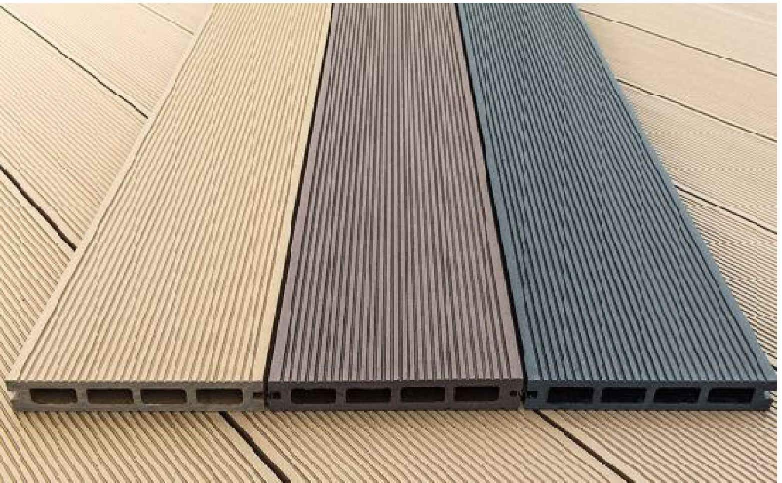
Chapter 14:
Polymer Structures

Chapter Notes

14.1 Introduction

Wood



Rubber

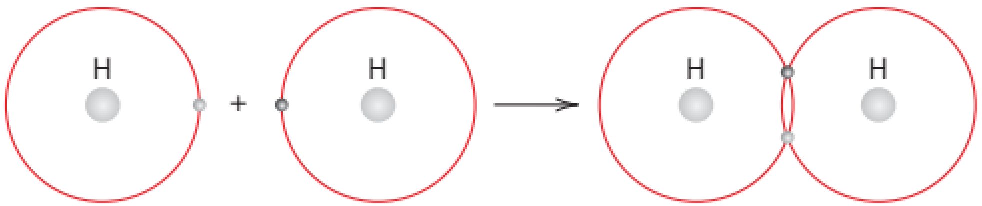
Leather

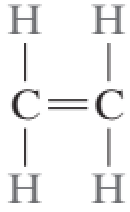
Concept Check!

- Is wool a polymer?

14.2: Hydrocarbon Molecules

- Hydrogen + Carbon
- Covalent
  - Single Bond
  - Double Bond
  - Tripple Bond
- Saturated
- Unsaturated





$$H_2C=CH_2$$

$H-C\equiv C-H$


porcupane
porcupene
porcupyne

14.2: Hydrocarbon Molecules

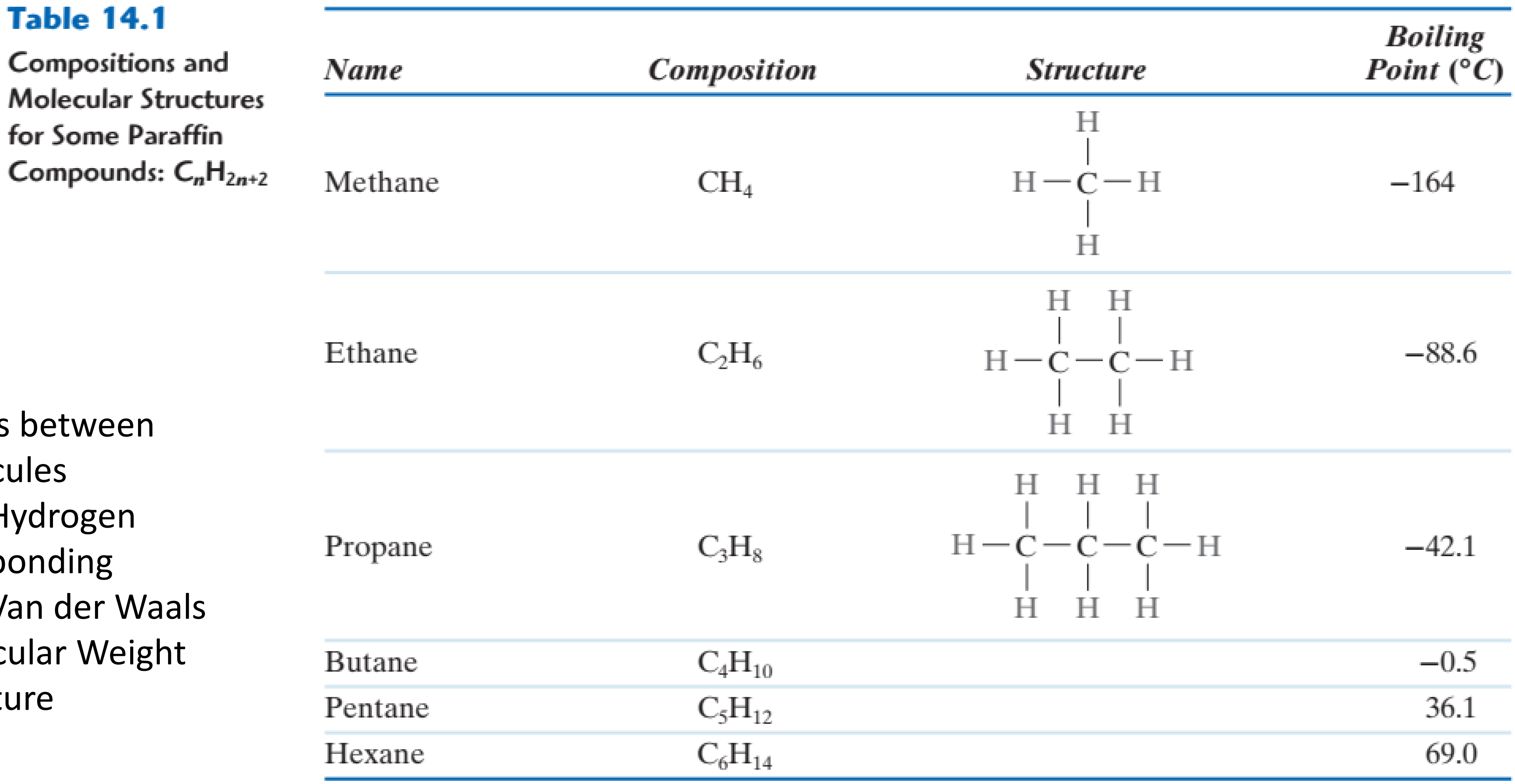


Table 14.1

Compositions and Molecular Structures for Some Paraffin Compounds: C_nH_{2n+2}

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

- Forces between molecules
  - Hydrogen bonding
  - Van der Waals
- Molecular Weight
- Structure

14.2: Hydrocarbon Molecules

- Isomerism
  - Same composition
  - Different atomic arrangement
  - Structure Effects Properties

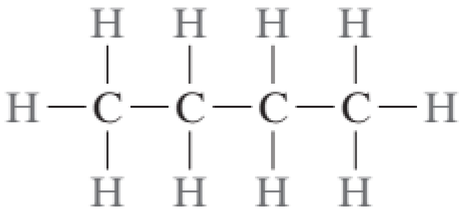
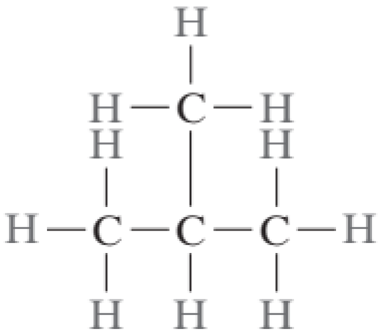
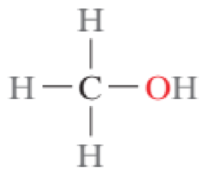
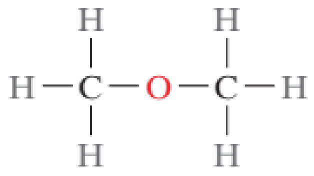
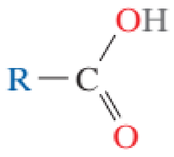
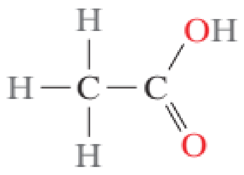
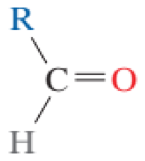
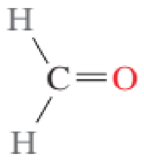
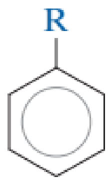
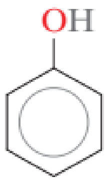
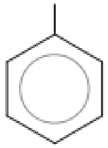
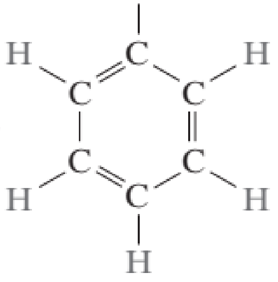
Molecule	Boiling Point
n-Butane 	-0.5°C
Isobutane 	-12.3°C

Table 14.2

Some Common Hydrocarbon Groups

Family	*Characteristic Unit*		*Representative Compound*
Alcohols	R—OH	 $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$	Methyl alcohol
Ethers	R—O—R′	 $\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-O-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H}$	Dimethyl ether
Acids			Acetic acid
Aldehydes			Formaldehyde
Aromatic hydrocarbons[a]			Phenol

[a] The simplified structure  denotes a phenyl group, 

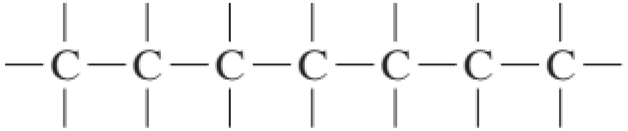
Concept Check!

- Are graphite (C) and diamond (C) isomers?
- Are Ethanol (H_6C_2O) and Dimethyl Ether (H_6C_2O)?
- Are Quartz (SO_2) and Glass (SO_2) isomers?

- Which has a higher vapor pressure at room temperature and pressure?
  - Hexane (C_6H_{14}) or Pentane (C_5H_{12})

- Is acetylene (C_2H_2) saturated or unsaturated?

14.3 Polymer Molecules



$$-C-C-C-C-C-C-C-$$

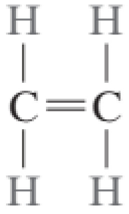
- Macromolecule: Very big molecules, lots of atoms
    - Covalent bonds
    - Carbon-chain polymers, string of carbon atoms
    - Side bonds can have different groups
- Repeat Unit: repeated structures along the chain
- Monomer: The small molecule that fuels a chain when making a polymer

Concept Check!

