sections, polymer molecules may be characterized in terms of their size, shape, and structure. Molecular size is specified in terms of molecular weight (or degree of polymerization). Molecular shape relates to the degree of chain twisting, coiling, and bending. Molecular structure depends on the manner in which structural units are joined together. Linear, branched, crosslinked,

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[11] For *cis*-isoprene the linear chain representation is as follows:



whereas the linear schematic for the trans structure is



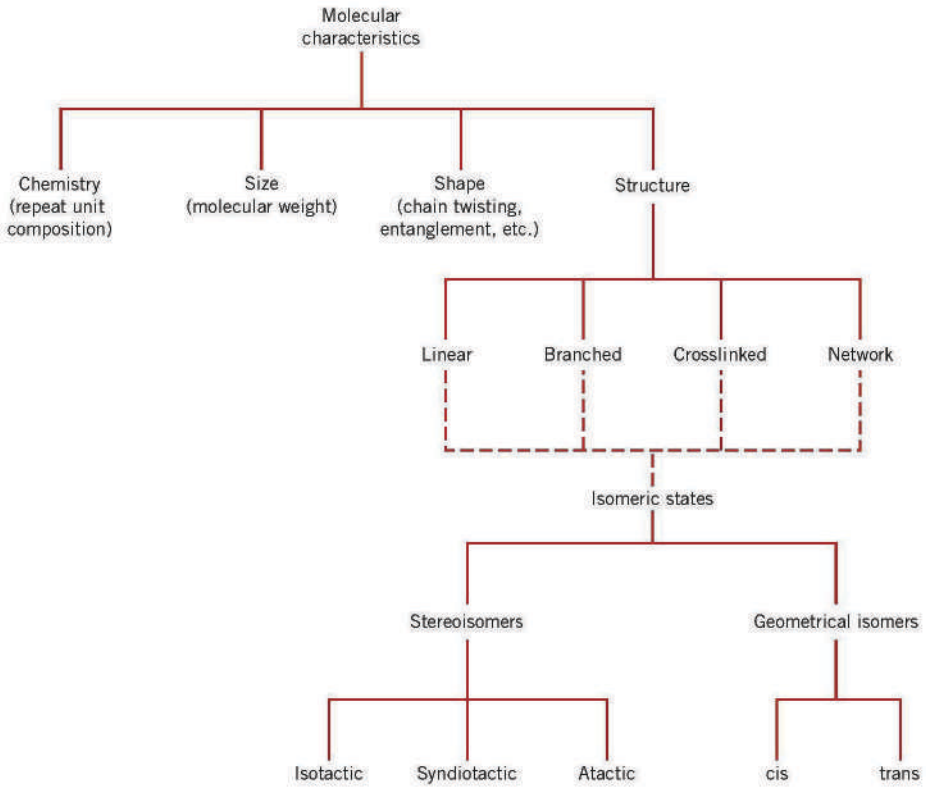


Figure 14.8 Classification scheme for the characteristics of polymer molecules.

and network structures are all possible, in addition to several isomeric configurations (isotactic, syndiotactic, atactic, cis, and trans). These molecular characteristics are presented in the taxonomic chart shown in Figure 14.8. Note that some of the structural elements are not mutually exclusive, and it may be necessary to specify molecular structure in terms of more than one. For example, a linear polymer may also be isotactic.

Concept Check 14.3

What is the difference between *configuration* and *conformation* in relation to polymer chains?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

14.9 THERMOPLASTIC AND THERMOSETTING POLYMERS

thermoplastic polymer

thermosetting polymer

The response of a polymer to mechanical forces at elevated temperatures is related to its dominant molecular structure. In fact, one classification scheme for these materials is according to behavior with rising temperature. *Thermoplastics* (or **thermoplastic polymers**) and *thermosets* (or **thermosetting polymers**) are the two subdivisions. Thermoplastics soften when heated (and eventually liquefy) and harden when cooled—processes that are totally reversible and may be repeated. On a molecular level, as the temperature is raised, secondary bonding forces are diminished (by increased molecular motion) so that the relative movement of

adjacent chains is facilitated when a stress is applied. Irreversible degradation results when a molten thermoplastic polymer is raised to too high a temperature. In addition, thermoplastics are relatively soft. Most linear polymers and those having some branched structures with flexible chains are thermoplastic. These materials are normally fabricated by the simultaneous application of heat and pressure (see Section 15.22). Examples of common thermoplastic polymers include polyethylene, polystyrene, poly(ethylene terephthalate), and poly(vinyl chloride).

Thermosetting polymers are network polymers. They become permanently hard during their formation and do not soften upon heating. Network polymers have covalent crosslinks between adjacent molecular chains. During heat treatments, these bonds anchor the chains together to resist the vibrational and rotational chain motions at high temperatures. Thus, the materials do not soften when heated. Crosslinking is usually extensive, in that 10 to 50% of the chain repeat units are crosslinked. Only heating to excessive temperatures will cause severance of these crosslink bonds and polymer degradation. Thermoset polymers are generally harder and stronger than thermoplastics and have better dimensional stability. Most of the crosslinked and network polymers, which include vulcanized rubbers, epoxies, and phenolics and some polyester resins, are thermosetting.

Concept Check 14.4

Some polymers (such as the polyesters) may be either thermoplastic or thermosetting. Suggest one reason for this.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

14.10 COPOLYMERS

Polymer chemists and scientists are continually searching for new materials that can be easily and economically synthesized and fabricated, with improved properties or better property combinations than are offered by the homopolymers previously discussed. One group of these materials are the copolymers.

Consider a copolymer that is composed of two repeat units as represented by ● and ● in Figure 14.9. Depending on the polymerization process and the relative fractions of these repeat unit types, different sequencing arrangements along the polymer chains are possible. For one, as depicted in Figure 14.9*a*, the two different units are randomly dispersed along the chain in what is termed a **random copolymer.** For an **alternating copolymer,** as the name suggests, the two repeat units alternate chain positions, as illustrated in Figure 14.9*b*. A **block copolymer** is one in which identical repeat units are clustered in blocks along the chain (Figure 14.9*c*). Finally, homopolymer side branches of one type may be grafted to homopolymer main chains that are composed of a different repeat unit; such a material is termed a **graft copolymer** (Figure 14.9*d*).

random copolymer

alternating copolymer

block copolymer

graft copolymer

When calculating the degree of polymerization for a copolymer, the value m in Equation 14.7 is replaced with the average value $\overline{m}$ that is determined from

Average repeat unit molecular weight for a copolymer

$$\overline{m} = \Sigma f_j m_j \tag{14.7}$$

In this expression, f_j and m_j are, respectively, the mole fraction and molecular weight of repeat unit j in the polymer chain.

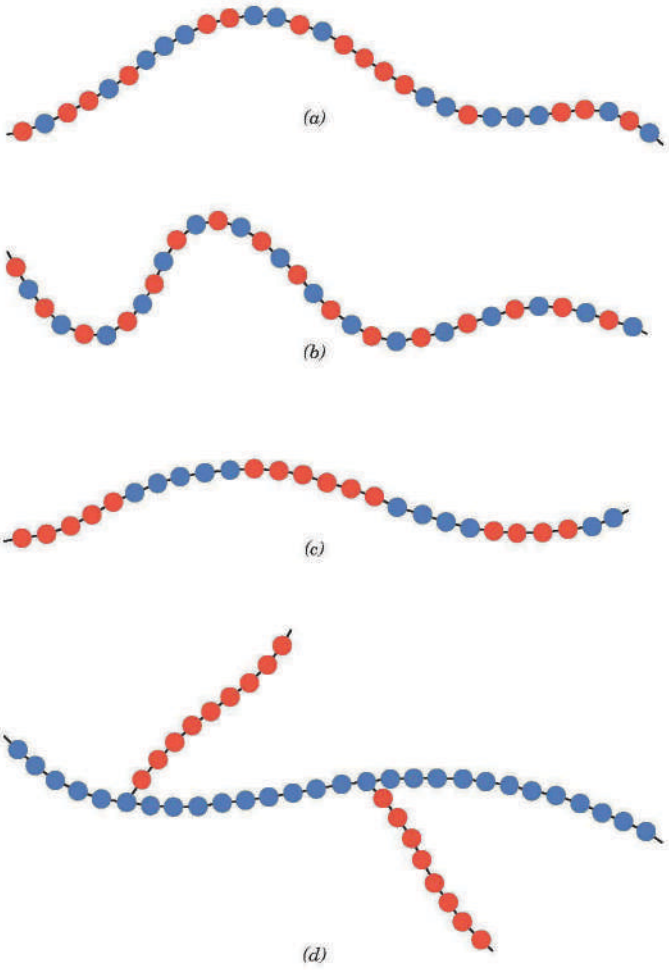


Figure 14.9 Schematic representations of (*a*) random, (*b*) alternating, (*c*) block, and (*d*) graft copolymers. The two different repeat unit types are designated by blue and red circles.

