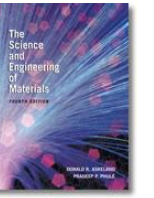


Polymers

introduction

- Discuss the classification of Polymers
- Learn two main ways of creating a Polymer
- Study the effect of temperature on Thermoplastics
- Study mechanical properties of Thermoplastics

- 1 Classification of Polymers
- 2 Addition Polymerization
- 3 Condensation Polymerization
- 4 Degree of Polymerization
- 5 Typical Thermoplastics
- 6 Structure–Property Relationships in Thermoplastics
- 7 Effect of Temperature on Thermoplastics

)

- 8 Mechanical Properties of Thermoplastics
- 9 Elastomers (Rubbers)
- 10 Thermosetting Polymers
- 11 Adhesives
- 12 Additives for Plastics
- 13 Polymer Processing and Recycling

Classification of Polymers

- Linear polymer - Any polymer in which molecules are in the form of spaghetti-like chains.
- Thermoplastics - Linear or branched polymers in which chains of molecules are not interconnected to one another.
- Thermosetting polymers - Polymers that are heavily cross-linked to produce a strong three dimensional network structure.
- Elastomers - These are polymers (thermoplastics or lightly cross-linked thermosets) that have an elastic deformation > 200%.

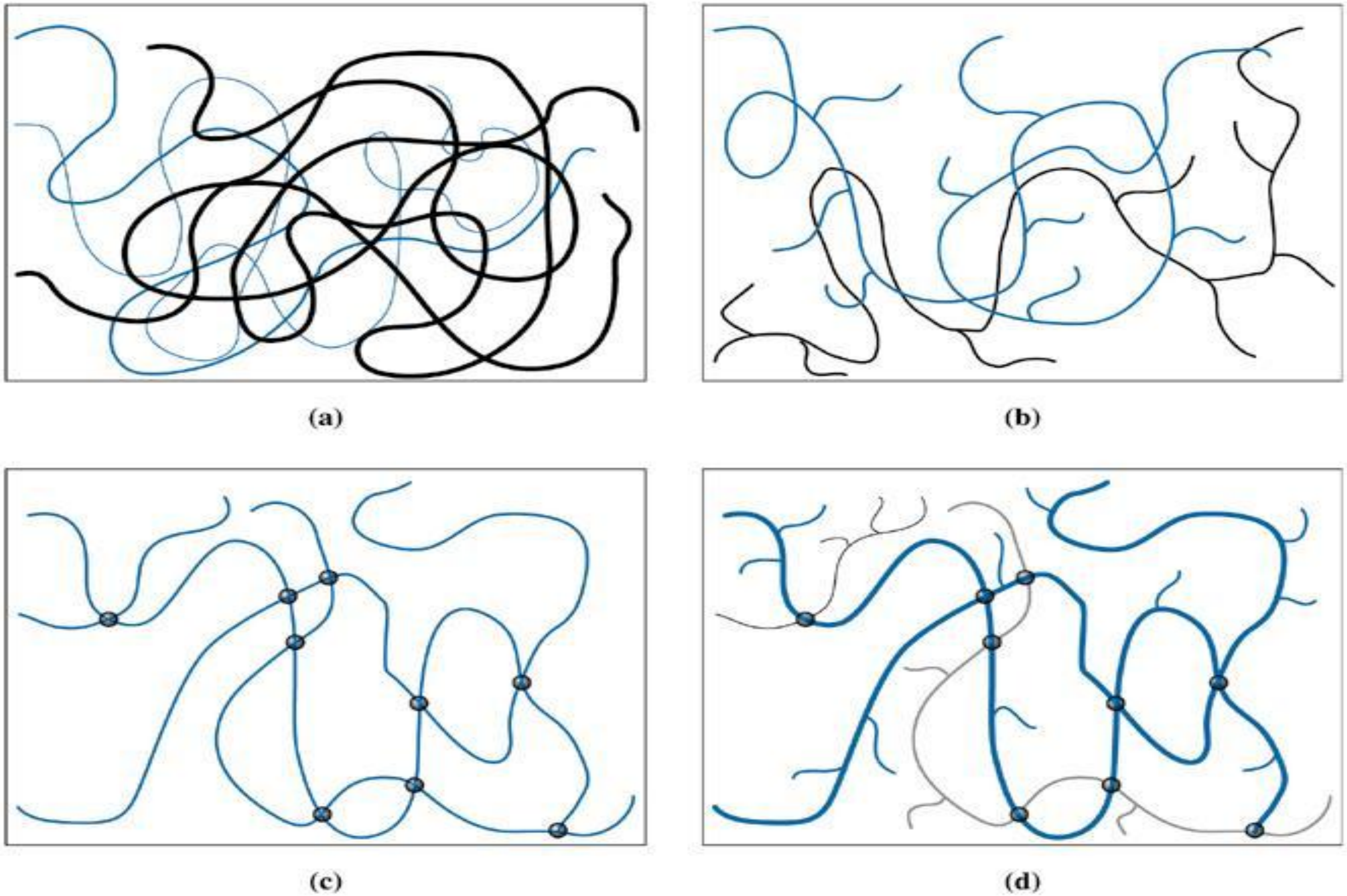
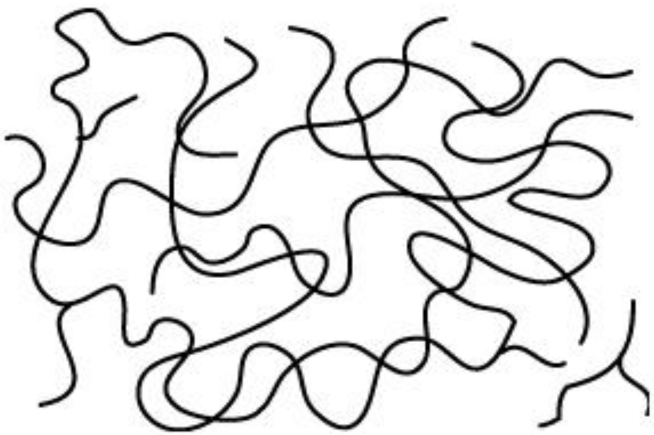


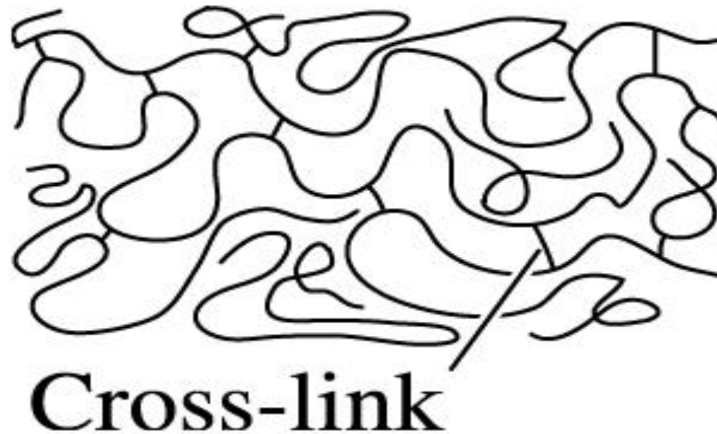
Figure 1 Schematic showing linear and branched polymers. Note that branching can occur in any type of polymer (e.g., thermoplastics, thermosets, and elastomers). (a) Linear unbranched polymer: notice chains are not straight lines and not connected. Different polymer chains are shown using different shades and design to show clearly that each chain is not connected to another. (b) Linear branched polymer: chains are not connected, however they have branches. (c) Thermoset polymer without branching: chains are connected to one another by covalent bonds but they do not have branches. Joining points are highlighted with solid circles, (d) Thermoset polymer that has branches and chains that are interconnected via covalent bonds. Different chains and branches are shown in different shades for better contrast. Places where chains are actually chemically bonded are shown with filled circles.