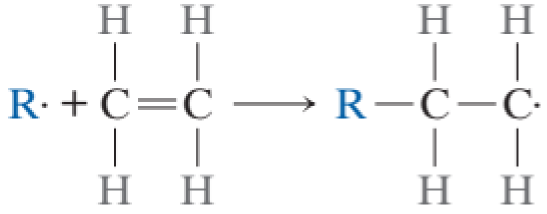
- Give an example of a macromolecule you have heard of before.

14.4 Chemistry of Polymer Molecules

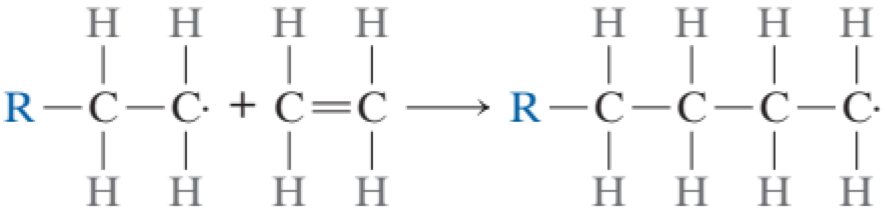
- Ethylene
- Polyethylene
    - Needs a Catalyst – R·
    - The chain keeps growing!
    - How does it stop?!? Is it all one long chain that extends until the fuel runs out?!?



$$\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}$$



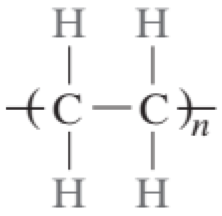
$$R\cdot + \underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \longrightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\cdot$$



$$R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\cdot + \underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}} \longrightarrow R-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\cdot$$

14.4 Chemistry of Polymer Molecules

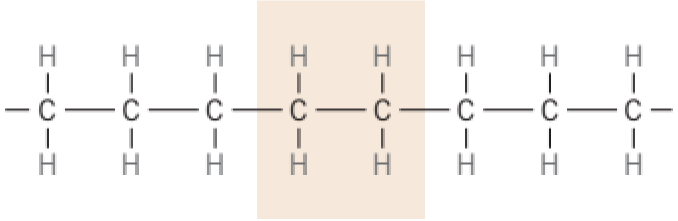
- How do you write down the chemical? The chain is so long, it will take forever.
- Shorthand!
- Simplified models
    - Differences between model (a) and (b)?
        - Angles
        - Atoms have volume
        - Atoms are different sizes



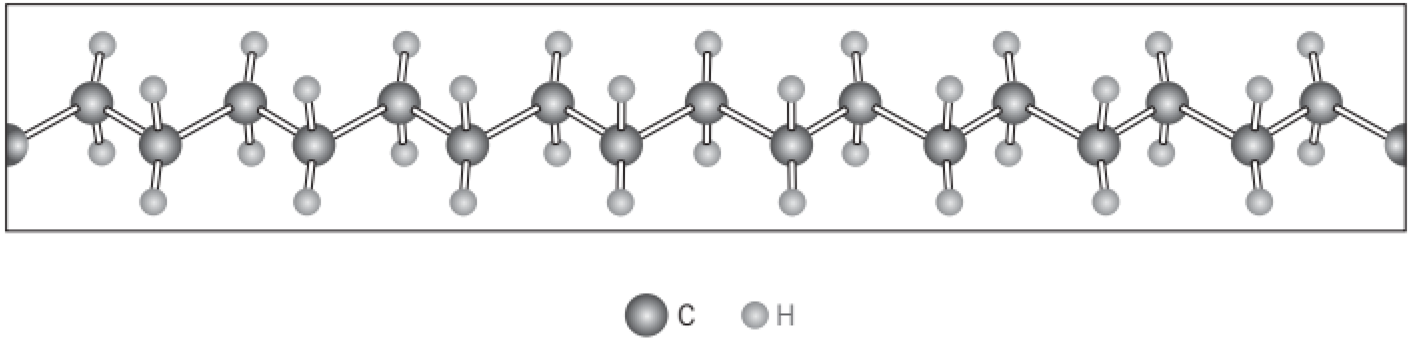
$$-\!\left(\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{C} \\ | \\ \mathrm{H} \end{array} - \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{C} \\ | \\ \mathrm{H} \end{array}\right)_{n}\!-$$

OR

$-\!(CH_2-CH_2)_n\!-$



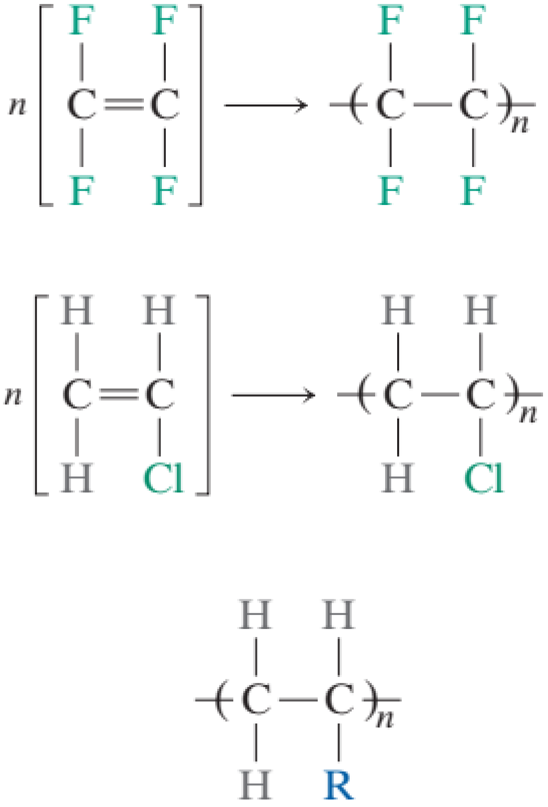
(a)



(b)

14.4 Chemistry of Polymer Molecules

- Other Polymers:
  - Swap out the H group for other things:
    - Fluoride: Polytetrafluoroethylene, (a.k.a. PTFE or Teflon) (Fluorocarbon)
    - Chloride: Poly (vinal chloride), (a.k.a. PVC) – makes good potato cannons
    - Organic Groups: Lots of different possibilities

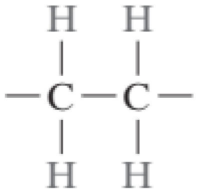
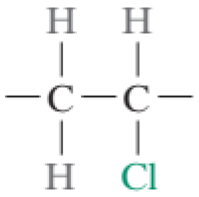
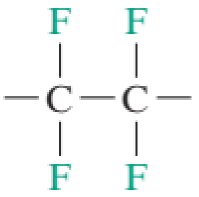
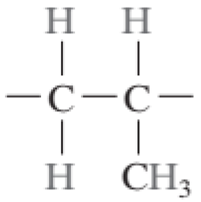
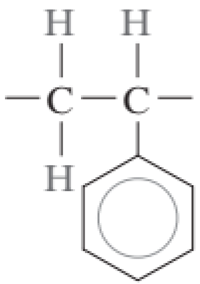


$$n\left[\begin{matrix} F & & F \\ | & & | \\ C & = & C \\ | & & | \\ F & & F \end{matrix}\right] \longrightarrow \left(\begin{matrix} F & & F \\ | & & | \\ C & - & C \\ | & & | \\ F & & F \end{matrix}\right)_n$$

$$n\left[\begin{matrix} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & Cl \end{matrix}\right] \longrightarrow \left(\begin{matrix} H & & H \\ | & & | \\ C & - & C \\ | & & | \\ H & & Cl \end{matrix}\right)_n$$

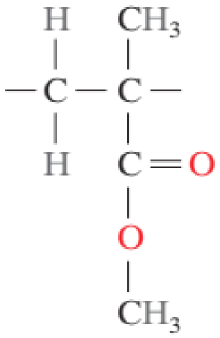
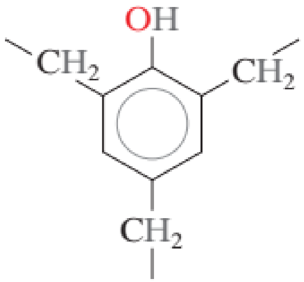
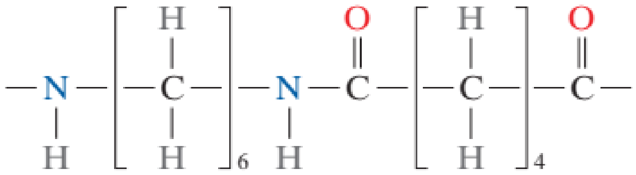
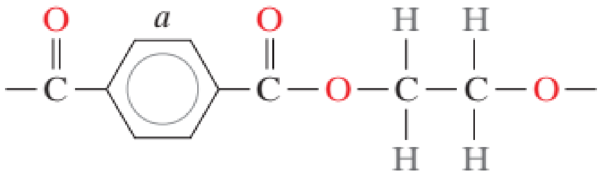
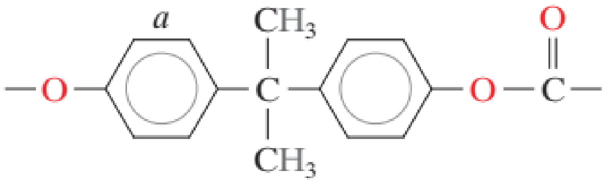
$$\left(\begin{matrix} H & & H \\ | & & | \\ C & - & C \\ | & & | \\ H & & R \end{matrix}\right)_n$$

Table 14.3 Repeat Units for Ten of the More Common Polymeric Materials

Polymer	*Repeat Unit*
Polyethylene (PE)	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$
Poly(vinyl chloride) (PVC)	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-$
Polytetrafluoroethylene (PTFE)	 $-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-$
Polypropylene (PP)	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-$
Polystyrene (PS)	

(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)	

14.4 Chemistry of Polymer Molecules

- Homopolymer: Only one repeating unit in a single polymer
- Copolymer: More than one different repeat units in one polymer