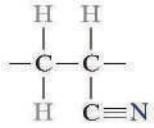
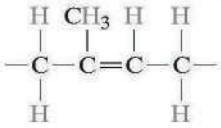
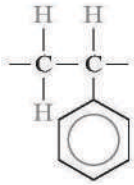
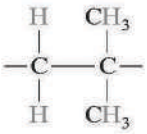
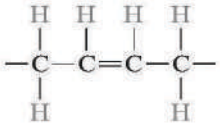
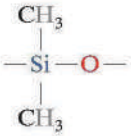
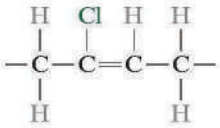
Synthetic rubbers, discussed in Section 15.16, are often copolymers; chemical repeat units that are employed in some of these rubbers are shown in Table 14.5. Styrene–butadiene rubber (SBR) is a common random copolymer from which automobile tires are made. Nitrile rubber (NBR) is another random copolymer composed of acrylonitrile and butadiene. It is also highly elastic and, in addition, resistant to swelling in organic solvents; gasoline hoses are made of NBR. Impact-modified polystyrene is a block copolymer that consists of alternating blocks of styrene and butadiene. The rubbery isoprene blocks act to slow cracks propagating through the material.

14.11 POLYMER CRYSTALLINITY

polymer crystallinity

The crystalline state may exist in polymeric materials. However, because it involves molecules instead of just atoms or ions, as with metals and ceramics, the atomic arrangements will be more complex for polymers. We think of **polymer crystallinity** as the packing of molecular chains to produce an ordered atomic array. Crystal structures may be specified in terms of unit cells, which are often quite complex. For example, Figure 14.10 shows the unit cell for polyethylene and its relationship to the molecular chain structure; this unit cell has orthorhombic geometry (Table 3.2). Of course, the chain molecules also extend beyond the unit cell shown in the figure.

Table 14.5 Chemical Repeat Units That Are Employed in Copolymer Rubbers

Repeat Unit Name	Repeat Unit Structure	Repeat Unit Name	Repeat Unit Structure
VMSE Acrylonitrile		VMSE Isoprene	
Repeat Units for Rubbers			
VMSE Styrene		VMSE Isobutylene	
VMSE Butadiene		VMSE Dimethylsiloxane	
VMSE Chloroprene			

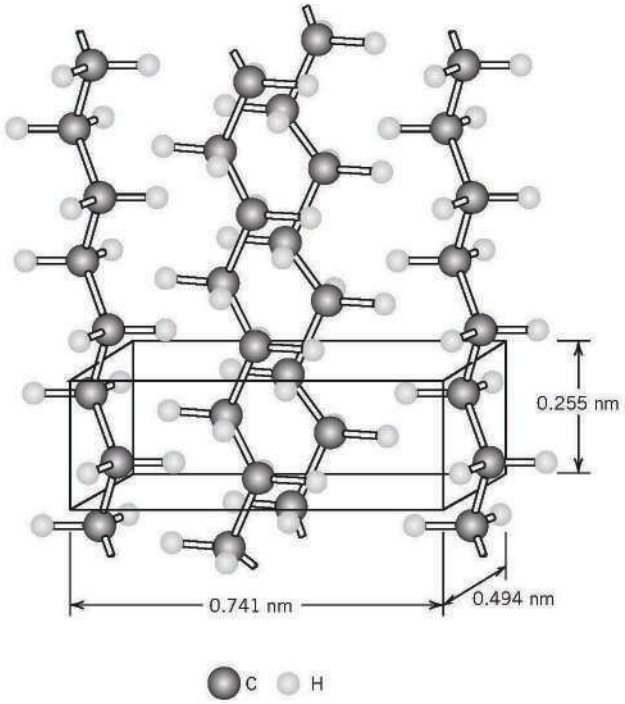


Figure 14.10 Arrangement of molecular chains in a unit cell for polyethylene. (Adapted from C. W. Bunn, *Chemical Crystallography*, Oxford University Press, Oxford, 1945, p. 233.)

Molecular substances having small molecules (e.g., water and methane) are normally either totally crystalline (as solids) or totally amorphous (as liquids). As a consequence of their size and often complexity, polymer molecules are often only partially crystalline (or semicrystalline), having crystalline regions dispersed within the remaining amorphous material. Any chain disorder or misalignment will result in an amorphous region, a condition that is fairly common, because twisting, kinking, and coiling of the chains prevent the strict ordering of every segment of every chain. Other structural effects are also influential in determining the extent of crystallinity, as discussed shortly.

The degree of crystallinity may range from completely amorphous to almost entirely (up to about 95%) crystalline; in contrast, metal specimens are almost always entirely crystalline, whereas many ceramics are either totally crystalline or totally noncrystalline. Semicrystalline polymers are, in a sense, analogous to two-phase metal alloys, discussed previously.

The density of a crystalline polymer will be greater than an amorphous one of the same material and molecular weight, because the chains are more closely packed together for the crystalline structure. The degree of crystallinity by weight may be determined from accurate density measurements, according to

Percent crystallinity (semicrystalline polymer)—dependence on specimen density, and densities of totally crystalline and totally amorphous materials

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \tag{14.8}$$

where ρ_s is the density of a specimen for which the percent crystallinity is to be determined, ρ_a is the density of the totally amorphous polymer, and ρ_c is the density of the perfectly crystalline polymer. The values of ρ_a and ρ_c must be measured by other experimental means.

The degree of crystallinity of a polymer depends on the rate of cooling during solidification as well as on the chain configuration. During crystallization upon cooling through the melting temperature, the chains, which are highly random and entangled in the viscous liquid, must assume an ordered configuration. For this to occur, sufficient time must be allowed for the chains to move and align themselves.

The molecular chemistry as well as chain configuration also influence the ability of a polymer to crystallize. Crystallization is not favored in polymers that are composed of chemically complex repeat units (e.g., polyisoprene). On the other hand, crystallization is not easily prevented in chemically simple polymers such as polyethylene and polytetrafluoroethylene, even for very rapid cooling rates.

For linear polymers, crystallization is easily accomplished because there are few restrictions to prevent chain alignment. Any side branches interfere with crystallization, such that branched polymers never are highly crystalline; in fact, excessive branching may prevent any crystallization whatsoever. Most network and crosslinked polymers are almost totally amorphous because the crosslinks prevent the polymer chains from rearranging and aligning into a crystalline structure. A few crosslinked polymers are partially crystalline. With regard to the stereoisomers, atactic polymers are difficult to crystallize; however, isotactic and syndiotactic polymers crystallize much more easily because the regularity of the geometry of the side groups facilitates the process of fitting together adjacent chains. Also, the bulkier or larger the side-bonded groups of atoms, the less tendency for crystallization.

For copolymers, as a general rule, the more irregular and random the repeat unit arrangements, the greater the tendency for the development of noncrystallinity. For alternating and block copolymers there is some likelihood of crystallization. On the other hand, random and graft copolymers are normally amorphous.

To some extent, the physical properties of polymeric materials are influenced by the degree of crystallinity. Crystalline polymers are usually stronger and more resistant to dissolution and softening by heat. Some of these properties are discussed in subsequent chapters.

Concept Check 14.5

(a) Compare the crystalline state in metals and polymers. **(b)** Compare the noncrystalline state as it applies to polymers and ceramic glasses.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

EXAMPLE PROBLEM 14.2

Computations of the Density and Percent Crystallinity of Polyethylene

(a) Compute the density of totally crystalline polyethylene. The orthorhombic unit cell for polyethylene is shown in Figure 14.10; also, the equivalent of two ethylene repeat units is contained within each unit cell.

(b) Using the answer to part (a), calculate the percent crystallinity of a branched polyethylene that has a density of 0.925 g/cm^3. The density for the totally amorphous material is 0.870 g/cm^3.

Solution

(a) Equation 3.5, used in Chapter 3 to determine densities for metals, also applies to polymeric materials and is used to solve this problem. It takes the same form—

$$\rho = \frac{nA}{V_C N_A}$$

where n represents the number of repeat units within the unit cell (for polyethylene $n = 2$), and A is the repeat unit molecular weight, which for polyethylene is

$$\begin{aligned} A &= 2(A_C) + 4(A_H) \\ &= (2)(12.01\ \text{g/mol}) + (4)(1.008\ \text{g/mol}) = 28.05\ \text{g/mol} \end{aligned}$$

Also, V_C is the unit cell volume, which is just the product of the three unit cell edge lengths in Figure 14.10; or

$$\begin{aligned} V_C &= (0.741\ \text{nm})(0.494\ \text{nm})(0.255\ \text{nm}) \\ &= (7.41 \times 10^{-8}\ \text{cm})(4.94 \times 10^{-8}\ \text{cm})(2.55 \times 10^{-8}\ \text{cm}) \\ &= 9.33 \times 10^{-23}\ \text{cm}^3/\text{unit cell} \end{aligned}$$

Now, substitution into Equation 3.5 of this value, values for n and A cited previously, and the value of N_A, leads to

$$\rho = \frac{nA}{V_C N_A}$$

$$= \frac{(2 \text{ repeat units/unit cell})(28.05 \text{ g/mol})}{(9.33 \times 10^{-23} \text{ cm}^3\text{/unit cell})(6.022 \times 10^{23} \text{ repeat units/mol})}$$

$$= 0.998 \text{ g/cm}^3$$

(b) We now use Equation 14.8 to calculate the percent crystallinity of the branched polyethylene with $\rho_c = 0.998$ g/cm^3, $\rho_a = 0.870$ g/cm^3, and $\rho_s = 0.925$ g/cm^3. Thus,