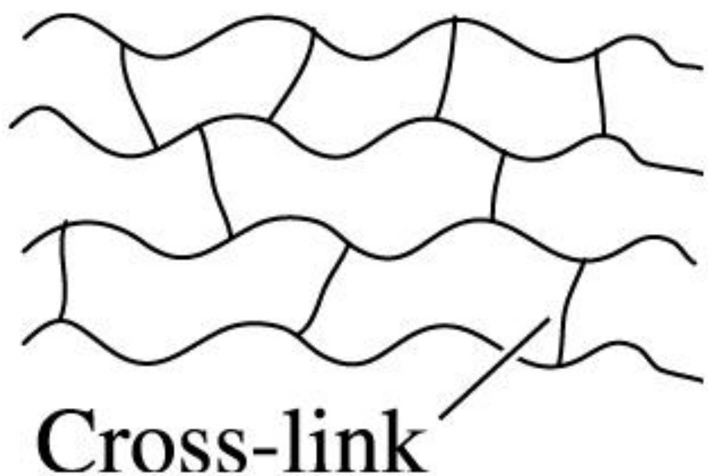
TABLE 15-1 ■ ***Comparison of the three polymer categories***

Behavior	General Structure	Example
Thermoplastic	Flexible linear chains (straight or branched)	Polyethylene
Thermosetting	Rigid three-dimensional network (chains may be linear or branched)	Polyurethanes
Elastomers	Thermoplastics or lightly cross-linked thermosets, consist of spring-like molecules	Natural rubber

Table 15.1 Comparison of the three polymer categories







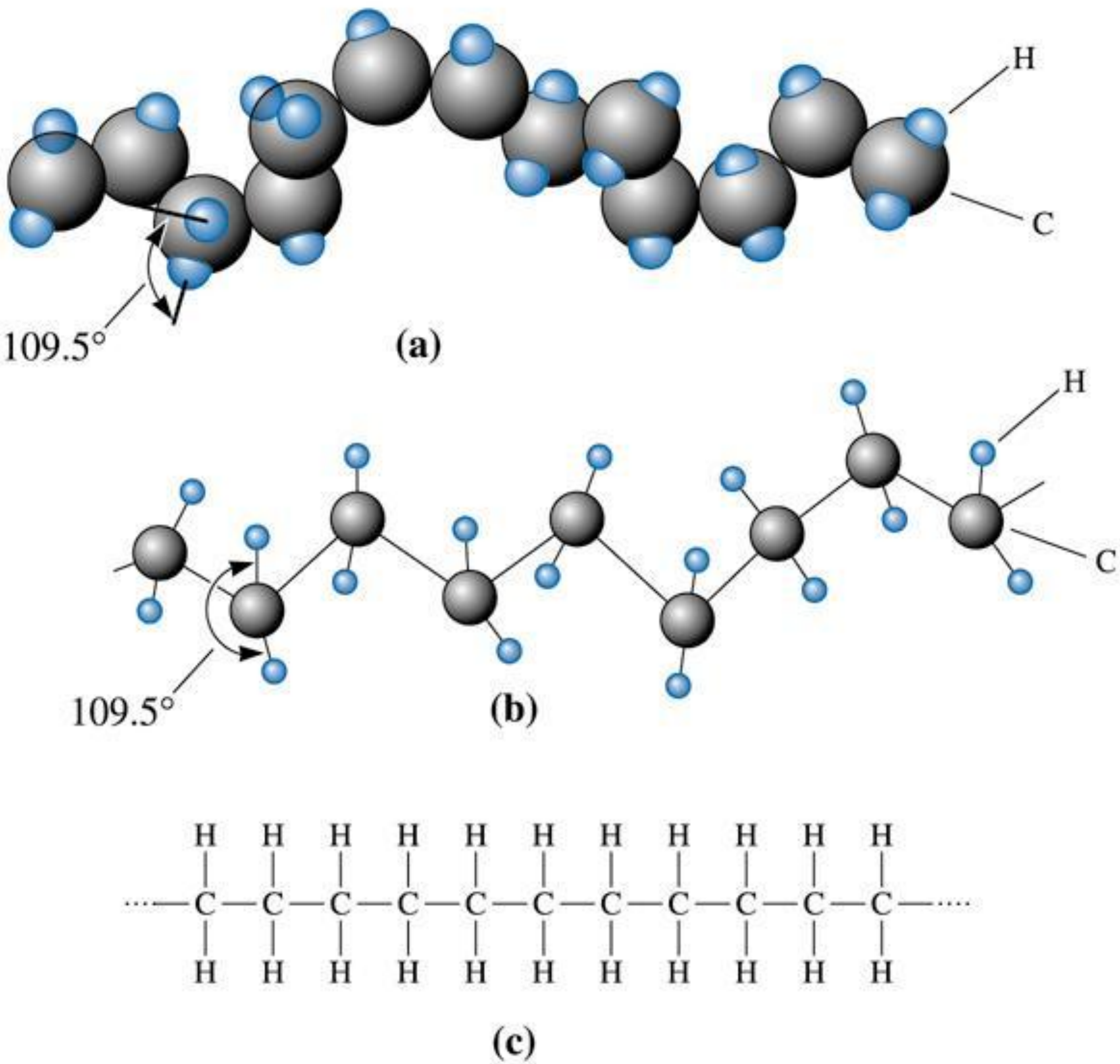
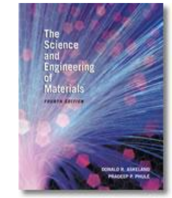


Figure 2 Three ways to represent the structure of polyethylene: (a) a solid three-dimensional model, (b) a three-dimensional "space" model, and (c) a simple two-dimensional model.