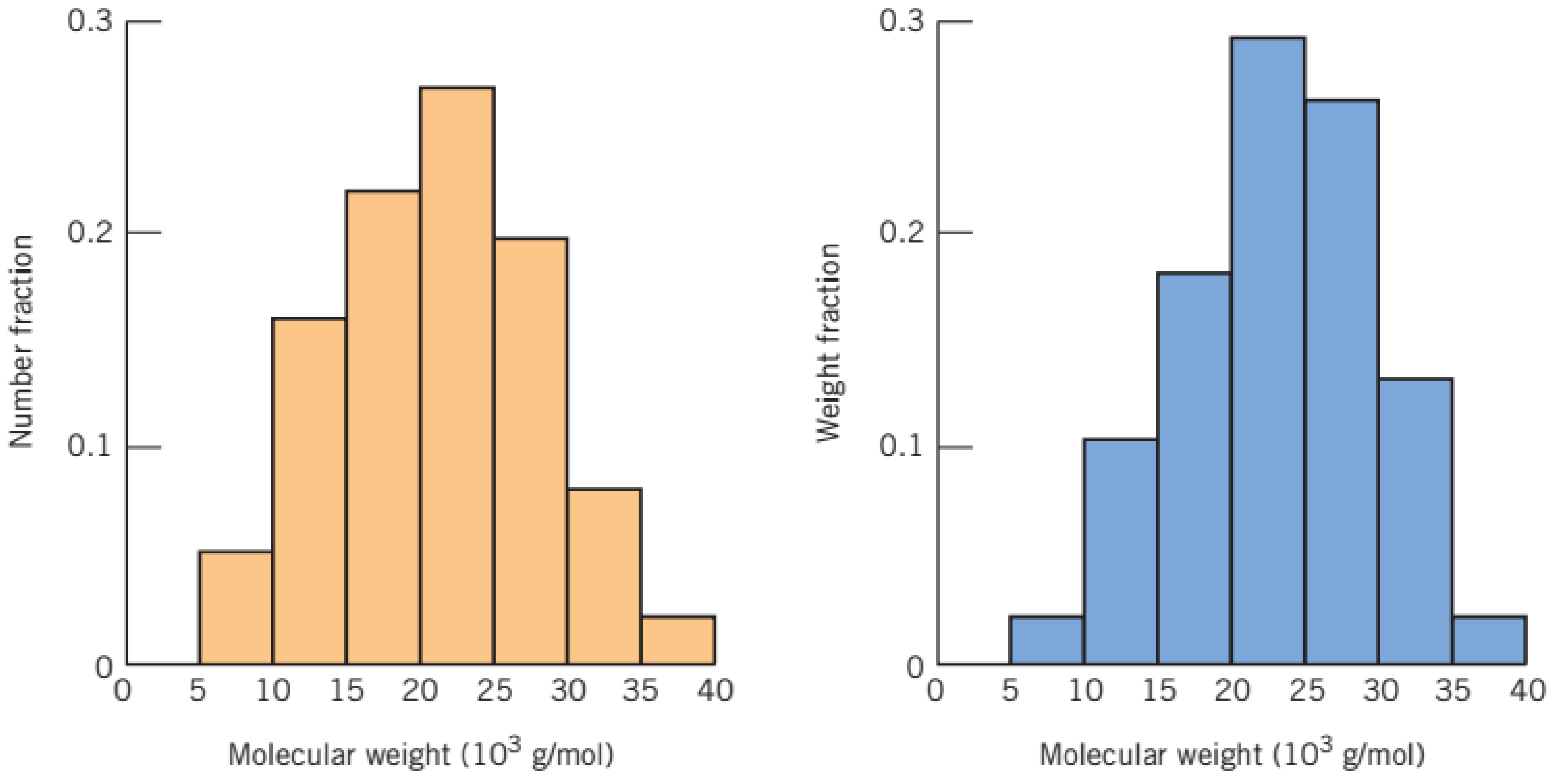
- Functionality: The number of bonds a monomer can form
- Bifunctional: Can form two new bonds; forms a chain structure.
- Trifunctional: Can form three new bonds; forms a web structure. (e.g. phenol-formaldehyde)

Concept Check!!!

- Draw poly (vinyl fluoride) (a.k.a. PVF) repeat structure.
- What is R?!? Give three examples of what R can be.

14.5 Molecular Weight (a.k.a. molar mass)

- Not all chains are the same length.
- Distribution of molar mass
- Use statistics to describe a distribution
  - Average, mean, mode, range, etc.
- Physical properties measurements can help determine molar mass.
  - Viscosity and osmotic pressure



(a) *(b)*

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

Number-average molecular weight

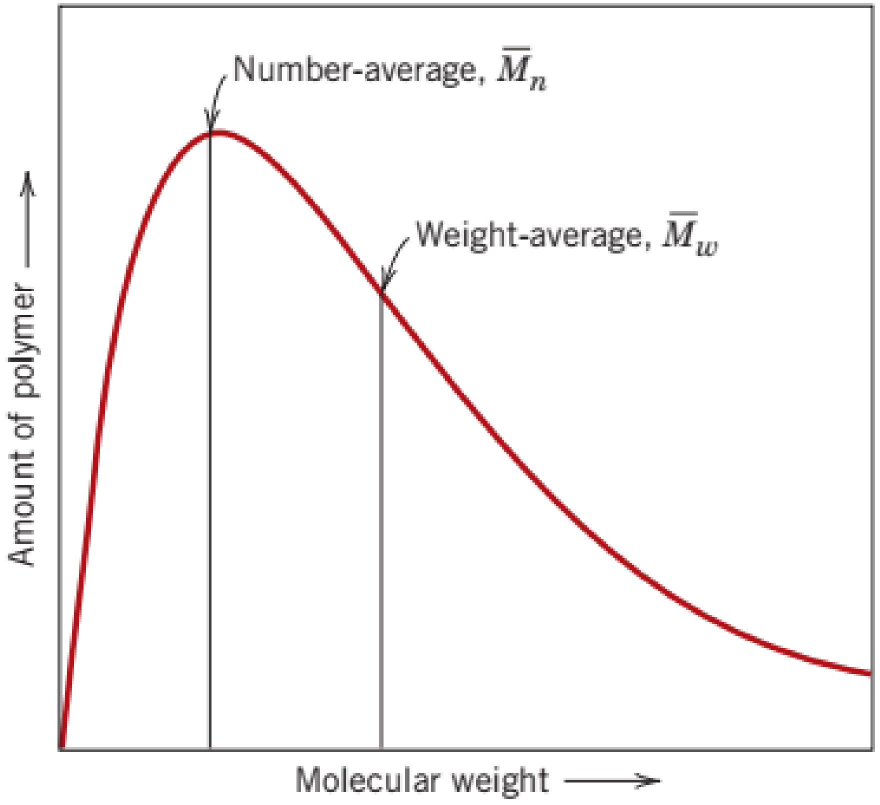
$$\overline{M}_n = \Sigma x_i M_i$$

Weight-average molecular weight

$$\overline{M}_w = \Sigma w_i M_i$$

14.5 Molecular Weight (a.k.a. molar mass)

Figure 14.4 Distribution of molecular weights for a typical polymer.



14.5 Molecular Weight (a.k.a. molar mass)

- Degree of Polymerization (DP)

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

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_iM_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
			$\overline{M}_n = \overline{21{,}150}$

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.

(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

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

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.

(c) Table 14.4b shows the data for the weight-average molecular weight, as taken from Figure 14.3*b*. The $w_i M_i$ 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	$w_i M_i$
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
			$\overline{M}_w = 23{,}200$

14.5 Molecular Weight (a.k.a. molar mass)

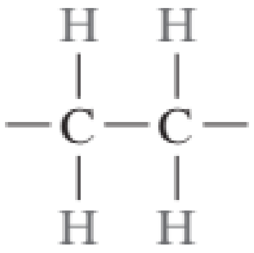
- Length of polymer chain changes physical properties!
  - Melting/softening temperature increases with increasing molecular weight
  - 100 g/mol ~ liquid at room temperature
  - 1000 g/mol ~ waxy solids, soft resins
  - 10,000+ g/mol ~ Solid

  - Elastic modulus
  - Strength

Concept Check!!!

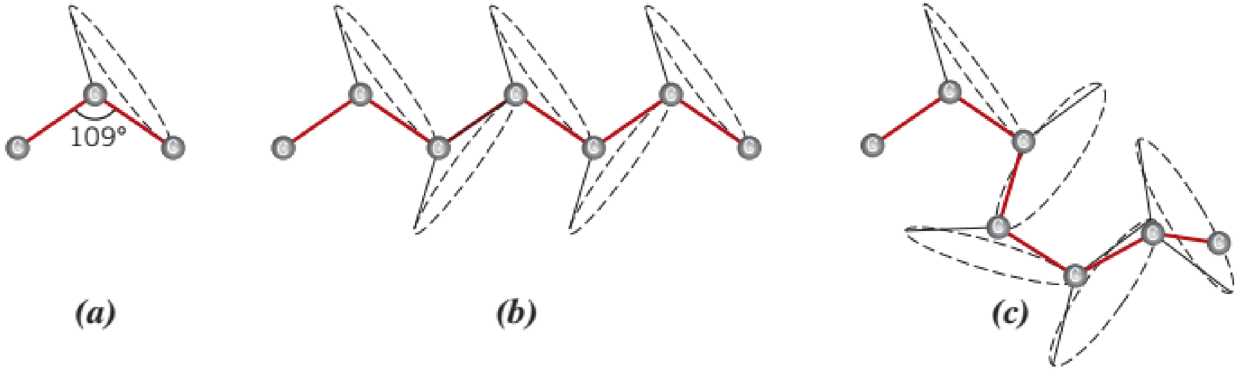
- Estimate the degree of polymerization in a grocery bag (polyethylene).

Polyethylene (PE)



14.6 Molecular Shape

- Single bonds can rotate
- Double bonds are rigid
- Polymer materials consist of large numbers of long chains.
  - Tangled fishing line
  - Spaghetti bowl
- Molecular entanglement
  - Elastic extensions
  - stretchy rubber
- Conformation



14.6 Molecular Shape

- Mechanical and thermal properties are dependent on polymer flexibility
  - Flexibility depends on repeat structure and chemistry
    - Double bonds? Single bonds?
    - Bulky attached groups

Concept Check!!!

- What polymer is more stretchy and flexible, polyethylene or polystyrene? Why?