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

$$= \frac{0.998 \text{ g/cm}^3\,(0.925 \text{ g/cm}^3 - 0.870 \text{ g/cm}^3)}{0.925 \text{ g/cm}^3\,(0.998 \text{ g/cm}^3 - 0.870 \text{ g/cm}^3)} \times 100$$

$$= 46.4\%$$

14.12 POLYMER CRYSTALS

crystallite

It has been proposed that a semicrystalline polymer consists of small crystalline regions (**crystallites**), each having a precise alignment, which are interspersed with amorphous regions composed of randomly oriented molecules. The structure of the crystalline regions may be deduced by examination of polymer single crystals, which may be grown from dilute solutions. These crystals are regularly shaped, thin platelets (or lamellae), approximately 10 to 20 nm thick, and on the order of 10 μm long. Frequently, these platelets will form a multilayered structure, like that shown in the electron micrograph of a single crystal of polyethylene in Figure 14.11. The molecular chains within each platelet fold back and forth on themselves, with folds occurring at the faces; this structure, aptly termed the **chain-folded model**, is

chain-folded model

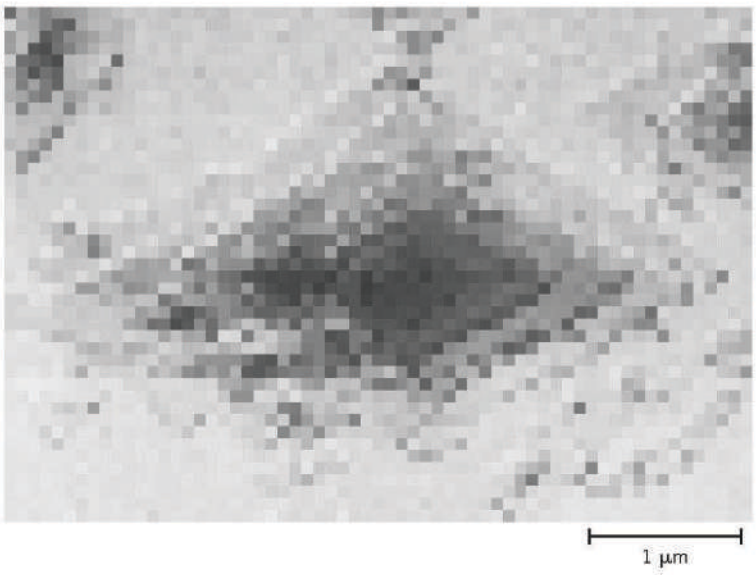


Figure 14.11 Electron micrograph of a polyethylene single crystal. 20,000×. [From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Editors), *Growth and Perfection of Crystals*. General Electric Company and John Wiley & Sons, Inc., 1958, p. 498.]

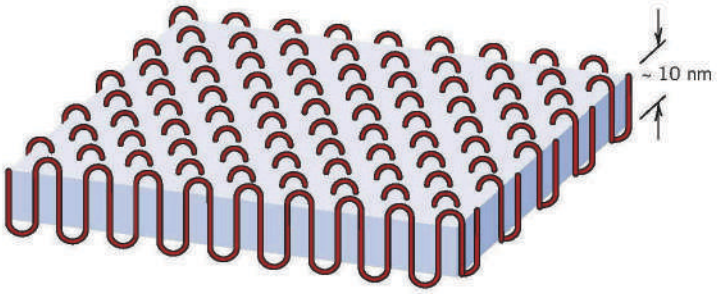


Figure 14.12 The chain-folded structure for a plate-shaped polymer crystallite.

illustrated schematically in Figure 14.12. Each platelet will consist of a number of molecules; however, the average chain length will be much greater than the thickness of the platelet.

spherulite

Many bulk polymers that are crystallized from a melt are semicrystalline and form a **spherulite** structure. As implied by the name, each spherulite may grow to be roughly spherical in shape; one of them, as found in natural rubber, is shown in the transmission electron micrograph in the (*d*) chapter-opening photograph for this chapter. The spherulite consists of an aggregate of ribbonlike chain-folded crystallites (lamellae) approximately 10 nm thick that radiate outward from a single nucleation site in the center. In this electron micrograph, these lamellae appear as thin white lines. The detailed structure of a spherulite is illustrated schematically in Figure 14.13. Shown here are the individual chain-folded lamellar crystals that are

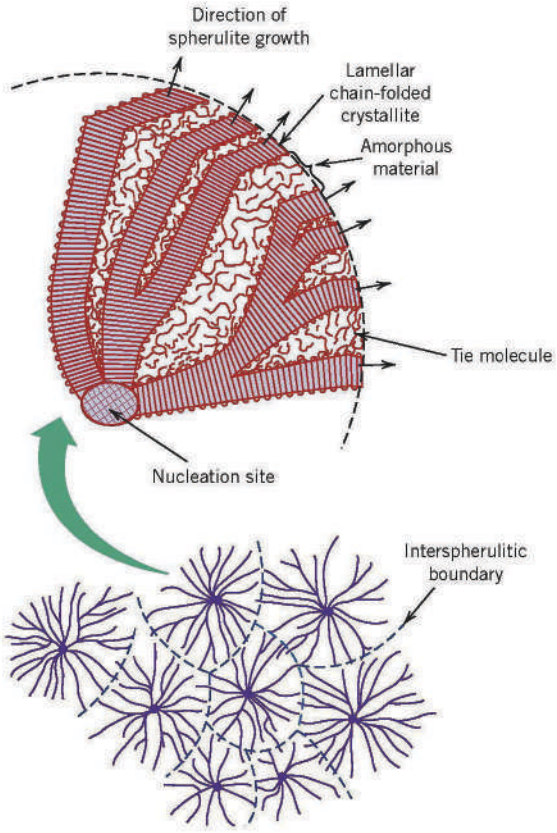


Figure 14.13 Schematic representation of the detailed structure of a spherulite.

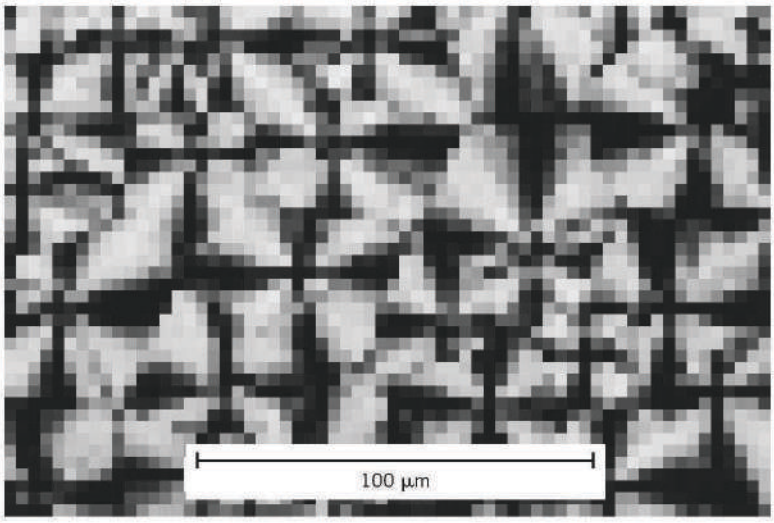


Figure 14.14 A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of polyethylene. Linear boundaries form between adjacent spherulites, and within each spherulite appears a Maltese cross. 525×. (Courtesy F. P. Price, General Electric Company.)

separated by amorphous material. Tie-chain molecules that act as connecting links between adjacent lamellae pass through these amorphous regions.

As the crystallization of a spherulitic structure nears completion, the extremities of adjacent spherulites begin to impinge on one another, forming more or less planar boundaries; prior to this time, they maintain their spherical shape. These boundaries are evident in Figure 14.14, which is a photomicrograph of polyethylene using cross-polarized light. A characteristic Maltese cross pattern appears within each spherulite. The bands or rings in the spherulite image result from twisting of the lamellar crystals as they extend like ribbons from the center.

Spherulites are considered to be the polymer analogue of grains in polycrystalline metals and ceramics. However, as discussed earlier, each spherulite is really composed of many different lamellar crystals and, in addition, some amorphous material. Polyethylene, polypropylene, poly(vinyl chloride), polytetrafluoroethylene, and nylon form a spherulitic structure when they crystallize from a melt.

14.13 DEFECTS IN POLYMERS

The point defect concept is different in polymers than in metals (Section 4.2) and ceramics (Section 12.5) as a consequence of the chainlike macromolecules and the nature of the crystalline state for polymers. Point defects similar to those found in metals have been observed in crystalline regions of polymeric materials; these include vacancies and interstitial atoms and ions. Chain ends are considered defects because they are chemically dissimilar to normal chain units. Vacancies are also associated with the chain ends (Figure 14.15). However, additional defects can result from branches in the polymer chain or chain segments that emerge from the crystal. A chain section can leave a polymer crystal and reenter it at another point, creating a loop, or can enter a second crystal to act as a tie molecule (see Figure 14.13). Screw dislocations also occur in polymer crystals (Figure 14.15). Impurity atoms/ions or groups of atoms/ions may be incorporated in the molecular structure as interstitials; they may also be associated with main chains or as short side branches.