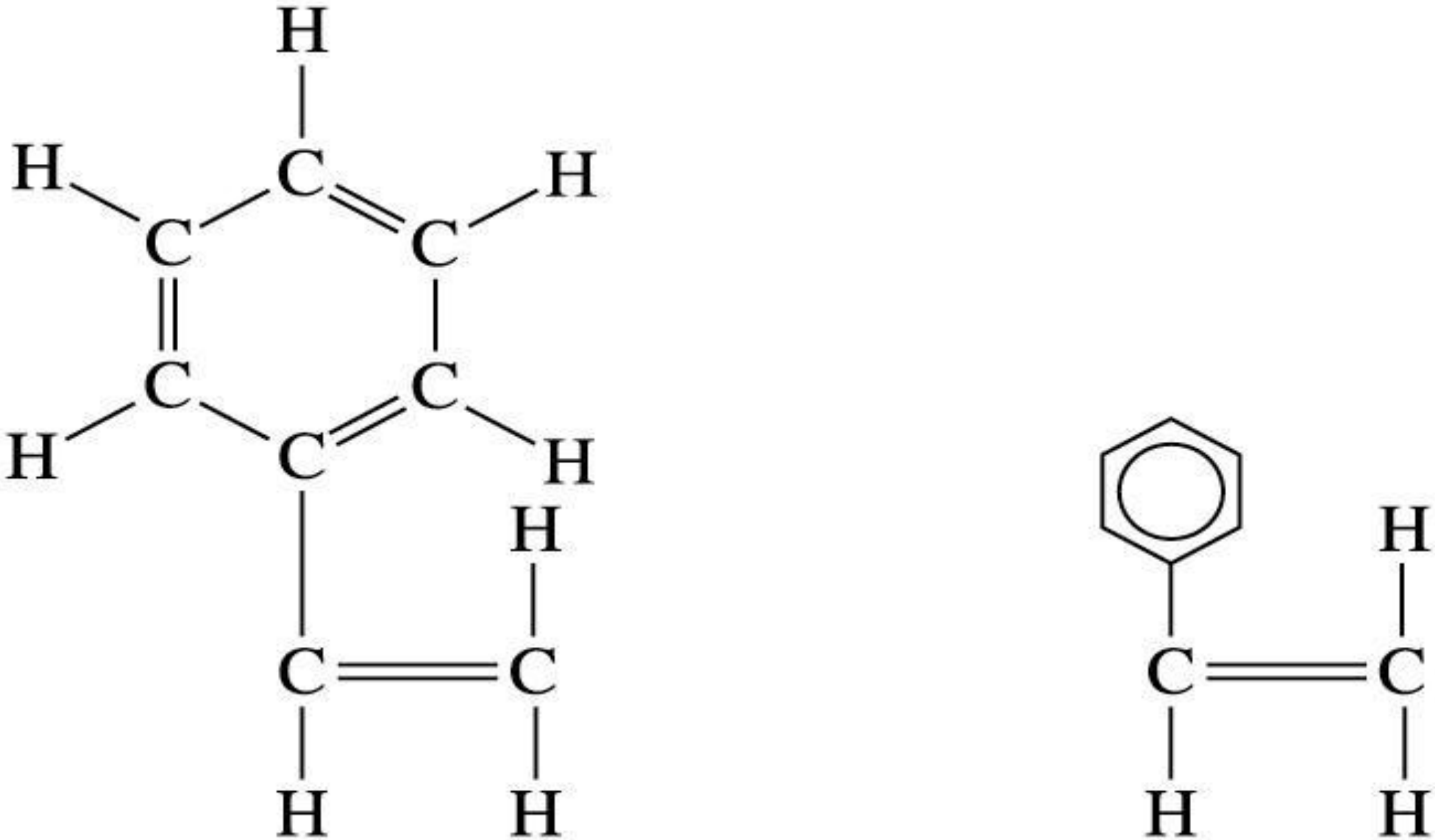
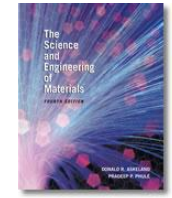


Figure 3 Two ways to represent the benzene ring. In this case, the benzene ring is shown attached to a pair of carbon atoms, producing styrene.



Example 1
Design/Materials Selection for Polymer Components

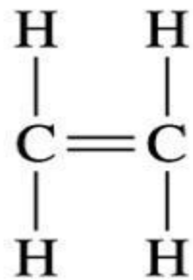
Design the type of polymer material you might select for the following applications: a surgeon's glove, a beverage container and a pulley.

Example 1 SOLUTION

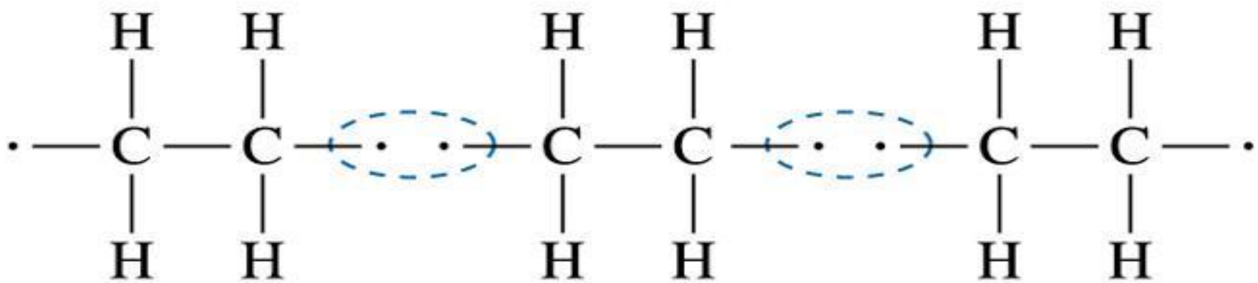
- The glove must be capable of stretching a great deal in order to slip onto the surgeon's hand. This requirement describes an elastomer.
- A thermoplastic such as polyethylene terephthalate (PET) will have the necessary formability and ductility needed for this application.
- A relatively strong, rigid, hard material is required to prevent wear, so a thermosetting polymer might be most appropriate.

Addition Polymerization

- Addition polymerization - Process by which polymer chains are built up by adding monomers together without creating a byproduct.
- Unsaturated bond - The double- or even triple-covalent bond joining two atoms together in an organic molecule.
- Functionality - The number of sites on a monomer at which polymerization can occur.

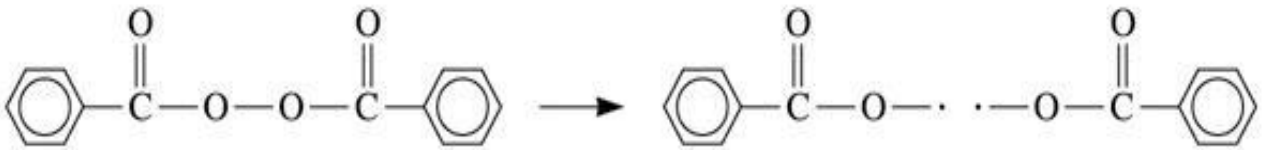


Ethylene monomer

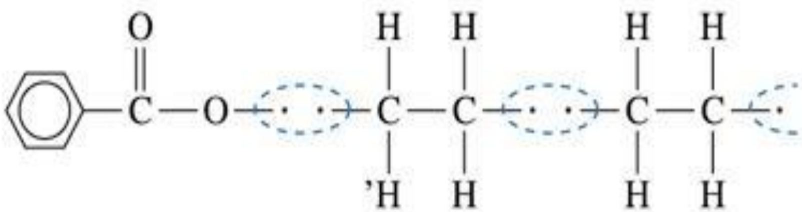


Ethylene repeat units

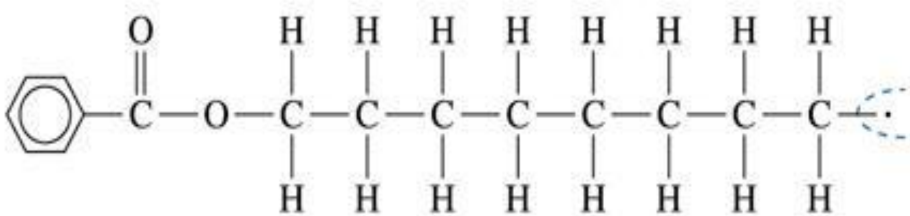
Figure 4 The addition reaction for producing polyethylene from ethylene molecules. The unsaturated double bond in the monomer is broken to produce active sites, which then attract additional repeat units to either end to produce a chain.



(a)



(b)



(c)

Figure 5 Initiation of a polyethylene chain by chain-growth may involve (a) producing free radicals from initiators such as benzoyl peroxide, (b) attachment of a polyethylene repeat unit to one of the initiator radicals, and (c) attachment of additional repeat units to propagate the chain.