14.7 Molecular Structure

- Molecular structure effects physical properties (remember isomers?)
  - Linear Polymers
    - Single chains, flexible, spaghetti-like.
  - Branched Polymers
    - Lower density, do not pack as well with the branches
  - Crosslinked Polymers
    - Long chains joined in places like a net. Usually used on rubbers in a process called vulcanization.
  - Network Polymers
    - Multifunctional monomers forming three or more active covalent bonds make three dimensional networks.

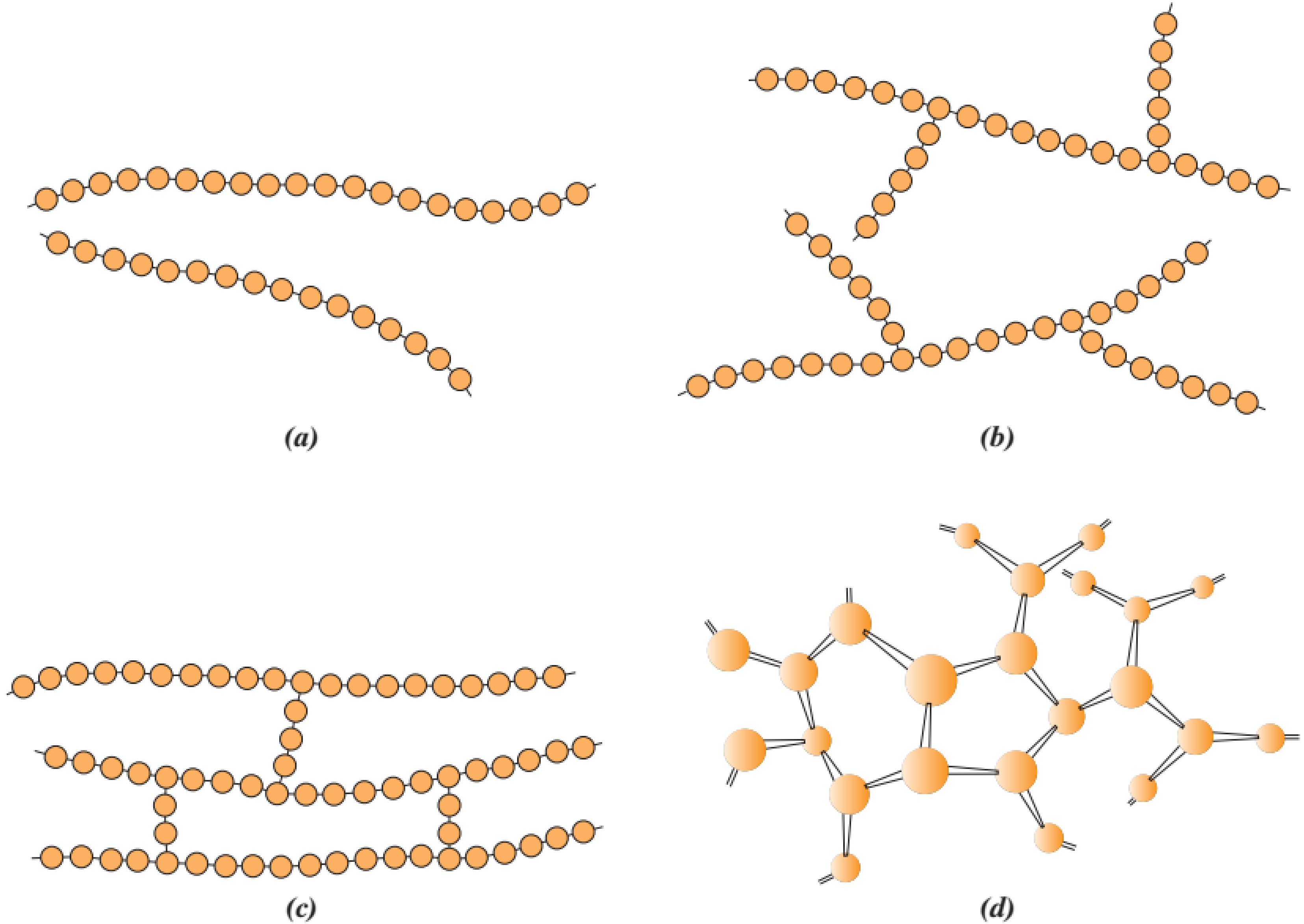


Figure 14.7 Schematic representations of (*a*) linear, (*b*) branched, (*c*) crosslinked, and (*d*) network (three-dimensional) molecular structures. Circles designate individual repeat units.

Concept Check!!!

- How does vulcanization change the physical properties of rubber?

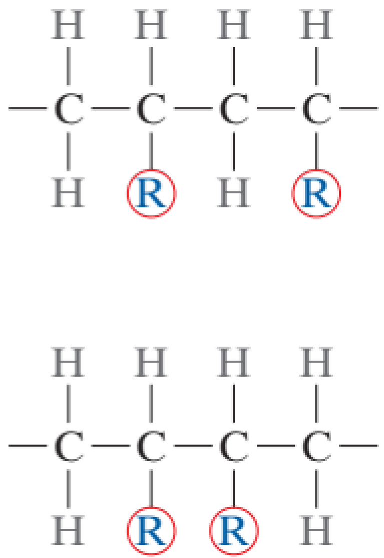
- Which polymer structure is the most rigid?

Pop Quiz!!!

- Which bonds are flexible and rotate?
- What characteristics have we covered so far that determine the physical properties of polymers?

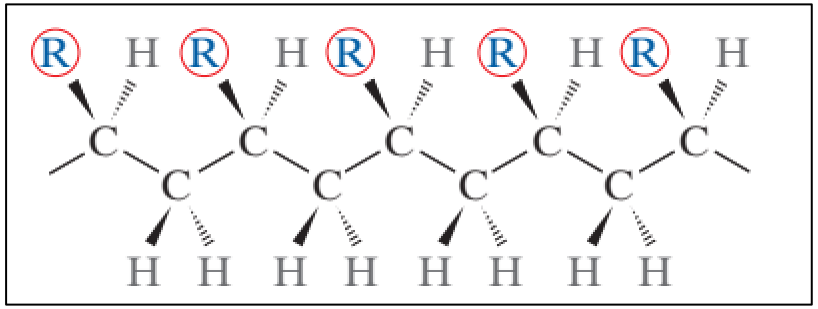
14.8 Molecular Configuration

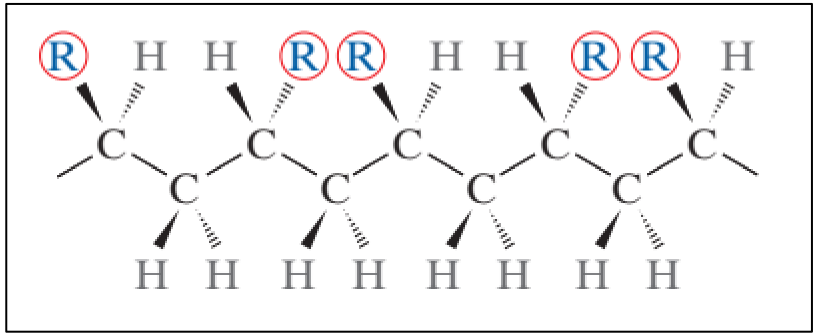
- The configuration of the repeating units can change physical properties. (Isomerism)
  - Heat-to-tail configuration predominates.
  - Head-to-head configuration is not chemically favorable.
    - Polar or geometric repulsion prevents this configuration sometimes

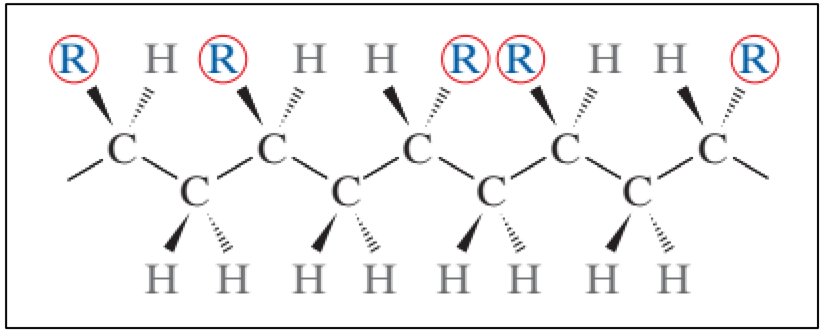


14.8 Molecular Configuration

- Stereoisomerism: Atoms linked together in the same order, but different spatial arrangement.
  - Isotactic configuration: R groups on the same side.
  - Syndiotactic configuration: R groups alternate sides.
  - Atactic configuration: R group placement is random.