Furthermore, the surfaces of chain-folded layers (Figure 14.13) are considered interfacial defects, as are also boundaries between two adjacent crystalline regions.

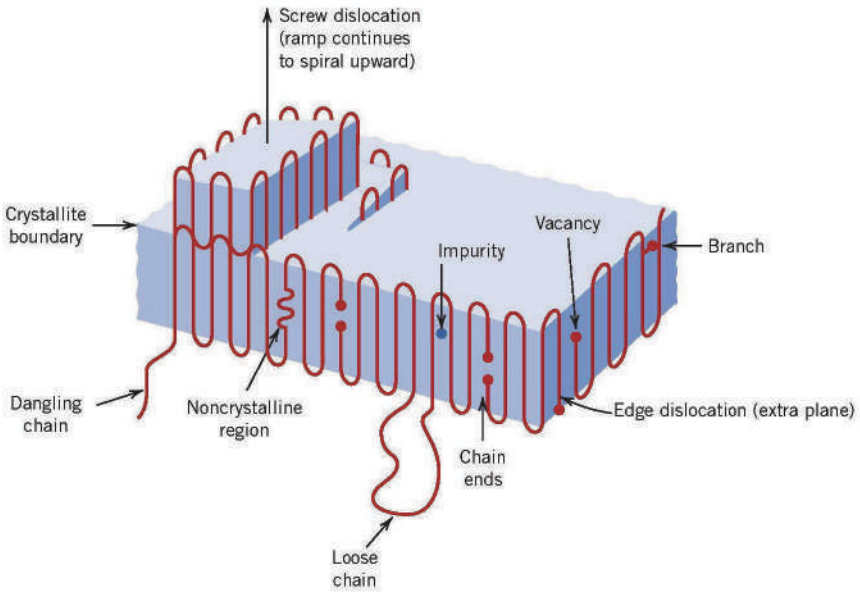


Figure 14.15 Schematic representation of defects in polymer crystallites.

14.14 DIFFUSION IN POLYMERIC MATERIALS

For polymeric materials, our interest is often in the diffusive motion of small foreign molecules (e.g., O_2, H_2O, CO_2, CH_4) between the molecular chains, rather than in the diffusive motion of chain atoms within the polymer structure. A polymer's permeability and absorption characteristics relate to the degree to which foreign substances diffuse into the material. Penetration of these foreign substances can lead to swelling and/or chemical reactions with the polymer molecules, and often a degradation of the material's mechanical and physical properties (Section 17.11).

Rates of diffusion are greater through amorphous regions than through crystalline regions; the structure of amorphous material is more "open." This diffusion mechanism may be considered analogous to interstitial diffusion in metals—that is, in polymers, diffusive movements occur through small voids between polymer chains from one open amorphous region to an adjacent open one.

Foreign molecule size also affects the diffusion rate: smaller molecules diffuse faster than larger ones. Furthermore, diffusion is more rapid for foreign molecules that are chemically inert than for those that interact with the polymer.

One step in diffusion through a polymer membrane is the dissolution of the molecular species in the membrane material. This dissolution is a time-dependent process, and, if slower than the diffusive motion, may limit the overall rate of diffusion. Consequently, the diffusion properties of polymers are often characterized in terms of a *permeability coefficient* (denoted by P_M), where for the case of steady-state diffusion through a polymer membrane, Fick's first law (Equation 5.3), is modified as

$$J = P_M \frac{\Delta P}{\Delta x} \tag{14.9}$$

In this expression, J is the diffusion flux of gas through the membrane [$(cm^3$ STP$)/(cm^2 \cdot s)$], P_M is the permeability coefficient, Δx is the membrane thickness, and ΔP is the difference in pressure of the gas across the membrane. For small molecules in nonglassy polymers the permeability coefficient can be approximated as

Table 14.6 Permeability Coefficients P_M at 25°C for Oxygen, Nitrogen, Carbon Dioxide, and Water Vapor in a Variety of Polymers

		P_M [$\times 10^{-13}$ (cm^3 STP)(cm)/($cm^2 \cdot s \cdot Pa$)]			
Polymer	*Acronym*	O_2	N_2	CO_2	H_2O
Polyethylene (low density)	LDPE	2.2	0.73	9.5	68
Polyethylene (high density)	HDPE	0.30	0.11	0.27	9.0
Polypropylene	PP	1.2	0.22	5.4	38
Poly(vinyl chloride)	PVC	0.034	0.0089	0.012	206
Polystyrene	PS	2.0	0.59	7.9	840
poly(vinylidene chloride)	PVDC	0.0025	0.00044	0.015	7.0
Poly(ethylene terephthalate)	PET	0.044	0.011	0.23	—
Poly(ethyl methacrylate)	PEMA	0.89	0.17	3.8	2380

Source: Adapted from J. Brandrup, E. H. Immergut, E. A. Grulke, A. Abe, and D. R. Bloch (Editors), *Polymer Handbook,* 4th edition. Copyright © 1999 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

the product of the diffusion coefficient (D) and solubility of the diffusing species in the polymer (S)—that is,

$$P_M = DS \tag{14.10}$$

Table 14.6 presents the permeability coefficients of oxygen, nitrogen, carbon dioxide, and water vapor in several common polymers.[12]

For some applications, low permeability rates through polymeric materials are desirable, as with food and beverage packaging and automobile tires and inner tubes. Polymer membranes are often used as filters, to selectively separate one chemical species from another (or others) (i.e., the desalination of water). In such instances it is normally the case that the permeation rate of the substance to be filtered is significantly greater than for the other substance(s).

EXAMPLE PROBLEM 14.3

Computations of Diffusion Flux of Carbon Dioxide through a Plastic Beverage Container and Beverage Shelf Life

The clear plastic bottles used for carbonated beverages (sometimes also called "soda," "pop," or "soda pop") are made from poly(ethylene terephthalate) (PET). The "fizz" in pop results from dissolved carbon dioxide (CO_2); because

[12] The units for permeability coefficients in Table 14.6 are unusual, which are explained as follows: When the diffusing molecular species is in the gas phase, solubility is equal to

$$S = \frac{C}{P}$$

where C is the concentration of the diffusing species in the polymer [in units of (cm^3 STP)/cm^3 gas] and P is the partial pressure (in units of Pa). STP indicates that this is the volume of gas at standard temperature and pressure [273 K (0°C) and 101.3 kPa (1 atm)]. Thus, the units for S are (cm^3 STP)/Pa·cm^3. Because D is expressed in terms of cm^2/s, the units for the permeability coefficient are (cm^3 STP)(cm)/(cm^2·s·Pa).

PET is permeable to CO_2, pop stored in PET bottles will eventually go "flat" (i.e., lose its fizz). A 20-oz. bottle of pop has a CO_2 pressure of about 400 kPa inside the bottle, and the CO_2 pressure outside the bottle is 0.4 kPa.

(a) Assuming conditions of steady state, calculate the diffusion flux of CO_2 through the wall of the bottle.

(b) If the bottle must lose 750 (cm^3 STP) of CO_2 before the pop tastes flat, what is the shelf life for a bottle of pop?
Note: assume that each bottle has a surface area of 500 cm^2 and a wall thickness of 0.05 cm.

Solution

(a) This is a permeability problem in which Equation 14.9 is employed. The permeability coefficient of CO_2 through PET (Table 14.6) is 0.23×10^{-13} (cm^3 STP)(cm)/(cm^2·s·Pa). Thus, the diffusion flux is equal to

$$J = -P_M \frac{\Delta P}{\Delta x} = -P_M \frac{P_2 - P_1}{\Delta x}$$

$$= -0.23 \times 10^{-13} \frac{(\text{cm}^3\ \text{STP})(\text{cm})}{(\text{cm}^2)(\text{s})(\text{Pa})} \frac{(400\ \text{Pa} - 400{,}000\ \text{Pa})}{0.05\ \text{cm}}$$

$$= 1.8 \times 10^{-7}\ (\text{cm}^3\ \text{STP})/(\text{cm}^2 \cdot \text{s})$$

(b) The flow rate of CO_2 through the wall of the bottle $\dot{V}_{CO_2}$ is equal to

$$\dot{V}_{CO_2} = JA$$

where A is the surface area of the bottle (i.e., 500 cm^2); therefore,

$$\dot{V}_{CO_2} = [1.8 \times 10^{-7}\ (\text{cm}^3\ \text{STP})/(\text{cm}^2 \cdot \text{s})]\ (500\ \text{cm}^2) = 9.0 \times 10^{-5}\ (\text{cm}^3\ \text{STP})/\text{s}$$

The time it will take for a volume (V) of 750 (cm^3 STP) to escape is calculated as

$$\text{time} = \frac{V}{\dot{V}_{CO_2}} = \frac{750\ (\text{cm}^3\ \text{STP})}{9.0 \times 10^{-5}\ (\text{cm}^3\ \text{STP})/\text{s}} = 8.3 \times 10^6\ \text{s}$$

$$= 97\ \text{days (or about 3 months)}$$

SUMMARY

Polymer Molecules

- Most polymeric materials are composed of very large molecular chains with side groups of various atoms (O, Cl, etc.) or organic groups such as methyl, ethyl, or phenyl groups.
- These macromolecules are composed of repeat units, smaller structural entities, which are repeated along the chain.