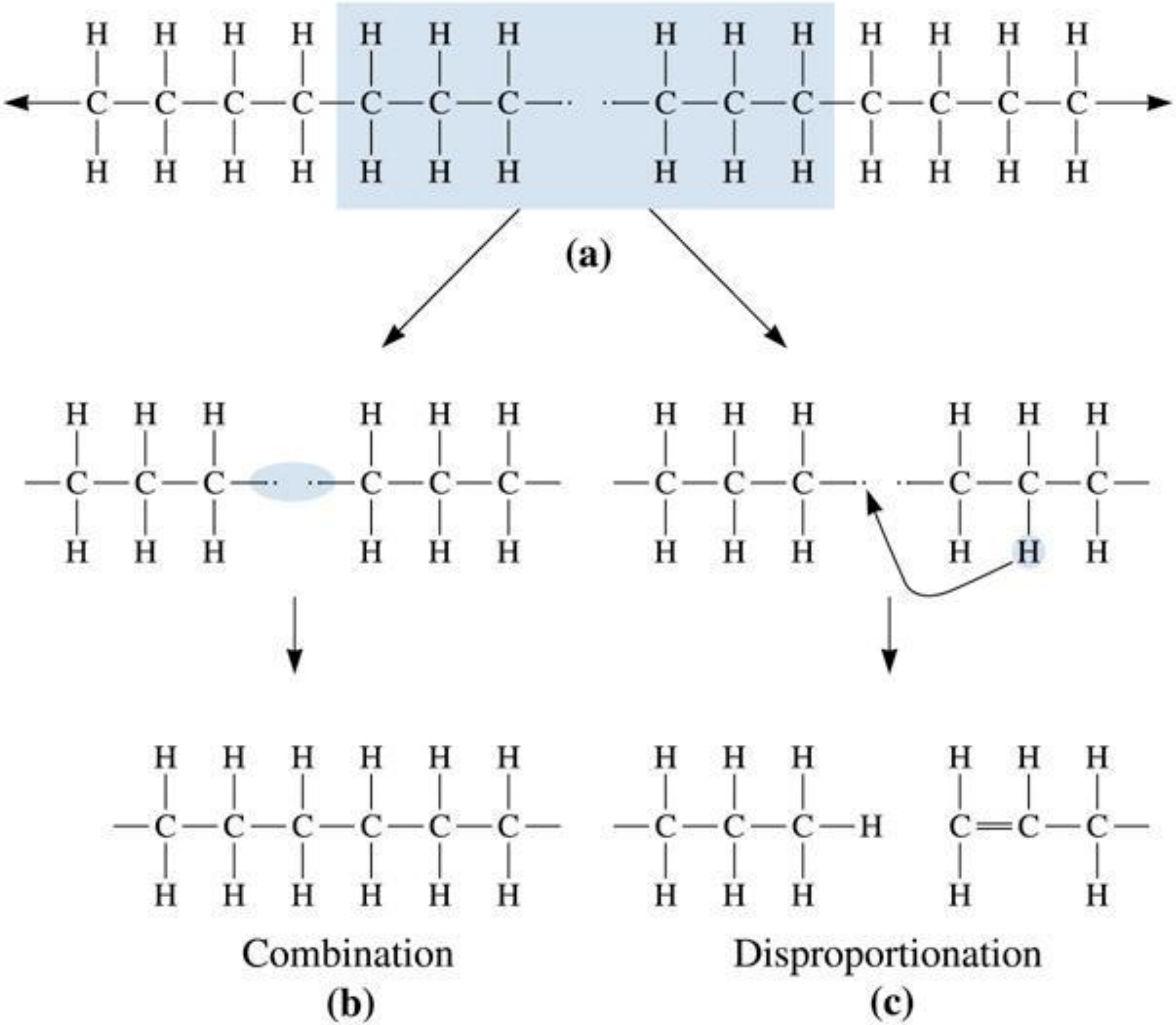


Figure 6 Termination of polyethylene chain growth: (a) the active ends of two chains come into close proximity, (b) the two chains undergo combination and become one large chain, and (c) rearrangement of a hydrogen atom and creation of a double covalent bond by disproportionation cause termination of two chains.

Example 2
Calculation of Initiator Required

Calculate the amount of benzoyl peroxide initiator required to produce 1 kg of polyethylene with an average molecular weight of 200,000 g/mol. What is the degree of polymerization? Assume that 20% of the initiator is actually effective and that all termination occurs by the combination mechanism.

Example 2 SOLUTION

The molecular weight of ethylene = (2 C)(12) + (4 H)(1) = 28 g/mol. Therefore, the degree of polymerization is:

$$\frac{200{,}000\ \text{g/mol}}{28\ \text{g/mol}} = 7143\ \text{ethylene molecules per average chain}$$

$$\frac{(1000\ \text{g polyethylene})(6.02\times10^{23}\ \text{monomers/mol})}{28\ \text{g/mol}} = 215\times10^{23}\ \text{monomers}$$

Example 2 SOLUTION (Continued)

The combination mechanism requires the number of benzoyl peroxide molecules to be:

$$\frac{215 \times 10^{23} \text{ ethylene molecules}}{7143 \text{ ethylene / chain}} = 0.03 \times 10^{23}$$

The molecular weight of benzoyl peroxide is (14 C)(12) + (10 H)(1) + (4 O)(16) = 242 g/mol. Therefore, the amount of initiator needed to form the ends of the chains is:

$$\frac{(0.03 \times 10^{23})(242 \text{ g/mol})}{6.02 \times 10^{23}} = 1.206 \text{ g}$$

Condensation Polymerization

- Condensation polymerization - A polymerization mechanism in which a small molecule (e.g., water, methanol, etc.) is condensed out as a byproduct.