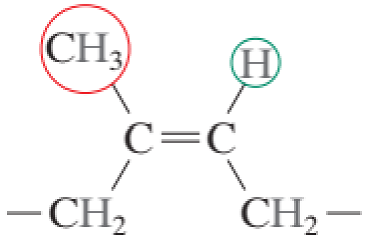




14.8 Molecular Configuration

- Geometric Isomerism
  - Repeat unit contains a rigid bond
  - Cis
  - Trans

Cis



Trans

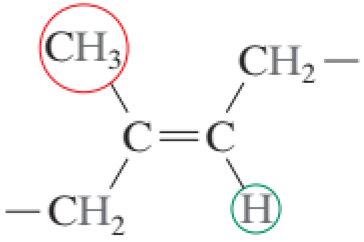
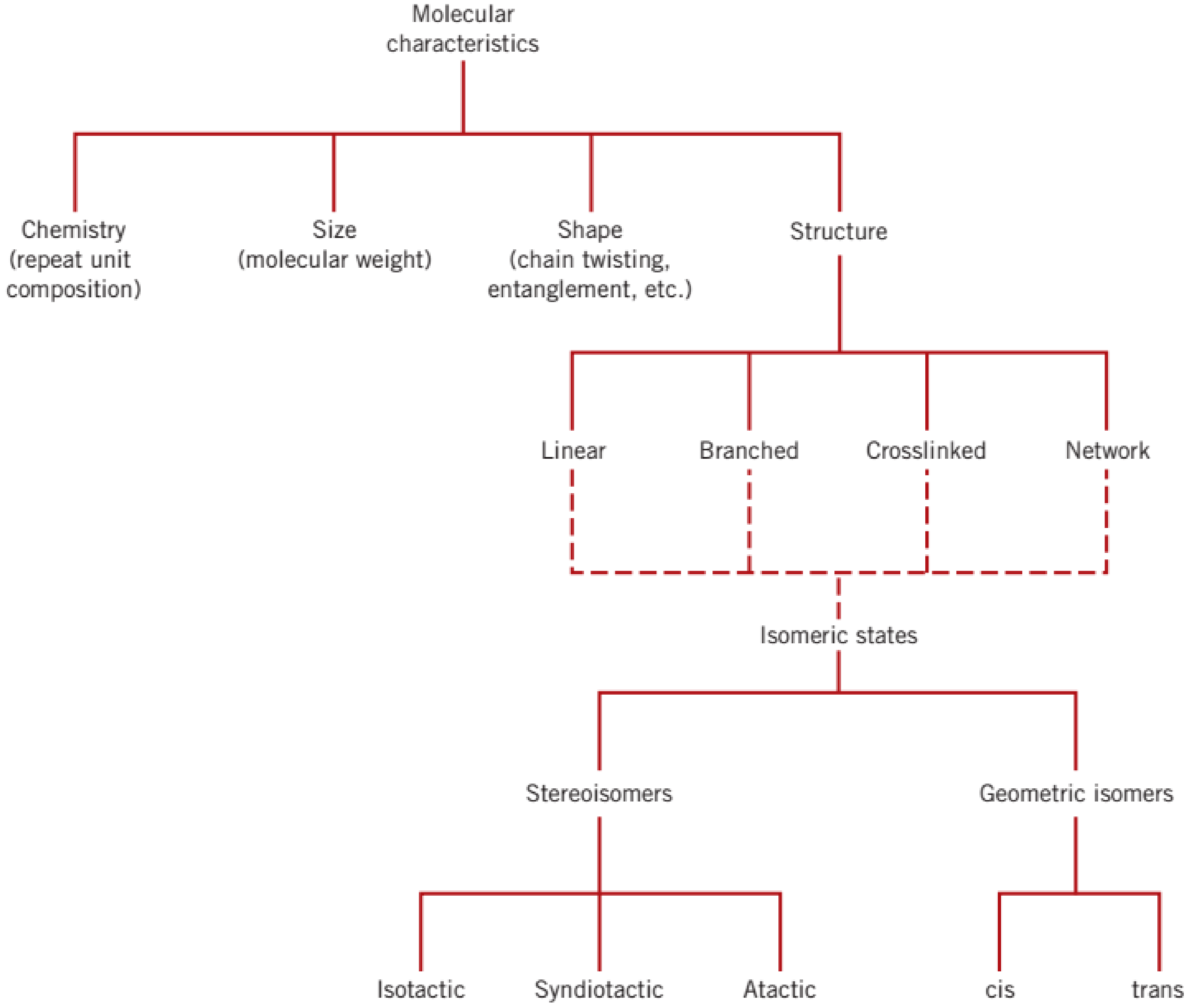


Figure 14.8
Classification scheme for the characteristics of polymer molecules.



Concept Check!!!

- What is the difference between conformation and configuration when discussing polymers?

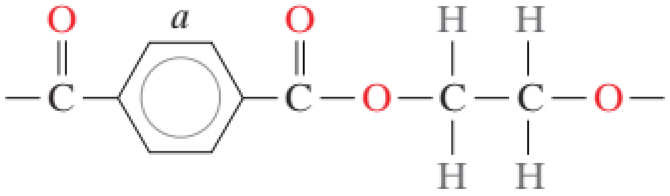
14.9 Thermoplastic and Thermosetting Polymers

- Thermoplastic polymer
  - Plastic means moldable and shapeable.
  - Reversibly soften (and melt) when heated and harden when cooled
  - Secondary bonding forces diminish with heat, molecules can move.
  - Don’t get too hot! Carbon bonds have their limit!
- Thermosetting polymer
  - Network and crosslink polymers.
  - Do not soften when heated.
  - Harder and stronger than plastics
  - 10%-50% of the chain repeat units are crosslinked

Concept Check!!!

- What type of bonds hold a thermoset polymer together? What bonds hold thermoplastic polymer together?
- Some polymers can be both thermoplastic or thermosetting. How does THAT work?

Poly(ethylene terephthalate)
(PET, a polyester)



14.10 Copolymers

- (a) Random Copolymer
- (b) Alternating Copolymer
- (c) Block Copolymer
- (d) Graft Copolymer
- Often used in rubbers

- Degree of Polymerization is modified.

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

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

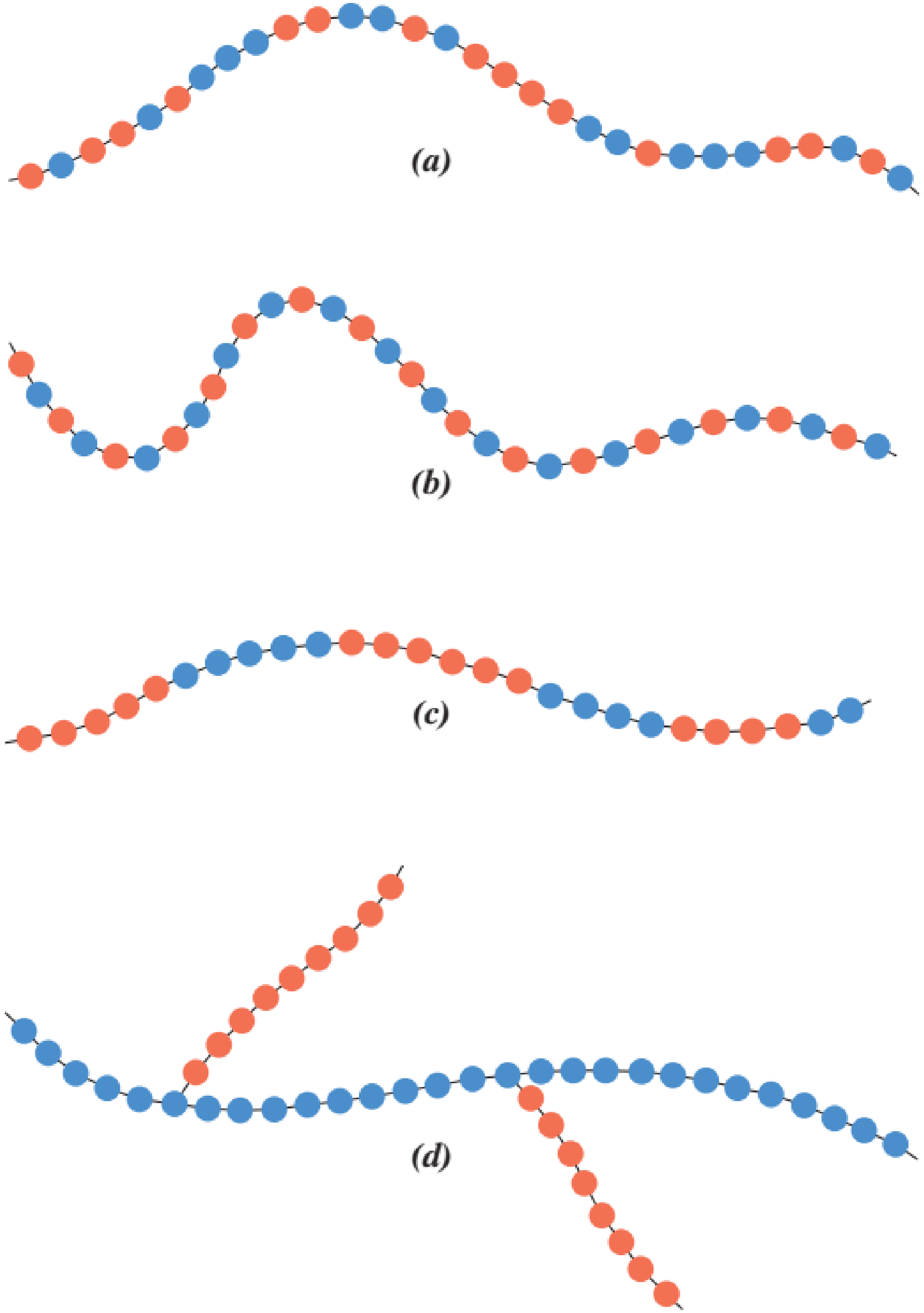
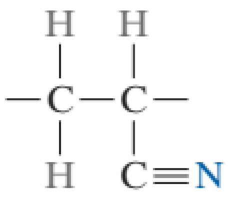
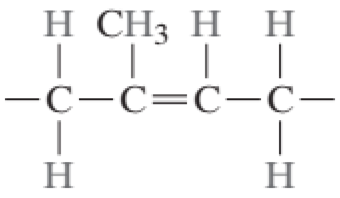
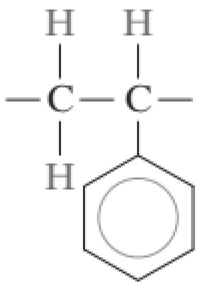
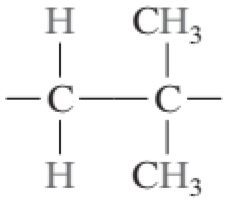
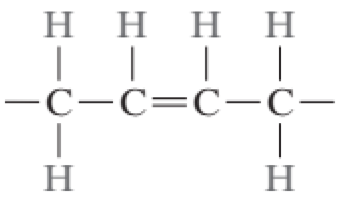
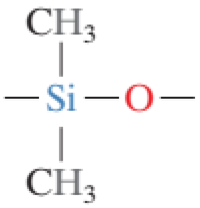
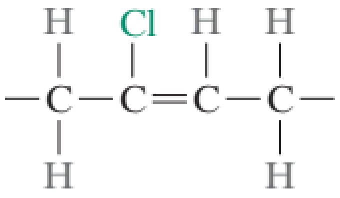


Table 14.5 Chemical Repeat Units That Are Employed in Copolymer Rubbers

Repeat Unit Name	*Repeat Unit Structure*	*Repeat Unit Name*	*Repeat Unit Structure*
VMSE Repeat Units for Rubbers Acrylonitrile	 $-\mathrm{CH_2}-\mathrm{CH}(\mathrm{C{\equiv}N})-$	**VMSE** Isoprene	 $-\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})=\mathrm{CH}-\mathrm{CH_2}-$
VMSE Styrene		**VMSE** Isobutylene	 $-\mathrm{CH_2}-\mathrm{C}(\mathrm{CH_3})_2-$
VMSE Butadiene	 $-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CH_2}-$	**VMSE** Dimethylsiloxane	 $-\mathrm{Si}(\mathrm{CH_3})_2-\mathrm{O}-$
VMSE Chloroprene	 $-\mathrm{CH_2}-\mathrm{C}(\mathrm{Cl})=\mathrm{CH}-\mathrm{CH_2}-$		

Concept Check!!!