The Chemistry of Polymer Molecules

- Repeat units for some of the chemically simple polymers [polyethylene, polytetrafluoroethylene, poly(vinyl chloride), polypropylene, etc.] are presented in Table 14.3.
- A homopolymer is one for which all of the repeat units are the same type. The chains for copolymers are composed of two or more kinds of repeat units.

- Repeat units are classified according to the number of active bonds (i.e., functionality):
  - For bifunctional, a two-dimensional chainlike structure results from a monomer that has two active bonds.
  - Trifunctional monomers have three active bonds, from which three-dimensional network structures form.

Molecular Weight

- Molecular weights for high polymers may be in excess of a million. Because all molecules are not of the same size, there is a distribution of molecular weights.
- Molecular weight is often expressed in terms of number and weight averages; values for these parameters may be determined using Equations 14.5a and 14.5b, respectively.
- Chain length may also be specified by degree of polymerization, the number of repeat units per average molecule (Equation 14.6).

Molecular Shape

- Molecular entanglements occur when the chains assume twisted, coiled, and kinked shapes or contours as a consequence of chain bond rotations.
- Rotational flexibility is diminished when double chain bonds are present, and also when bulky side groups are part of the repeat unit.

Molecular Structure

- Four different polymer molecular chain structures are possible: linear (Figure 14.7*a*), branched (Figure 14.7*b*), crosslinked (Figure 14.7*c*), and network (Figure 14.7*d*).

Molecular Configurations

- For repeat units that have more than one side atom or groups of atoms bonded to the main chain:
  - Head-to-head and head-to-tail configurations are possible.
  - Differences in spatial arrangements of these side atoms or groups of atoms lead to isotactic, syndiotactic, and atactic stereoisomers.
- When a repeat unit contains a double chain bond, both cis and trans geometrical isomers are possible.

Thermoplastic and Thermosetting Polymers

- With regard to behavior at elevated temperatures, polymers are classified as either thermoplastic or thermosetting.
  - Thermoplastic polymers have linear and branched structures; they soften when heated and harden when cooled.
  - In contrast, thermosetting polymers, once they have hardened, will not soften upon heating; their structures are crosslinked and network.

Copolymers

- The copolymers include random (Figure 14.9*a*), alternating (Figure 14.9*b*), block (Figure 14.9*c*), and graft (Figure 14.9*d*) types.
- Repeat units that are employed in copolymer rubber materials are presented in Table 14.5.

Polymer Crystallinity

- When the molecular chains are aligned and packed in an ordered atomic arrangement, the condition of crystallinity is said to exist.
- Amorphous polymers are also possible wherein the chains are misaligned and disordered.
- In addition to being entirely amorphous, polymers may also exhibit varying degrees of crystallinity; that is, crystalline regions are interdispersed within amorphous areas.
- Crystallinity is facilitated for polymers that are chemically simple and that have regular and symmetrical chain structures.
- The percent crystallinity of a semicrystalline polymer is dependent on its density as well as the densities of the totally crystalline and totally amorphous materials according to Equation 14.8.

Polymer Crystals

- Crystalline regions (or crystallites) are plate-shaped and have a chain-folded structure (Figure 14.12)—chains within the platelet are aligned and fold back and forth on themselves, with folds occurring at the faces.
- Many semicrystalline polymers form spherulites; each spherulite consists of a collection of ribbonlike chain-folded lamellar crystallites that radiate outward from its center.

Defects in Polymers

- Although the point defect concept in polymers is different than in metals and ceramics, vacancies, interstitial atoms, and impurity atoms/ions and groups of atoms/ions as interstitials have been found to exist in crystalline regions.
- Other defects include chain ends, dangling and loose chains, and dislocations (Figure 14.15).

Diffusion in Polymeric Materials

- With regard to diffusion in polymers, small molecules of foreign substances diffuse between molecular chains by an interstitial-type mechanism from one void to an adjacent one.
- Diffusion (or permeation) of gaseous species is often characterized in terms of the permeability coefficient, which is the product of the diffusion coefficient and solubility in the polymer (Equation 14.10).
- Permeation flow rates are expressed using a modified form of Fick's first law (Equation 14.9).

Equation Summary

Equation Number	*Equation*	*Solving for*	*Page Number*
14.5a	$\overline{M}_n = \Sigma x_i M_i$	Number-average molecular weight	541
14.5b	$\overline{M}_w = \Sigma w_i M_i$	Weight-average molecular weight	542
14.6	$DP = \frac{\overline{M}_n}{m}$	Degree of polymerization	542

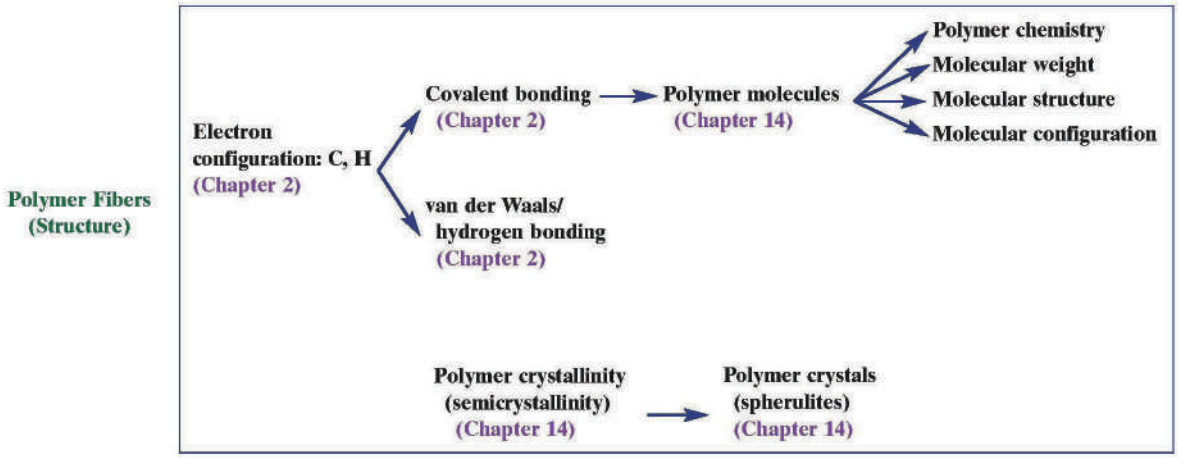
14.7	$\overline{m} = \Sigma f_j m_j$	For a copolymer, average repeat unit molecular weight	551
14.8	$\%\ \text{crystallinity} = \dfrac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$	Percent crystallinity, by weight	554
14.9	$J = P_M \dfrac{\Delta P}{\Delta x}$	Diffusion flux for steady-state diffusion through a polymer membrane	559

List of Symbols

Symbol	*Meaning*
f_j	Mole fraction of repeat unit j in a copolymer chain
m	Repeat unit molecular weight
M_i	Mean molecular weight within the size range i
m_j	Molecular weight of repeat unit j in a copolymer chain
ΔP	Difference in gas pressure from one side of a polymer membrane to the other side
P_M	Permeability coefficient for steady-state diffusion through a polymer membrane
x_i	Fraction of the total number of molecular chains that lie within the size range i
Δx	Thickness of polymer membrane across which diffusion is occurring
w_i	Weight fraction of molecules that lie within the size range i
ρ_a	Density of a totally amorphous polymer
ρ_c	Density of a completely crystalline polymer
ρ_s	Density of polymer specimen for which percent crystallinity is to be determined

Processing/Structure/Properties/Performance Summary

In the following diagram, we illustrate relationships among the various structural components for polymers, as discussed in this chapter (as well as Chapter 2), that influence the properties and processing of polymer fibers, as discussed in Chapter 15.



Important Terms and Concepts

alternating copolymer
atactic configuration
bifunctional
block copolymer
branched polymer
chain-folded model
cis (structure)
copolymer
crosslinked polymer
crystallinity (polymer)
crystallite
degree of polymerization
functionality
graft copolymer
homopolymer
isomerism
isotactic configuration
linear polymer
macromolecule
molecular chemistry
molecular structure
molecular weight
monomer
network polymer
polymer
random copolymer
repeat unit
saturated
spherulite
stereoisomerism
syndiotactic configuration
thermoplastic polymer
thermosetting polymer
trans (structure)
trifunctional
unsaturated

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QUESTIONS AND PROBLEMS

Hydrocarbon Molecules
Polymer Molecules
The Chemistry of Polymer Molecules

14.1 On the basis of the structures presented in this chapter, sketch repeat unit structures for the following polymers: **(a)** polychlorotrifluoroethylene, and **(b)** poly(vinyl alcohol).

Molecular Weight

14.2 Compute repeat unit molecular weights for the following: **(a)** poly(vinyl chloride), **(b)** poly(ethylene terephthalate), **(c)** polycarbonate, and **(d)** polydimethylsiloxane.