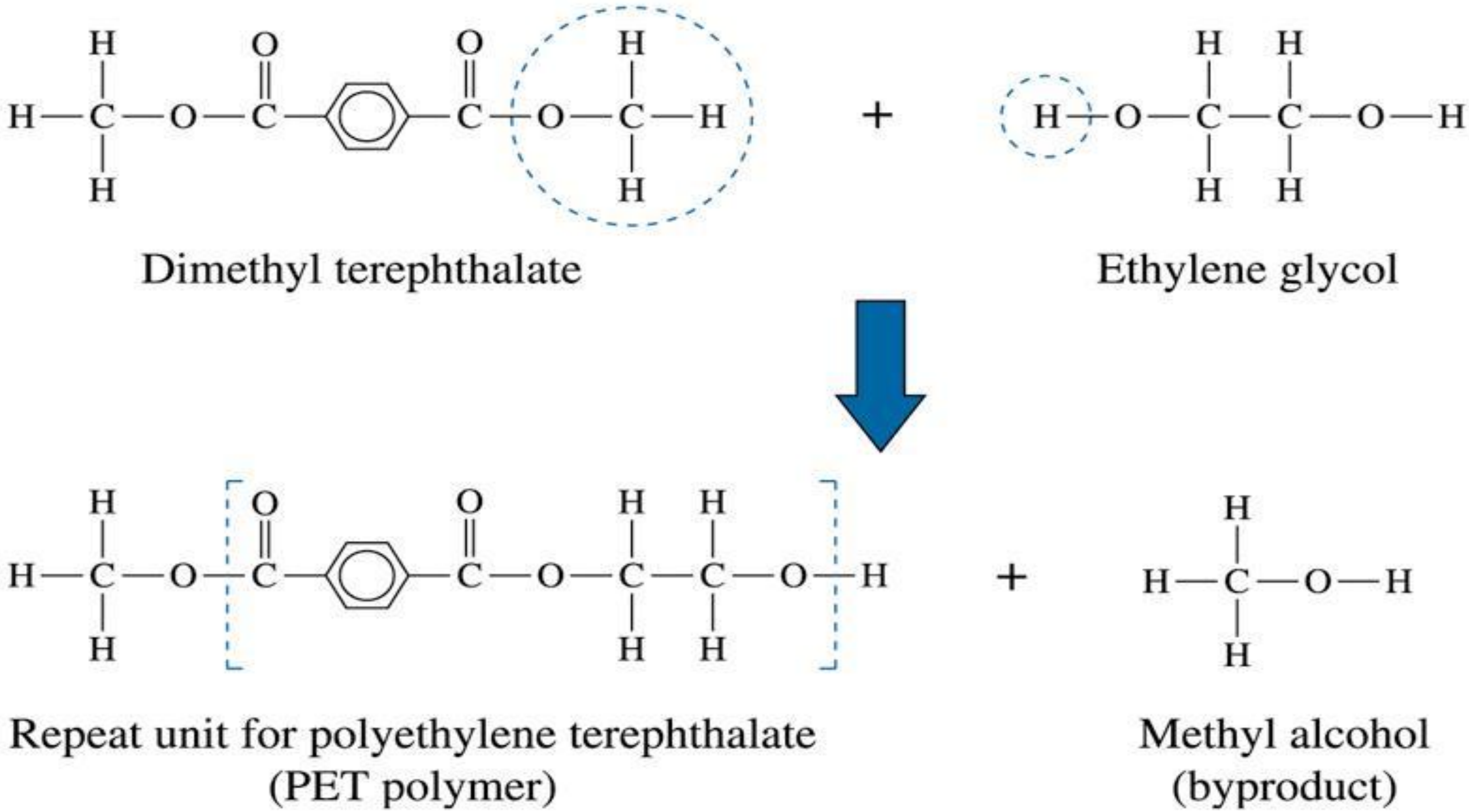


Figure 7 The condensation reaction for polyethylene terephthalate (PET), a common polyester. The OCH3 group and a hydrogen atom are removed from the monomers, permitting the two monomers to join and producing methyl alcohol as a byproduct.

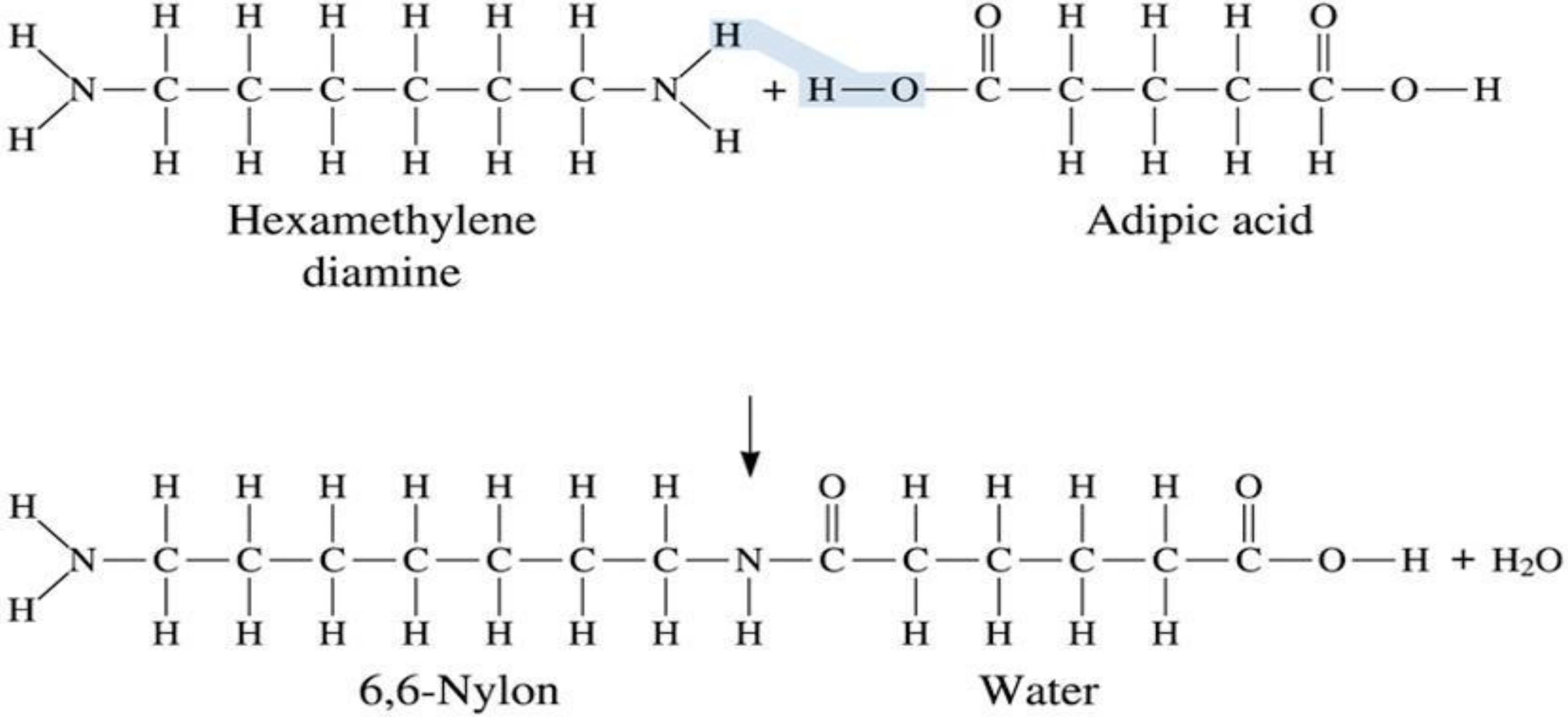
Example 3
Condensation Polymerization of 6,6-Nylon

Nylon was first reported by Wallace Hume Carothers, of du Pont in about 1934. In 1939, du Pont's Charles Stine reported the discovery of this first synthetic fiber to a group of 3000 women gathered for the New York World's Fair. The first application was nylon stockings that were strong. Today nylon is used in hundreds of applications. Prior to nylon, Carothers had discovered neoprene (an elastomer).

The linear polymer 6,6-nylon is to be produced by combining 1000 g of hexamethylene diamine with adipic acid. A condensation reaction then produces the polymer. Show how this reaction occurs and determine the byproduct that forms. How many grams of adipic acid are needed, and how much 6,6- nylon is produced, assuming 100% efficiency?

Example 3 SOLUTION

The molecular structures of the monomers are shown below. The linear nylon chain is produced when a hydrogen atom from the hexamethylene diamine combines with an OH group from adipic acid to form a water molecule.



Example 3 SOLUTION (Continued)

Molecular weight of hexamethylene diamine is 116 g/mol, of adipic acid is 146 g/mol, and of water is 18 g/mol. The number of moles of hexamethylene diamine added (calculated below) is equal to the number of moles of adipic acid:

$$\frac{1000g}{116\ g/mol} = 8.621\,moles = \frac{x\ g}{146\ g/mol}$$

x = 1259 g of adipic acid required

The number of moles of water lost is also 8.621:
$\mathbf{y}$ = (8.621 moles) (18 g/mol) = 155.2 g H_2O

Total amount of nylon produced is
1000 g + 1259 g – 2(155.2 g) = 1948.6 g.