- How is a graft polymer different from a crosslinked polymer?

14.11 Polymer Crystallinity

- The packing of molecular chains to produce an ordered atomic array.
- Crystal structures are called Unit Cells

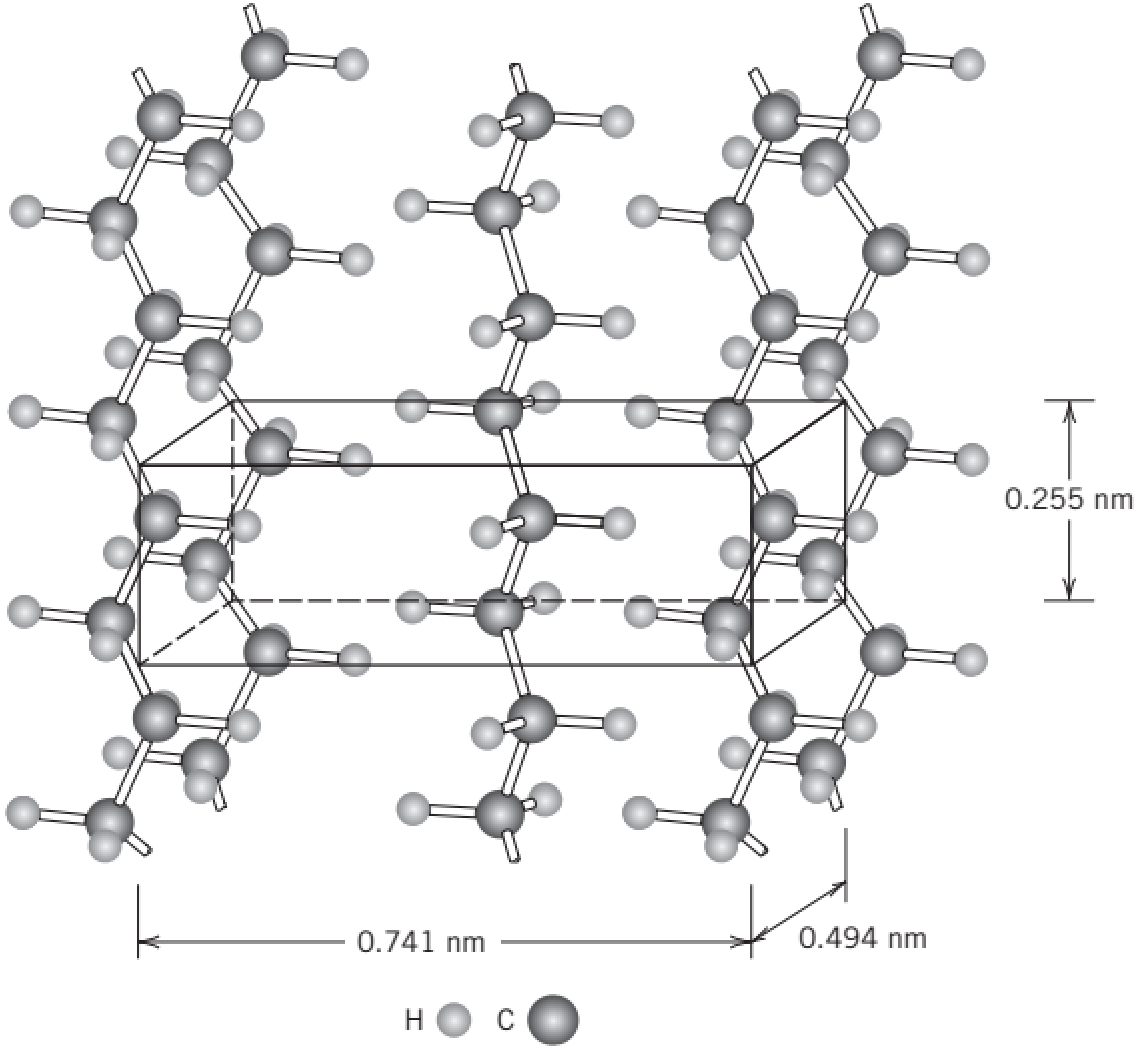
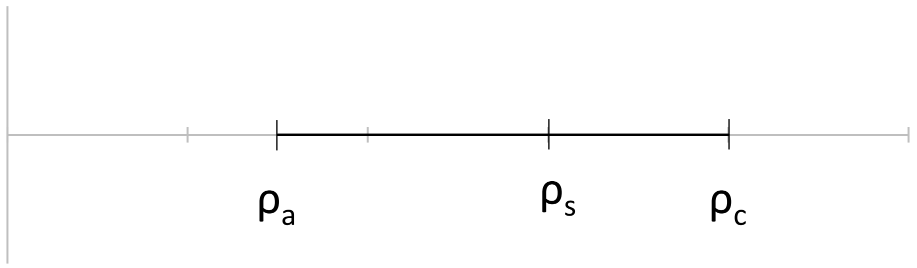


Figure 14.10 Arrangement of molecular chains in a unit cell for polyethylene.

14.11 Polymer Crystallinity

- Small molecules are usually binary; amorphous (liquid) or solid
- Polymers exist on the spectrum of crystallinity.
  - Some segments of chains can form unit cells and pack in crystal form. Other areas will have twists, kings, and coils that prevent close packing.
- % Crystallinity is calculated from the density of the material.

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



14.11 Polymer Crystallinity

- Degree of crystallinity
  - Depends on cooling rate. Slower means more crystals.
  - Depends on functional groups and configuration.
    - Linear polymers, readily crystalize.
    - Side branches prevent local crystallization.
    - Crosslinks and networks prevent crystallization.
    - Atactic polymers do not crystalize readily
    - Bulky side bonds hinder crystallization.
    - Ordered copolymers can crystallize, while random configurations will not.
- Crystal structure compared to amorphous
  - Stronger
  - Resistant to dissolution and softening by heat

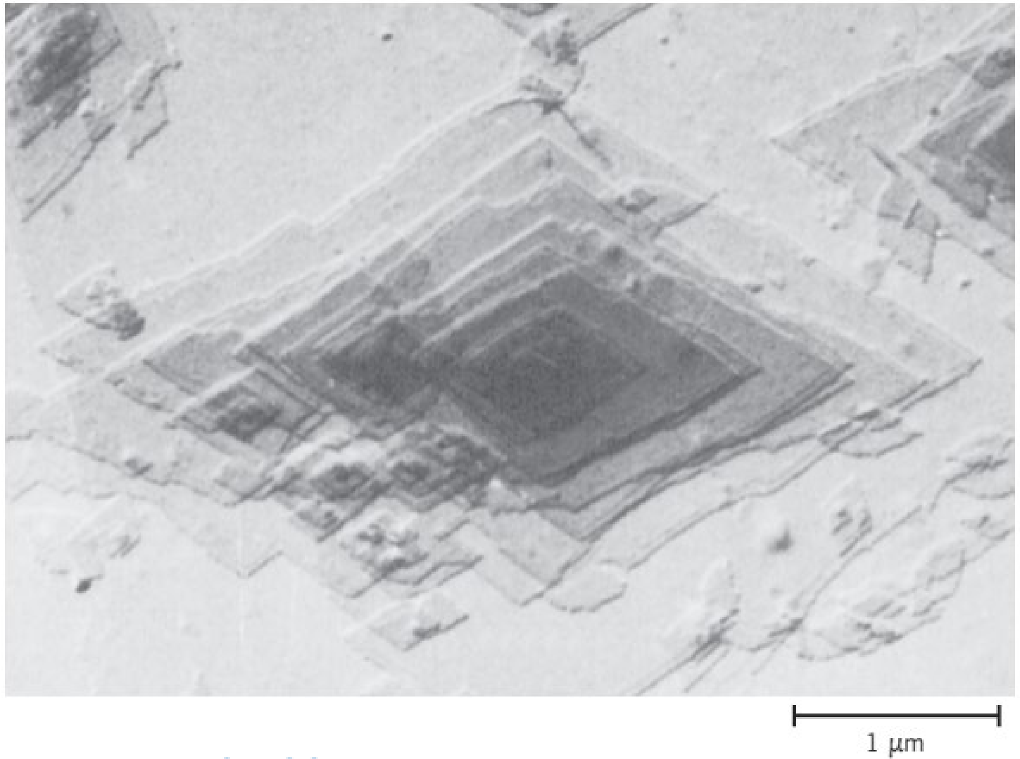
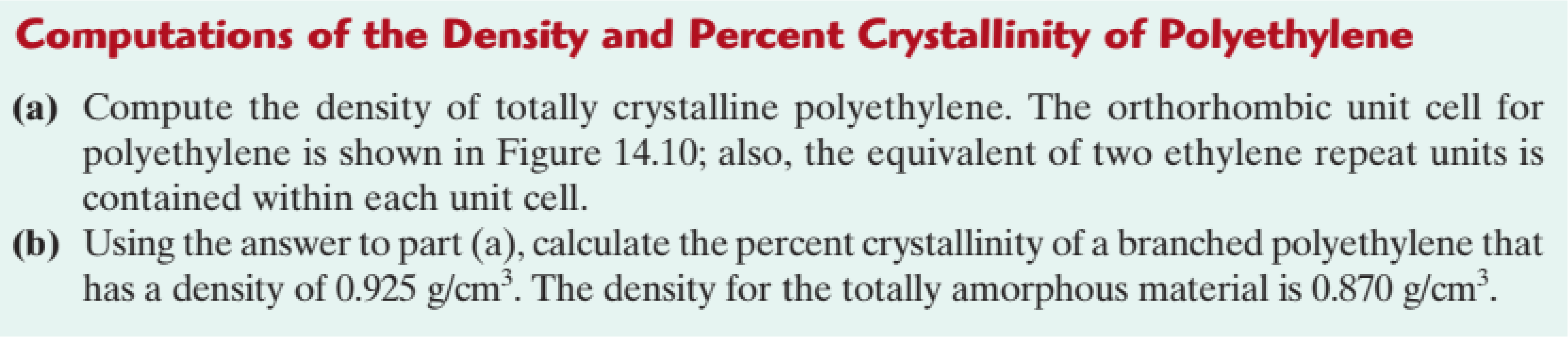


Figure 14.11 Electron micrograph of a polyethylene single crystal. 20,000×. [From A. Keller, R. H. Doremus, B. W. Roberts, and D. Turnbull (Editors), *Growth and Perfection of Crystals.* General Electric Company and John Wiley & Sons, Inc., 1958, p. 498. Reprinted with permission of John Wiley & Sons,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



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.