14.3 The number-average molecular weight of a polypropylene is 1,000,000 g/mol. Compute the degree of polymerization.

14.4 **(a)** Compute the repeat unit molecular weight of polystyrene.

(b) Compute the number-average molecular weight for a polystyrene for which the degree of polymerization is 25,000.

14.5 The following table lists molecular weight data for a polypropylene material. Compute **(a)** the number-average molecular weight, **(b)** the weight-average molecular weight, and **(c)** the degree of polymerization.

Molecular Weight Range (g/mol)	x_i	w_i
8,000–16,000	0.05	0.02
16,000–24,000	0.16	0.10
24,000–32,000	0.24	0.20
32,000–40,000	0.28	0.30
40,000–48,000	0.20	0.27
48,000–56,000	0.07	0.11

14.6 Molecular weight data for some polymer are tabulated here. Compute **(a)** the number-

average molecular weight and **(b)** the weight-average molecular weight. **(c)** If it is known that this material's degree of polymerization is 710, which one of the polymers listed in Table 14.3 is this polymer? Why?

Molecular Weight Range (g/mol)	x_i	w_i
15,000–30,000	0.04	0.01
30,000–45,000	0.07	0.04
45,000–60,000	0.16	0.11
60,000–75,000	0.26	0.24
75,000–90,000	0.24	0.27
90,000–105,000	0.12	0.16
105,000–120,000	0.08	0.12
120,000–135,000	0.03	0.05

14.7 Is it possible to have a poly(methyl methacrylate) homopolymer with the following molecular weight data and a degree of polymerization of 527? Why or why not?

Molecular Weight Range (g/mol)	w_i	x_i
8,000–20,000	0.02	0.05
20,000–32,000	0.08	0.15
32,000–44,000	0.17	0.21
44,000–56,000	0.29	0.28
56,000–68,000	0.23	0.18
68,000–80,000	0.16	0.10
80,000–92,000	0.05	0.03

14.8 High-density polyethylene may be chlorinated by inducing the random substitution of chlorine atoms for hydrogen.

(a) Determine the concentration of Cl (in wt%) that must be added if this substitution occurs for 5% of all the original hydrogen atoms.

(b) In what ways does this chlorinated polyethylene differ from poly(vinyl chloride)?

Molecular Shape

14.9 For a linear freely rotating polymer molecule, the total extended chain length L depends on the bond length between chain atoms d, the total number of bonds in the molecule N, and the angle between adjacent backbone chain atoms θ, as follows:

$$L = Nd \sin\left(\frac{\theta}{2}\right) \qquad (14.11)$$

Furthermore, the average end-to-end distance r for a randomly winding polymer molecule in Figure 14.6 is equal to

$$r = d\sqrt{N} \qquad (14.12)$$

A linear polytetrafluoroethylene has a number-average molecular weight of 500,000 g/mol; compute average values of L and r for this material.

14.10 Using the definitions for total chain molecule length L (Equation 14.11) and average chain end-to-end distance r (Equation 14.12), for a linear polyethylene determine the following:

(a) the number-average molecular weight for $L = 2500$ nm

(b) the number-average molecular weight for $r = 20$ nm

Molecular Configurations

14.11 Sketch portions of a linear polystyrene molecule that are **(a)** syndiotactic, **(b)** atactic, and **(c)** isotactic. Use two-dimensional schematics per footnote 8 of this chapter.

14.12 Sketch cis and trans structures for **(a)** butadiene, and **(b)** chloroprene. Use two-dimensional schematics per footnote 11 of this chapter.

Thermoplastic and Thermosetting Polymers

14.13 Make comparisons of thermoplastic and thermosetting polymers **(a)** on the basis of mechanical characteristics upon heating and **(b)** according to possible molecular structures.

14.14 **(a)** Is it possible to grind up and reuse phenol-formaldehyde? Why or why not?

(b) Is it possible to grind up and reuse polypropylene? Why or why not?

Copolymers

14.15 Sketch the repeat structure for each of the following alternating copolymers: **(a)** poly (butadiene-chloroprene), **(b)** poly(styrene-methyl methacrylate), and **(c)** poly(acrylonitrile-vinyl chloride).

14.16 The number-average molecular weight of a poly(styrene-butadiene) alternating copolymer is 1,350,000 g/mol; determine the aver-

age number of styrene and butadiene repeat units per molecule.

14.17 Calculate the number-average molecular weight of a random nitrile rubber [poly (acrylonitrile-butadiene) copolymer] in which the fraction of butadiene repeat units is 0.30; assume that this concentration corresponds to a degree of polymerization of 2000.

14.18 An alternating copolymer is known to have a number-average molecular weight of 250,000 g/mol and a degree of polymerization of 3420. If one of the repeat units is styrene, which of ethylene, propylene, tetrafluoroethylene, and vinyl chloride is the other repeat unit? Why?

14.19 **(a)** Determine the ratio of butadiene to styrene repeat units in a copolymer having a number-average molecular weight of 350,000 g/mol and degree of polymerization of 4425.

(b) Which type(s) of copolymer(s) will this copolymer be, considering the following possibilities: random, alternating, graft, and block? Why?

14.20 Crosslinked copolymers consisting of 60 wt% ethylene and 40 wt% propylene may have elastic properties similar to those for natural rubber. For a copolymer of this composition, determine the fraction of both repeat unit types.

14.21 A random poly(isobutylene-isoprene) copolymer has a number-average molecular weight of 200,000 g/mol and a degree of polymerization of 3000. Compute the fraction of isobutylene and isoprene repeat units in this copolymer.

Polymer Crystallinity

14.22 Explain briefly why the tendency of a polymer to crystallize decreases with increasing molecular weight.

14.23 For each of the following pairs of polymers, do the following: (1) state whether it is possible to determine whether one polymer is more likely to crystallize than the other; (2) if it is possible, note which is the more likely and then cite reason(s) for your choice; and (3) if it is not possible to decide, then state why.

(a) Linear and syndiotactic poly(vinyl chloride); linear and isotactic polystyrene

(b) Network phenol-formaldehyde; linear and heavily crosslinked *cis*-isoprene

(c) Linear polyethylene; lightly branched isotactic polypropylene

(d) Alternating poly(styrene-ethylene) copolymer; random poly(vinyl chloride-tetrafluoroethylene) copolymer

14.24 The density of totally crystalline polypropylene at room temperature is 0.946 g/cm^3. Also, at room temperature the unit cell for this material is monoclinic with the following lattice parameters:

$$a = 0.666 \text{ nm} \qquad \alpha = 90°$$
$$b = 2.078 \text{ nm} \qquad \beta = 99.62°$$
$$c = 0.650 \text{ nm} \qquad \gamma = 90°$$

If the volume of a monoclinic unit cell, V_{mono}, is a function of these lattice parameters as

$$V_{mono} = abc \sin \beta$$

determine the number of repeat units per unit cell.

14.25 The density and associated percent crystallinity for two polytetrafluoroethylene materials are as follows:

ρ (g/cm^3)	crystallinity (%)
2.144	51.3
2.215	74.2

(a) Compute the densities of totally crystalline and totally amorphous polytetrafluoroethylene.

(b) Determine the percent crystallinity of a specimen having a density of 2.26 g/cm^3.

14.26 The density and associated percent crystallinity for two nylon 6,6 materials are as follows:

ρ (g/cm^3)	crystallinity (%)
1.188	67.3
1.152	43.7

(a) Compute the densities of totally crystalline and totally amorphous nylon 6,6.

(b) Determine the density of a specimen having 55.4% crystallinity.

Diffusion in Polymeric Materials

14.27 Consider the diffusion of water vapor through a polypropylene (PP) sheet 2 mm thick. The pressures of H_2O at the two faces are 1 kPa and 10 kPa, which are maintained constant. Assuming conditions of steady state, what is the diffusion flux [in (cm^3 STP)/cm^2·s] at 298 K?

14.28 Argon diffuses through a high-density polyethylene (HDPE) sheet 40 mm thick at a rate of 4.0×10^{-7} (cm^3 STP)/cm^2·s at 325 K. The pressures of argon at the two faces are 5000 kPa and 1500 kPa, which are maintained constant. Assuming conditions of steady state, what is the permeability coefficient at 325 K?

14.29 The permeability coefficient of a type of small gas molecule in a polymer is dependent on absolute temperature according to the following equation:

$$P_M = P_{M_0} \exp\left(-\frac{Q_p}{RT}\right)$$

where P_{M_0} and Q_p are constants for a given gas-polymer pair. Consider the diffusion of hydrogen through a poly(dimethyl siloxane) (PDMSO) sheet 20 mm thick. The hydrogen pressures at the two faces are 10 kPa and 1 kPa, which are maintained constant. Compute the diffusion flux [in (cm^3 STP)/cm^2·s] at 350 K. For this diffusion system

$$P_{M_0} = 1.45 \times 10^{-8} (cm^3\ STP)(cm)/cm^2 \cdot s \cdot Pa$$

$$Q_p = 13.7\ kJ/mol$$

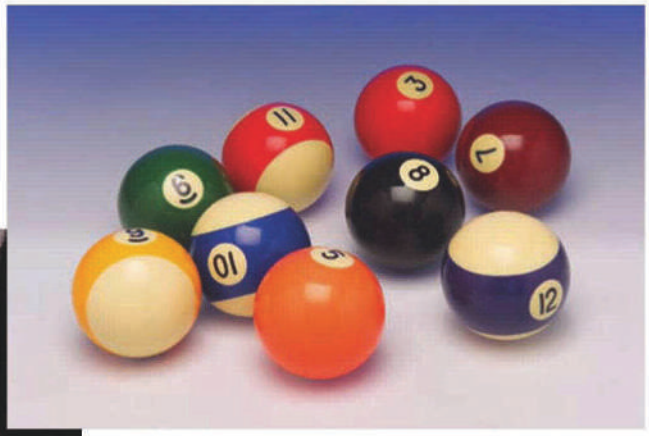
Also, assume a condition of steady state diffusion.