Degree of Polymerization

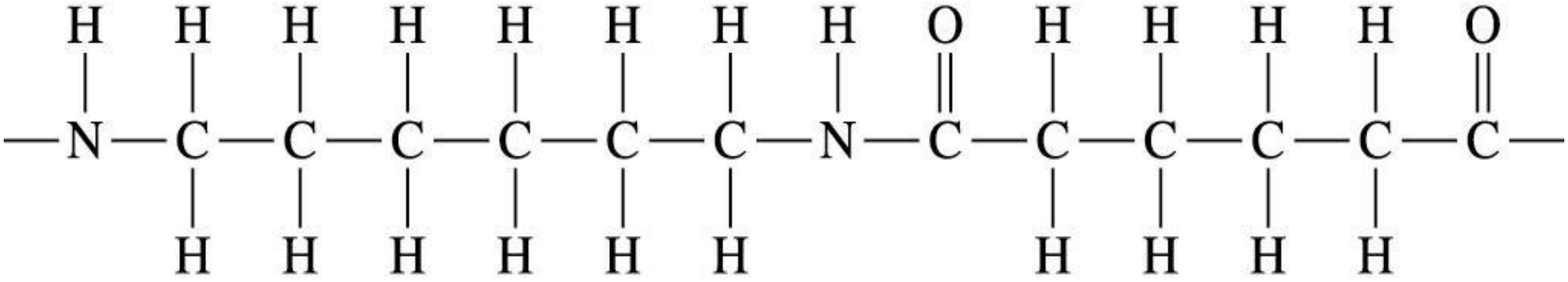
- **Degree of polymerization** - The average molecular weight of the polymer divided by the molecular weight of the monomer.

Example 4
Degree of Polymerization for 6,6-Nylon

Calculate the degree of polymerization if 6,6-nylon has a molecular weight of 120,000 g/mol.

Example 15.4 SOLUTION

The molecular weights are 116 g/mol for hexamethylene diamine, 146 g/mol for adipic acid, and 18 g/mol for water. The repeat unit for 6,6-nylon is:



Example 4 SOLUTION (Continued)

The molecular weight of the repeat unit is the sum of the molecular weights of the monomers, minus that of the two water molecules that are evolved:

$M_{repeat\ unit} = 116 + 146 - 2(18) = 226$ g/mol

Degree of polymerization = 120,000/226 = 531

The degree of polymerization refers to the total number of repeat units in the chain. The chain contains 531 hexamethylene diamine and 531 adipic acid molecules.

Example 5
Number and Weight Average Molecular Weights

We have a polyethylene sample containing 4000 chains with molecular weights between 0 and 5000 g/mol, 8000 chains with molecular weights between 5000 and 10,000 g/mol, 7000 chains with molecular weights between 10,000 and 15,000 g/mol, and 2000 chains with molecular weights between 15,000 and 20,000 g/mol. Determine both the number and weight average molecular weights.

Example 5 SOLUTION

First we need to determine the number fraction x_i and weight fraction f_i for each of the four ranges. We can then use Equations 15-2 and 15-3 to find the molecular weights.

Example 5 SOLUTION (Continued)

Number of Chains	Mean M per Chain	x_i	$x_i M_i$	Weight	f_i	$f_i M_i$
4000	2500	0.191	477.5	10×10^6	0.0519	129.75
8000	7500	0.381	2857.5	60×10^6	0.3118	2338.50
7000	12,500	0.333	4162.5	87.5×10^6	0.4545	5681.25
2000	17,500	0.095	1662.5	35×10^6	0.1818	3181.50
$\sum = 21{,}000$		$\sum = 1.00$	$\sum = 9160$	$\sum = 192.5 \times 10^6$	$\sum = 1$	$\sum = 11{,}331$

$$\overline{M}_n = \sum x_i M_i = 9160 \text{ g/mol}$$

$$\overline{M}_w = \sum f_i M_i = 11{,}331 \text{ g/mol}$$

The weight average molecular weight is larger than the number average molecular weight.

Typical Thermoplastics

TABLE 15-2 ■ *Properties of selected thermoplastics*

	Tensile Strength (psi)	% Elongation	Elastic Modulus (psi)	Density (g/cm^3)	Izod Impact (ft lb/in.)
Polyethylene (PE):					
Low-density	3,000	800	40,000	0.92	9.0
High-density	5,500	130	180,000	0.96	4.0
Ultrahigh molecular weight	7,000	350	100,000	0.934	30.0
Polyvinyl chloride (PVC)	9,000	100	600,000	1.40	
Polypropylene (PP)	6,000	700	220,000	0.90	1.0
Polystyrene (PS)	8,000	60	450,000	1.06	0.4
Polyacrylonitrile (PAN)	9,000	4	580,000	1.15	4.8
Polymethyl methacrylate (PMMA) (acrylic, Plexiglas)	12,000	5	450,000	1.22	0.5
Polychlorotrifluoroethylene	6,000	250	300,000	2.15	2.6
Polytetrafluoroethylene (PTFE, Teflon)	7,000	400	80,000	2.17	3.0
Polyoxymethylene (POM) (acetal)	12,000	75	520,000	1.42	2.3
Polyamide (PA) (nylon)	12,000	300	500,000	1.14	2.1
Polyester (PET)	10,500	300	600,000	1.36	0.6
Polycarbonate (PC)	11,000	130	400,000	1.20	16.0
Polyimide (PI)	17,000	10	300,000	1.39	1.5
Polyetheretherketone (PEEK)	10,200	150	550,000	1.31	1.6
Polyphenylene sulfide (PPS)	9,500	2	480,000	1.30	0.5
Polyether sulfone (PES)	12,200	80	350,000	1.37	1.6
Polyamide-imide (PAI)	27,000	15	730,000	1.39	4.0

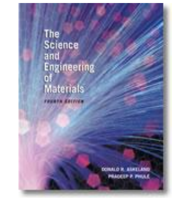


TABLE 15-3 ■ ***Repeat units and applications for selected addition thermoplastics***

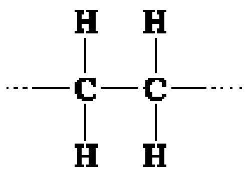
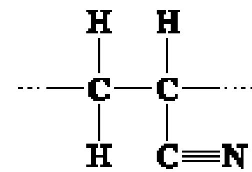
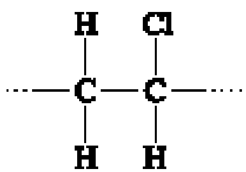
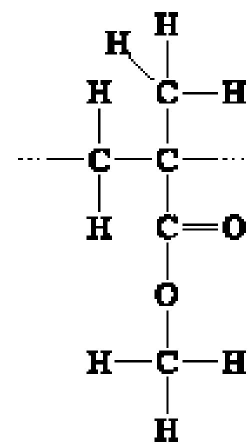
Polymer	Repeat Unit	Application	Polymer	Repeat Unit	Application
Polyethylene (PE)		Packing films, wire insulation, squeeze bottles, tubing, household items	Polyacrylonitrile (PAN)		Textile fibers, precursor for carbon fibers, food container
Polyvinyl chloride (PVC)		Pipe, valves, fittings, floor tile, wire insulation, vinyl automobile roofs	Polymethyl methacrylate (PMMA) (acrylic-Plexiglas)		Windows, windshields, coatings, hard contact lenses, lighted signs

Table 15.3 (Continued)

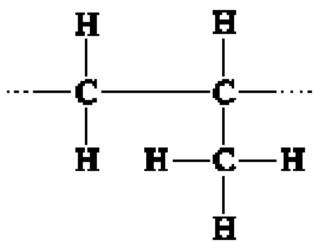
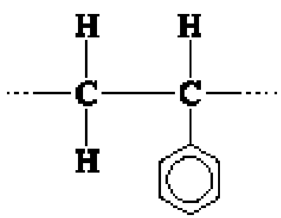
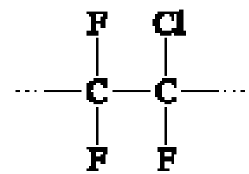
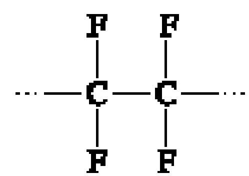
Polypropylene (PP)		Tanks, carpet fibers, rope, packaging
Polystyrene (PS)		Packaging and insulation foams, lighting panels, appliance components, egg cartons
Polychlorotri-fluoroethylene		Valve components, gaskets, tubing, electrical insulation
Polytetrafluoro-ethylene (Teflon) (PTFE)		Seals, valves, nonstick coatings