(a) Equation 3.8, 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, namely,

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

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 3.8 of this value, values for n and A cited previously, and the value of N_A leads to

$$\begin{aligned} \rho &= \frac{nA}{V_C N_A} \\ &= \frac{(2\ \text{repeat units/unit cell})(28.05\ \text{g/mol})}{(9.33 \times 10^{-23}\ \text{cm}^3/\text{unit cell})(6.022 \times 10^{23}\ \text{repeat units/mol})} \\ &= 0.998\ \text{g/cm}^3 \end{aligned}$$

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.

(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,

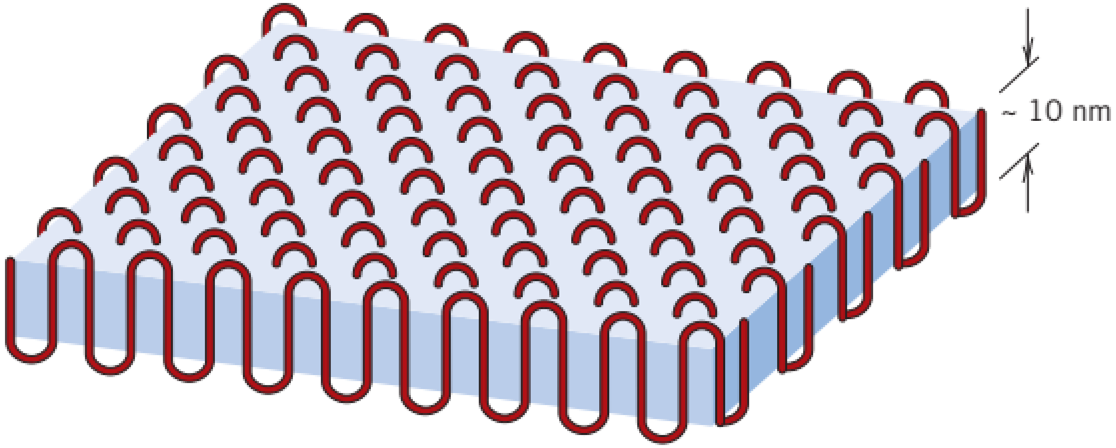
$$\begin{aligned}\%\text{ crystallinity} &= \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100 \\ &= \frac{0.998\text{ g/cm}^3\,(0.925\text{ g/cm}^3 - 0.870\text{ g/cm}^3)}{0.925\text{ g/cm}^3\,(0.998\text{ g/cm}^3 - 0.870\text{ g/cm}^3)} \times 100 \\ &= 46.4\%\end{aligned}$$

Concept Check!!!

- Does polyisoprene readily form a crystalline structure? Why/why not?
- Compare the crystalline state in metals and polymers.
- Compare the non-crystalline state as it applies to polymers and ceramic glasses.

14.12 Polymer Crystals

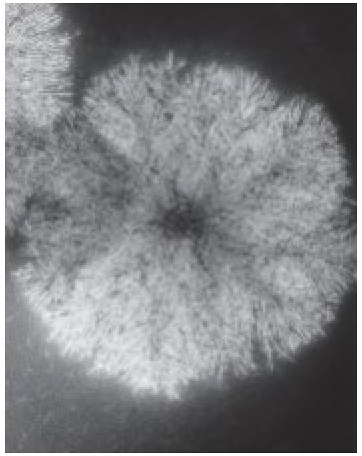
- Crystallites: small crystal regions in a polymer
    - Form thin plates called lamellae (10-12 nm thick, 10 μm long)
    - Plates for multilayer structures called chain-folded model



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

14.12 Polymer Crystals

- Spherulite
  - Ribbon-like growth (lamellae) from a central nucleation point at the center.



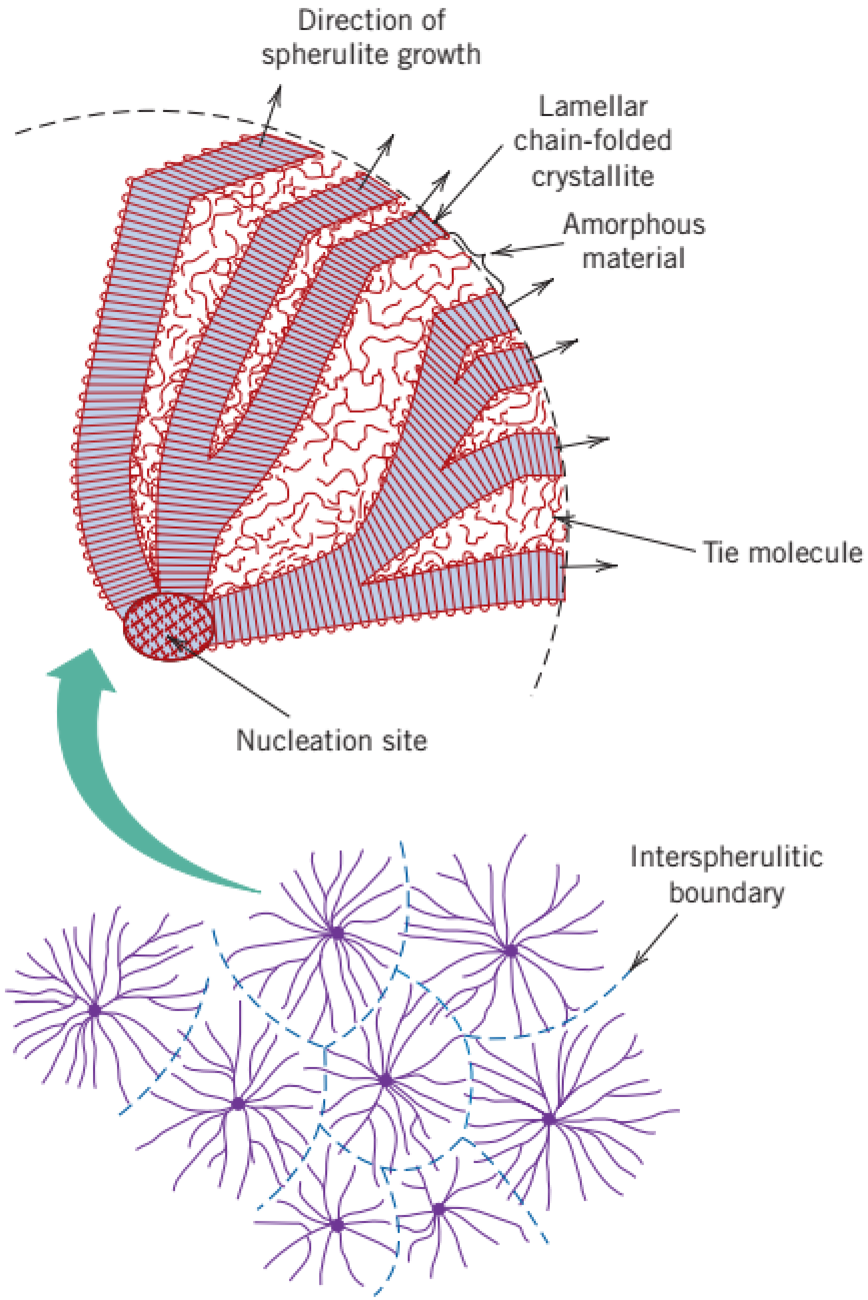
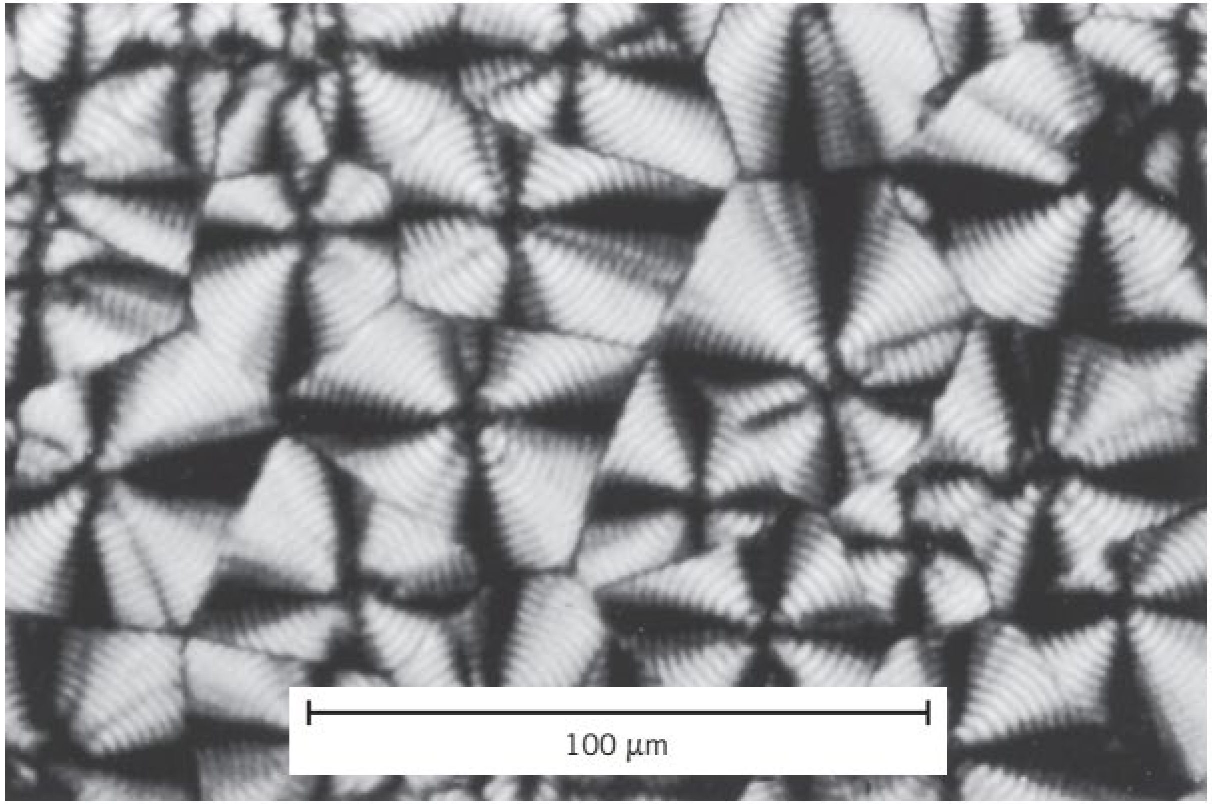


Figure 14.13 Schematic representation of the detailed structure of a spherulite.