Spreadsheet Problem

14.1SS For a specific polymer, given at least two density values and their corresponding percents crystallinity, develop a spreadsheet that allows the user to determine the following: **(a)** the density of the totally crystalline polymer, **(b)** the density of the totally amorphous polymer, **(c)** the percent crystallinity of a specified density, and **(d)** the density for a specified percent crystallinity.

Chapter 15 Characteristics, Applications, and Processing of Polymers

Top: Photograph of several billiard balls that are made of phenol-formaldehyde (Bakelite). The Materials of Importance piece that follows Section 15.15 discusses the invention of phenol-formaldehyde and its replacement of ivory for billiard balls. Bottom: Photograph of a woman playing billiards. (iStockphoto)





There are several reasons why an engineer should know something about the characteristics, applications, and processing of polymeric materials. Polymers are used in a wide variety of applications, such as construction materials and microelectronics processing. Thus, most engineers will be required to work with polymers at some point in their careers. Understanding the mechanisms by which polymers elastically and plastically deform allows one to alter and control their moduli of elasticity and strengths (Sections 15.7 and 15.8). Also, additives may be incorporated into polymeric materials to modify a host of properties, including strength, abrasion resistance, toughness, thermal stability, stiffness, deteriorability, color, and flammability resistance (Section 15.21).

In the processing/structure/properties/performance scheme for polymer fibers, reasons for studying the characteristics, applications, and processing of polymers are as follows:

- Polymeric materials that are used for fibers in textiles (i.e., clothing) must be relatively strong. In this chapter we discuss the mechanical characteristics of polymers, the mechanisms (on a molecular scale) by which semicrystalline polymers plastically deform, and, finally, techniques that are available to strengthen these materials.
- Several techniques are used to form polymer fibers; in one fabrication procedure the fibers are spun from the molten material. This chapter discusses the phenomenon of melting for polymers, the concept of melting temperature, and structural characteristics of polymers that influence melting temperature. The magnitude of a fiber's melting temperature will influence the manner in which it is processed as well as the maximum temperature at which it may be used.

Learning Objectives

After studying this chapter you should be able to do the following:

1. **Make schematic plots of the three characteristic stress–strain behaviors observed for polymeric materials.**
2. **Describe/sketch the various stages in the elastic and plastic deformations of a semicrystalline (spherulitic) polymer.**
3. **Discuss the influence of the following factors on polymer tensile modulus and/or strength: (a) molecular weight, (b) degree of crystallinity, (c) predeformation, and (d) heat treating of undeformed materials.**
4. **Describe the molecular mechanism by which elastomeric polymers deform elastically.**
5. **List four characteristics or structural components of a polymer that affect both its melting and glass transition temperatures.**
6. **Cite the seven different polymer application types and, for each, note its general characteristics.**
7. **Briefly describe addition and condensation polymerization mechanisms.**
8. **Name the five types of polymer additives and, for each, indicate how it modifies the properties.**
9. **Name and briefly describe five fabrication techniques used for plastic polymers.**

15.1 INTRODUCTION

This chapter discusses some of the characteristics important to polymeric materials and, the various types and processing techniques.

Mechanical Behavior of Polymers

15.2 STRESS–STRAIN BEHAVIOR

The mechanical properties of polymers are specified with many of the same parameters that are used for metals—that is, modulus of elasticity and yield and tensile strengths. For many polymeric materials, the simple stress–strain test is used to

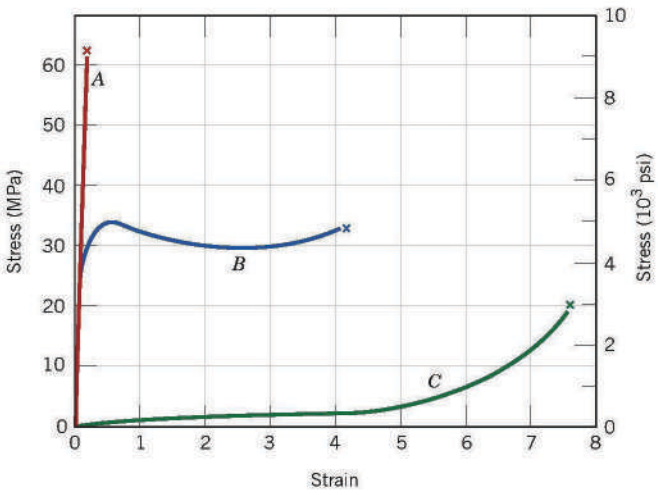


Figure 15.1 The stress–strain behavior for brittle (curve *A*), plastic (curve *B*), and highly elastic (elastomeric) (curve *C*) polymers.

characterize some of these mechanical parameters.[1] The mechanical characteristics of polymers, for the most part, are highly sensitive to the rate of deformation (strain rate), the temperature, and the chemical nature of the environment (the presence of water, oxygen, organic solvents, etc.). Some modifications of the testing techniques and specimen configurations used for metals (Chapter 6) are necessary with polymers, especially for the highly elastic materials, such as rubbers.

VMSE



Polymers

Three typically different types of stress–strain behavior are found for polymeric materials, as represented in Figure 15.1. Curve *A* illustrates the stress–strain character for a brittle polymer, inasmuch as it fractures while deforming elastically. The behavior for a plastic material, curve *B*, is similar to that for many metallic materials; the initial deformation is elastic, which is followed by yielding and a region of plastic deformation. Finally, the deformation displayed by curve *C* is totally elastic; this rubberlike elasticity (large recoverable strains produced at low stress levels) is displayed by a class of polymers termed the **elastomers.**

elastomer

Modulus of elasticity (termed *tensile modulus* or sometimes just *modulus* for polymers) and ductility in percent elongation are determined for polymers in the same manner as for metals (Section 6.6). For plastic polymers (curve *B*, Figure 15.1), the yield point is taken as a maximum on the curve, which occurs just beyond the termination of the linear-elastic region (Figure 15.2). The stress at this maximum is

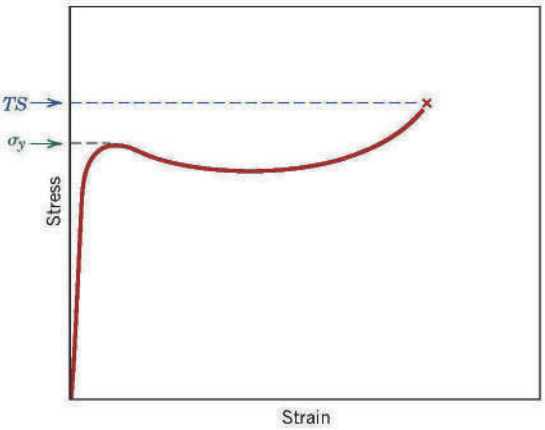


Figure 15.2 Schematic stress–strain curve for a plastic polymer showing how yield and tensile strengths are determined.

[1] ASTM Standard D 638, "Standard Test Method for Tensile Properties of Plastics."

Table 15.1 Room-Temperature Mechanical Characteristics of Some of the More Common Polymers

Material	*Specific Gravity*	*Tensile Modulus [GPa (ksi)]*	*Tensile Strength [MPa (ksi)]*	*Yield Strength [MPa (ksi)]*	*Elongation at Break (%)*
Polyethylene (low density)	0.917–0.932	0.17–0.28 (25–41)	8.3–31.4 (1.2–4.55)	9.0–14.5 (1.3–2.1)	100–650
Polyethylene (high density)	0.952–0.965	1.06–1.09 (155–158)	22.1–31.0 (3.2–4.5)	26.2–33.1 (3.8–4.8)	10–1200
Poly(vinyl chloride)	1.30–1.58	2.4–4.1 (350–600)	40.7–51.7 (5.9–7.5)	40.7–44.8 (5.9–6.5)	40–80
Polytetrafluoroethylene	2.14–2.20	0.40–0.55 (58–80)	20.7–34.5 (3.0–5.0)	13.8–15.2 (2.0–2.2)	200–400
Polypropylene	0.90–0.91	1.14–1.55 (165–225)	31–41.4 (4.5–6.0)	31.0–37.2 (4.5–5.4)	100–600
Polystyrene	1.04–1.05	2.28–3.28 (330–475)	35.9–51.7 (5.2–7.5)	25.0–69.0 (3.63–10.0)	1.2–2.5
Poly(methyl methacrylate)	1.17–1.20	2.24–3.24 (325–470)	48.3–72.4 (7.0–10.5)	53.8–73.1 (7.8–10.6)	2.0–5.5
Phenol-formaldehyde	1.24–1.32	2.76–4.83 (400–700)	34.5–62.1 (5.0–9.0)	—	1.5–2.0
Nylon 6,6	1.13–1.15	1.58–3.80 (230–550)	75.9–94.5 (11.0–13.7)	44.8–82.8 (6.5–12)	15–300
Polyester (PET)	1.29–1.40	2.8–4.1 (400–600)	48.3–72.4 (7.0–10.5)	59.3 (8.6)	30–300
Polycarbonate	1.20	2.38 (345)	62.8–72.4 (9.1–10.5)	62.1 (9.0)	110–150

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the yield strength (σ_y). Furthermore, tensile strength (*TS*) corresponds to the stress at which fracture occurs (Figure 15.2); *TS* may be greater than or less than σ_y. Strength, for these plastic polymers, is normally taken as tensile strength. Table 15.1 gives these mechanical properties for several polymeric materials; more comprehensive lists are provided in Tables B.2, B.3, and B.4, Appendix B.