TABLE 15-4 ■ ***Repeat units and applications for complex thermoplastics***

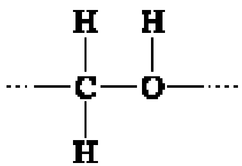
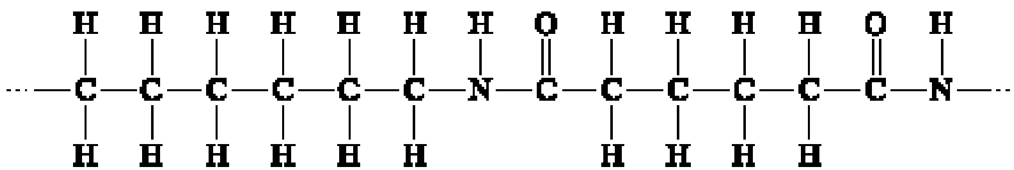
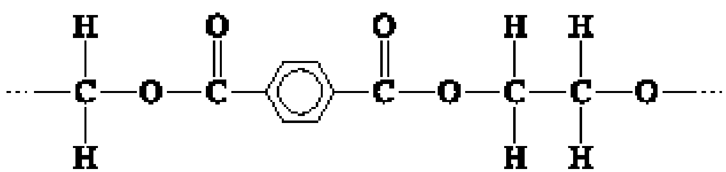
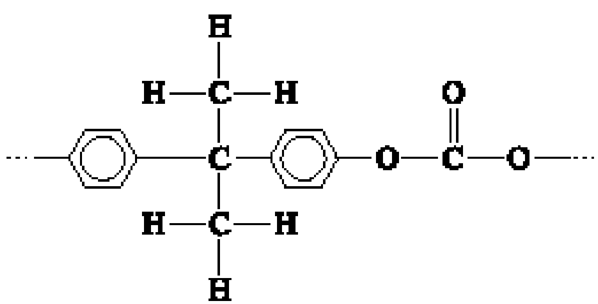
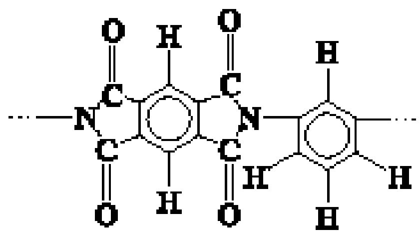
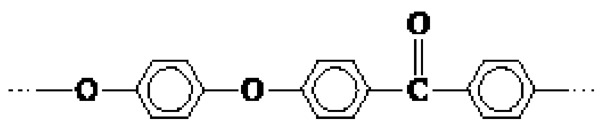
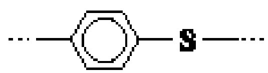
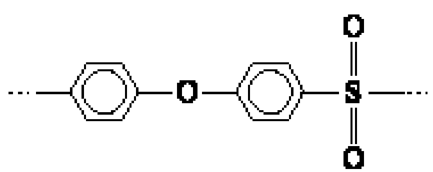
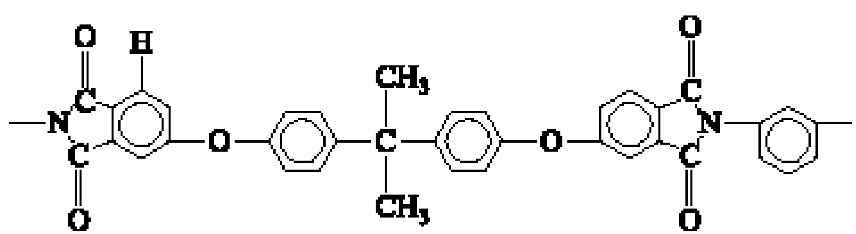
Polymer	Repeat Unit	Applications
Polyoxymethylene (acetal)(POM)		Plumbing fixtures, pens, bearings, gears, fan blades
Polyamide (nylon) (PA)		Bearings, gears, fibers, rope, automotive components, electrical components
Polyester (PET)		Fibers, photographic film, recording tape, boil-in-bag containers, beverage containers
Polycarbonate (PC)		Electrical and appliance housings, automotive components, football helmets, returnable bottles

Table 15.4 (Continued)

Polyimide (PI)		Adhesives, circuit boards, fibers for space shuttle
Polyetheretherketone (PEEK)		High-temperature electrical insulation and coatings
Polyphenylene sulfide (PPS)		Coatings, fluid-handling components, electronic components, hair dryer components
Polyether sulfone (PES)		Electrical components, coffeemakers, hair dryers, microwave oven components
Polyamide-imide (PAI)		Electronic components, aerospace and automotive applications

Section 6 Structure–Property Relationships in Thermoplastics

- Branched polymer - Any polymer consisting of chains that consist of a main chain and secondary chains that branch off from the main chain.
- Crystallinity is important in polymers since it affects mechanical and optical properties.
- Tacticity - Describes the location in the polymer chain of atoms or atom groups in nonsymmetrical monomers.
- Liquid-crystalline polymers - Exceptionally stiff polymer chains that act as rigid rods, even above their melting point.

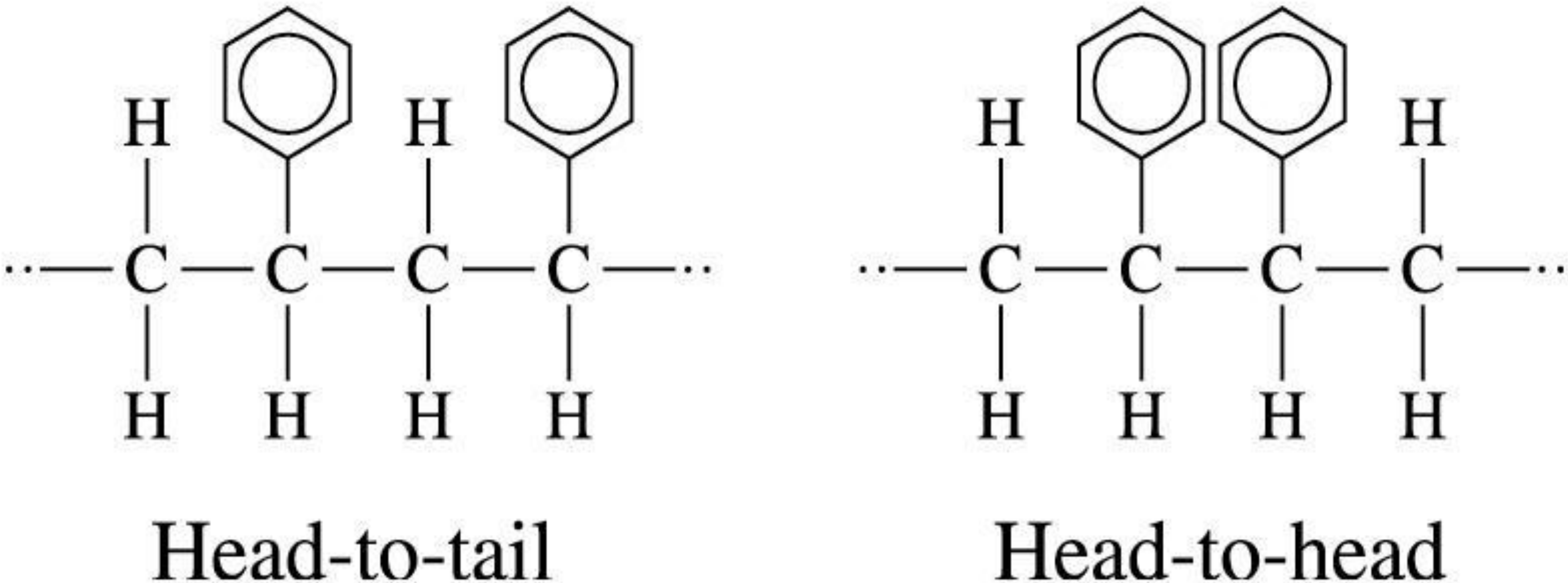
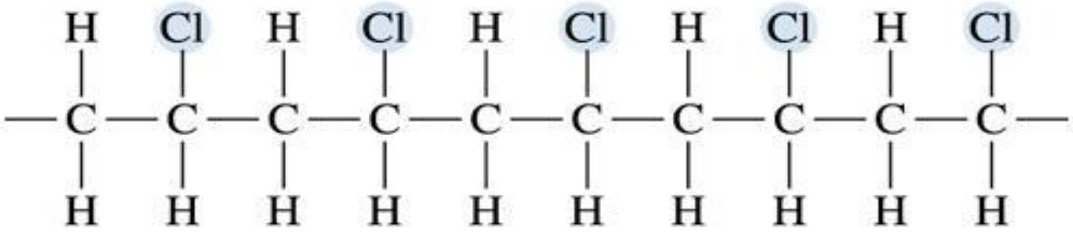
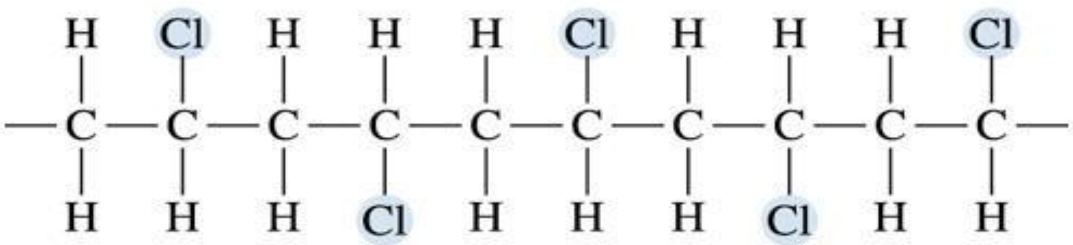