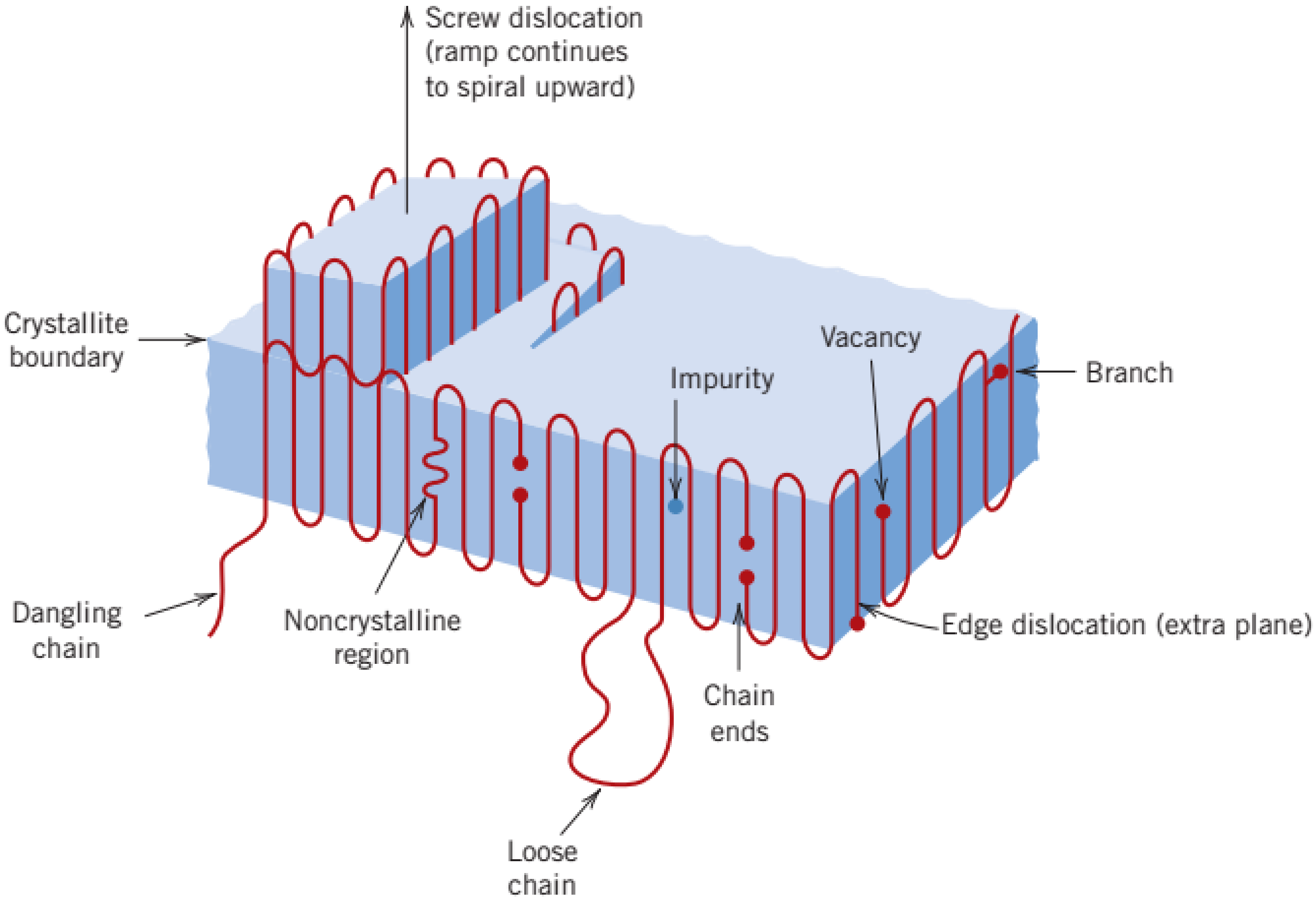
Figure 14.14 A transmission photomicrograph (using cross-polarized light) showing the spherulite structure of polyethylene. Linear boundaries form between adjacent spherulites, and within each spherulite appears a Maltese cross. 525×.



Courtesy F. P. Price, General Electric Company

14.13 Defects in Polymers

- Point defects:
  - Similar, but different from metals and ceramics
  - Vacancies and interstitial atoms and ions occur
  - Chain ends are defects because they are chemically different from repeating units (also create vacancies).
  - Branches make defects
  - Chains can leave, and then reenter, or join another crystal



Concept Check!!!

- What fills in the space between the lamellae?

14.14 Diffusion in Polymeric Materials

- Small molecules can move through polymer molecular chain structures. (Permeability and Absorption)
  - Permeability can lead to swelling and/or chemical reactions, disrupting the crystal structures.
- Diffusion is faster for the a foreign molecule (e.g.,O_2, H_2O, CO_2, CH_4) when it is:
  - Moving in amorphous section and not crystal section.
  - Small
  - Inert (doesn’t chemically interact with the polymer chain structures)

14.14 Diffusion in Polymeric Materials

- Two steps in permeation through a polymer membrane:
  - Dissolution
  - Diffusion
- Estimate permeability coefficient:
  - Small molecules in non-glassy polymers

Steady-state diffusion

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

Permeability coefficient model

$$P_M = DS$$

Table 14.6

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

		P_M [× 10^{-13} (cm³ STP)(cm)/(cm²·s·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.

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[13] The units for permeability coefficients in Table 14.6 are unusual and 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 (cm³ STP gas)/cm³ polymer] 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 (cm³ STP)/Pa·cm³. Because D is expressed in terms of cm²/s, the units for the permeability coefficient are (cm³ STP)(cm)/(cm²·s·Pa).

Concept Check!!!

- What are some applications where you want to have gasses pass through a membrane?
- What are some applications where you **DO NOT** want to have gasses pass through a membrane?

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 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.

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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)/($\text{cm}^2 \cdot \text{s} \cdot \text{Pa}$). Thus, the diffusion flux is

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

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

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

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 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.

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Note: Assume that each bottle has a surface area of 500 cm^2 and a wall thickness of 0.05 cm.

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

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

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

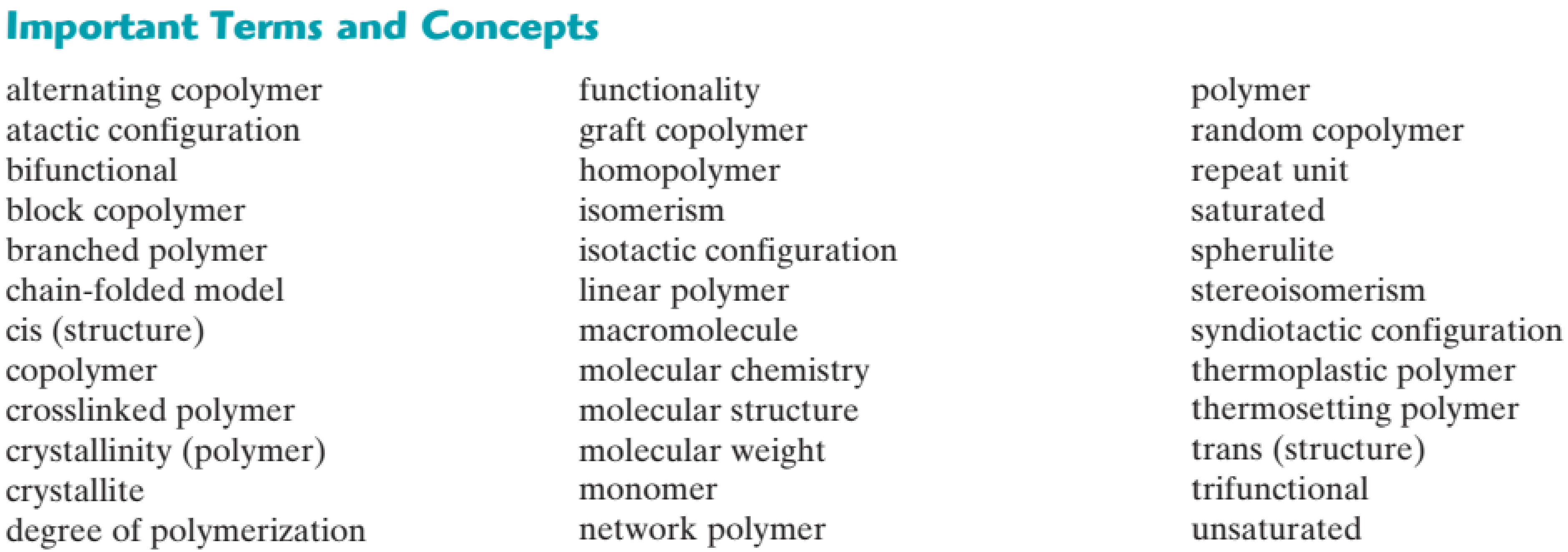
$$\dot{V}_{CO_2} = [1.8 \times 10^{-7}(\text{cm}^3\text{STP})/(\text{cm}^2\cdot\text{s})](500\ \text{cm}^2) = 9.0 \times 10^{-5}\,(\text{cm}^3\ \text{STP})/\text{s}$$

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

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

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

Concept Check!!!



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

Equation Summary

Equation Number	Equation	Solving For
14.5a	$\overline{M}_n = \Sigma x_i M_i$	Number-average molecular weight
14.5b	$\overline{M}_w = \Sigma w_i M_i$	Weight-average molecular weight
14.6	$DP = \dfrac{\overline{M}_n}{m}$	Degree of polymerization
14.7	$\overline{m} = \Sigma f_j m_j$	For a copolymer, average repeat unit molecular weight
14.8	$\% \text{ crystallinity} = \dfrac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$	Percent crystallinity, by weight
14.9	$J = -P_M \dfrac{\Delta P}{\Delta x}$	Diffusion flux for steady-state diffusion through a polymer membrane

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