Polymers are, in many respects, mechanically dissimilar to metals (Figures 1.4, 1.5, and 1.6). For example, the modulus for highly elastic polymeric materials may be as low as 7 MPa (10^3 psi), but may run as high as 4 GPa (0.6×10^6 psi) for some of the very stiff polymers; modulus values for metals are much larger and range between 48 and 410 GPa (7×10^6 to 60×10^6 psi). Maximum tensile strengths for polymers are about 100 MPa (15,000 psi)—for some metal alloys 4100 MPa (600,000 psi). And, whereas metals rarely elongate plastically to more than 100%, some highly elastic polymers may experience elongations to greater than 1000%.

In addition, the mechanical characteristics of polymers are much more sensitive to temperature changes near room temperature. Consider the stress–strain behavior for poly(methyl methacrylate) (Plexiglas) at several temperatures between 4 and 60°C (40 and 140°F) (Figure 15.3). Increasing the temperature produces (1) a decrease in elastic modulus, (2) a reduction in tensile strength, and (3) an enhancement of ductility—at 4°C (40°F) the material is totally brittle, whereas there is considerable plastic deformation at both 50 and 60°C (122 and 140°F).

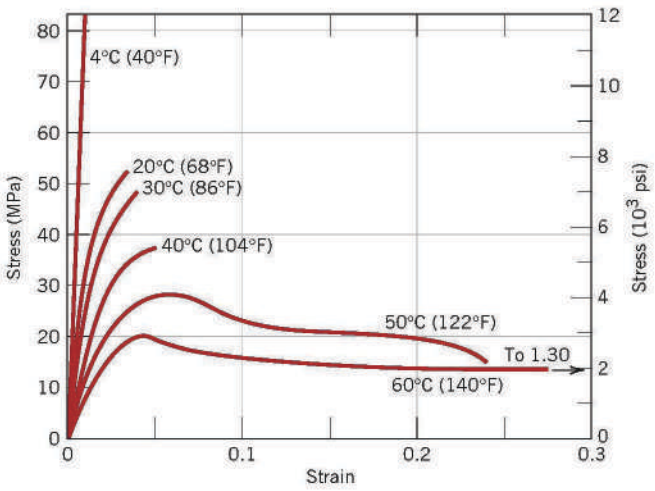


Figure 15.3 The influence of temperature on the stress–strain characteristics of poly(methyl methacrylate). (From T. S. Carswell and H. K. Nason, "Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics," *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, 1944. Copyright, ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission.)

The influence of strain rate on the mechanical behavior may also be important. In general, decreasing the rate of deformation has the same influence on the stress–strain characteristics as increasing the temperature; that is, the material becomes softer and more ductile.

15.3 MACROSCOPIC DEFORMATION



Some aspects of the macroscopic deformation of semicrystalline polymers deserve our attention. The tensile stress–strain curve for a semicrystalline material, which was initially undeformed, is shown in Figure 15.4; also included in the figure are schematic representations of the specimen profiles at various stages of deformation. Both upper and lower yield points are evident on the curve, which are followed by a near horizontal region. At the upper yield point, a small neck forms within the gauge section of the specimen. Within this neck, the chains become oriented (i.e., chain axes become aligned parallel to the elongation direction, a condition that is represented schematically in Figure 15.13*d*), which leads to localized strengthening. Consequently, there is a resistance to continued deformation at this point, and specimen elongation proceeds by the propagation of this neck region along the gauge length; the chain orientation phenomenon (Figure 15.13*d*) accompanies this neck extension. This tensile behavior may be contrasted to that found for ductile metals (Section 6.6), wherein once a neck has formed, all subsequent deformation is confined to within the neck region.

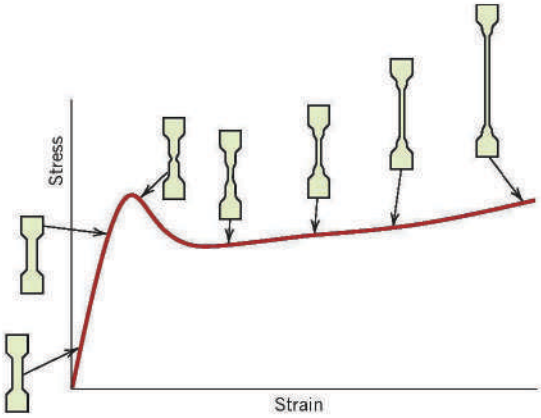


Figure 15.4 Schematic tensile stress–strain curve for a semicrystalline polymer. Specimen contours at several stages of deformation are included. (From Jerold M. Schultz, *Polymer Materials Science*, copyright © 1974, p. 488. Reprinted by permission of Prentice Hall, Inc., Englewood Cliffs, NJ.)

Concept Check 15.1

When citing the ductility as percent elongation for semicrystalline polymers, it is not necessary to specify the specimen gauge length, as is the case with metals. Why is this so?

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site).*]

15.4 VISCOELASTIC DEFORMATION

An amorphous polymer may behave like a glass at low temperatures, a rubbery solid at intermediate temperatures [above the glass transition temperature (Section 15.12)], and a viscous liquid as the temperature is further raised. For relatively small deformations, the mechanical behavior at low temperatures may be elastic; that is, in conformity to Hooke's law, $\sigma = E\epsilon$. At the highest temperatures, viscous or liquid-like behavior prevails. For intermediate temperatures the polymer is a rubbery solid that exhibits the combined mechanical characteristics of these two extremes; the condition is termed **viscoelasticity.**

viscoelasticity

Elastic deformation is instantaneous, which means that total deformation (or strain) occurs the instant the stress is applied or released (i.e., the strain is independent of time). In addition, upon release of the external stress, the deformation is totally recovered—the specimen assumes its original dimensions. This behavior is represented in Figure 15.5*b* as strain versus time for the instantaneous load–time curve, shown in Figure 15.5*a*.

By way of contrast, for totally viscous behavior, deformation or strain is not instantaneous; that is, in response to an applied stress, deformation is delayed or dependent on time. Also, this deformation is not reversible or completely recovered after the stress is released. This phenomenon is demonstrated in Figure 15.5*d*.

For the intermediate viscoelastic behavior, the imposition of a stress in the manner of Figure 15.5*a* results in an instantaneous elastic strain, which is followed by a viscous, time-dependent strain, a form of anelasticity (Section 6.4); this behavior is illustrated in Figure 15.5*c*.

A familiar example of these viscoelastic extremes is found in a silicone polymer that is sold as a novelty and known by some as "Silly Putty." When rolled into

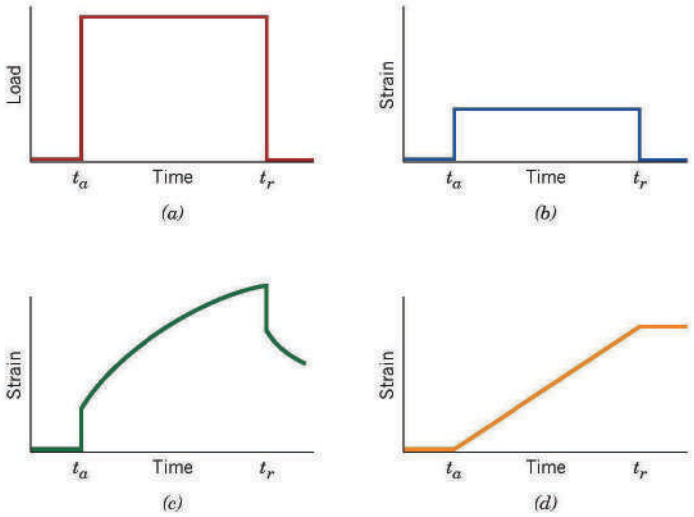


Figure 15.5 (*a*) Load versus time, where load is applied instantaneously at time t_a and released at t_r. For the load–time cycle in (*a*), the strain-versus-time responses are for totally elastic (*b*), viscoelastic (*c*), and viscous (*d*) behaviors.