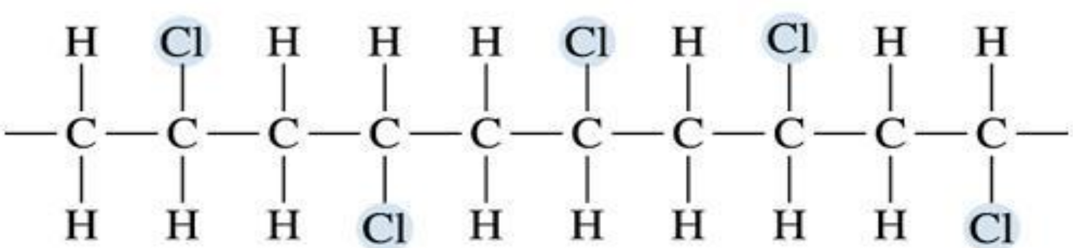
Figure 15.8 Head-to-tail versus head-to-head arrangement of repeat units. The head-to-tail arrangement is most typical.



(a)



(b)



(c)

Figure 9 Three possible arrangements of nonsymmetrical monomers: (a) isotactic, (b)syndiotactic, and (c)atactic.

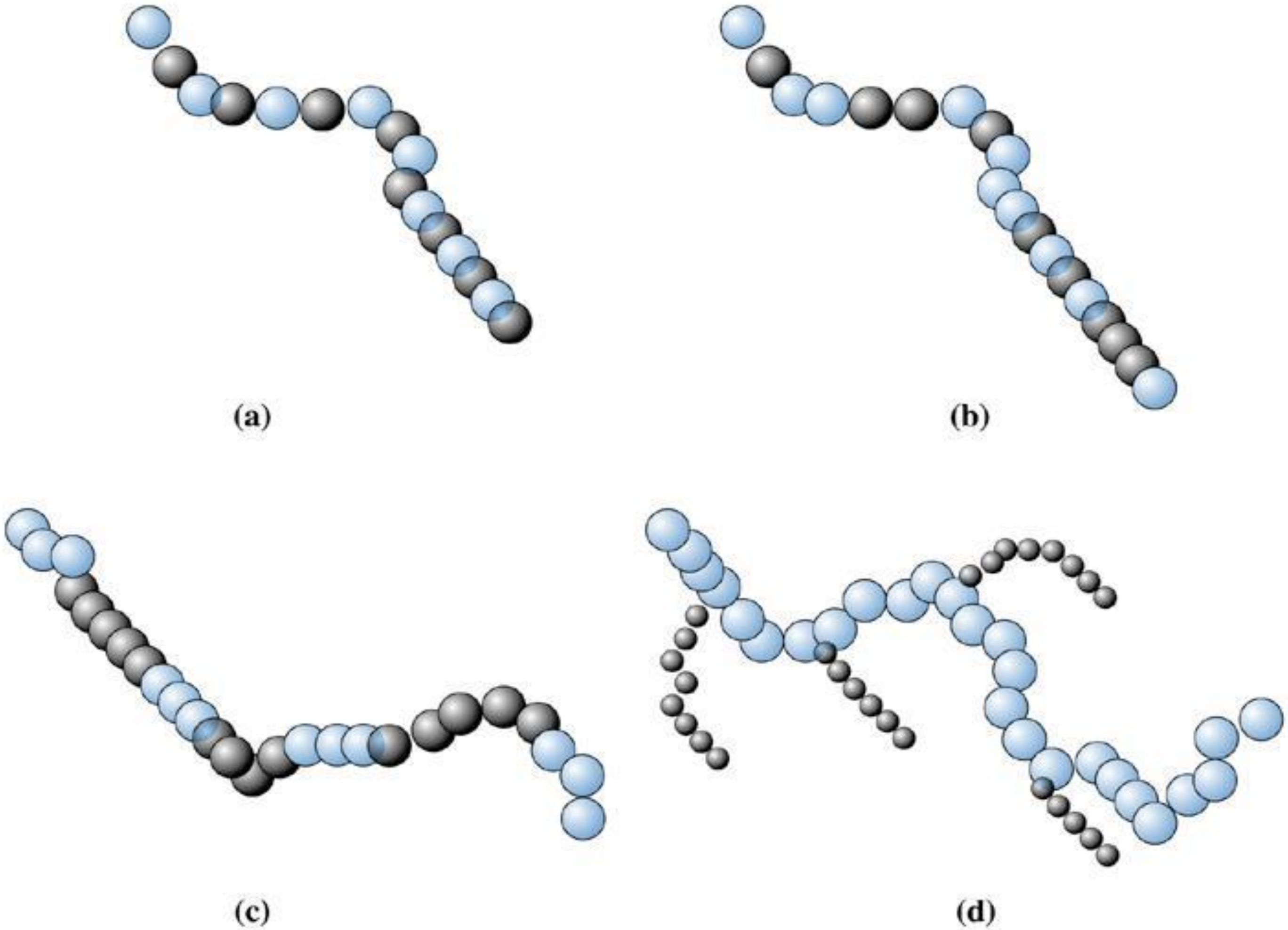
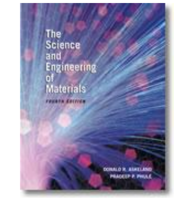


Figure 10 Four types of copolymers: (a) alternating monomers, (b) random monomers, (c) block copolymers, and (d) grafted copolymers. Circles of different colors or sizes represent different monomers.



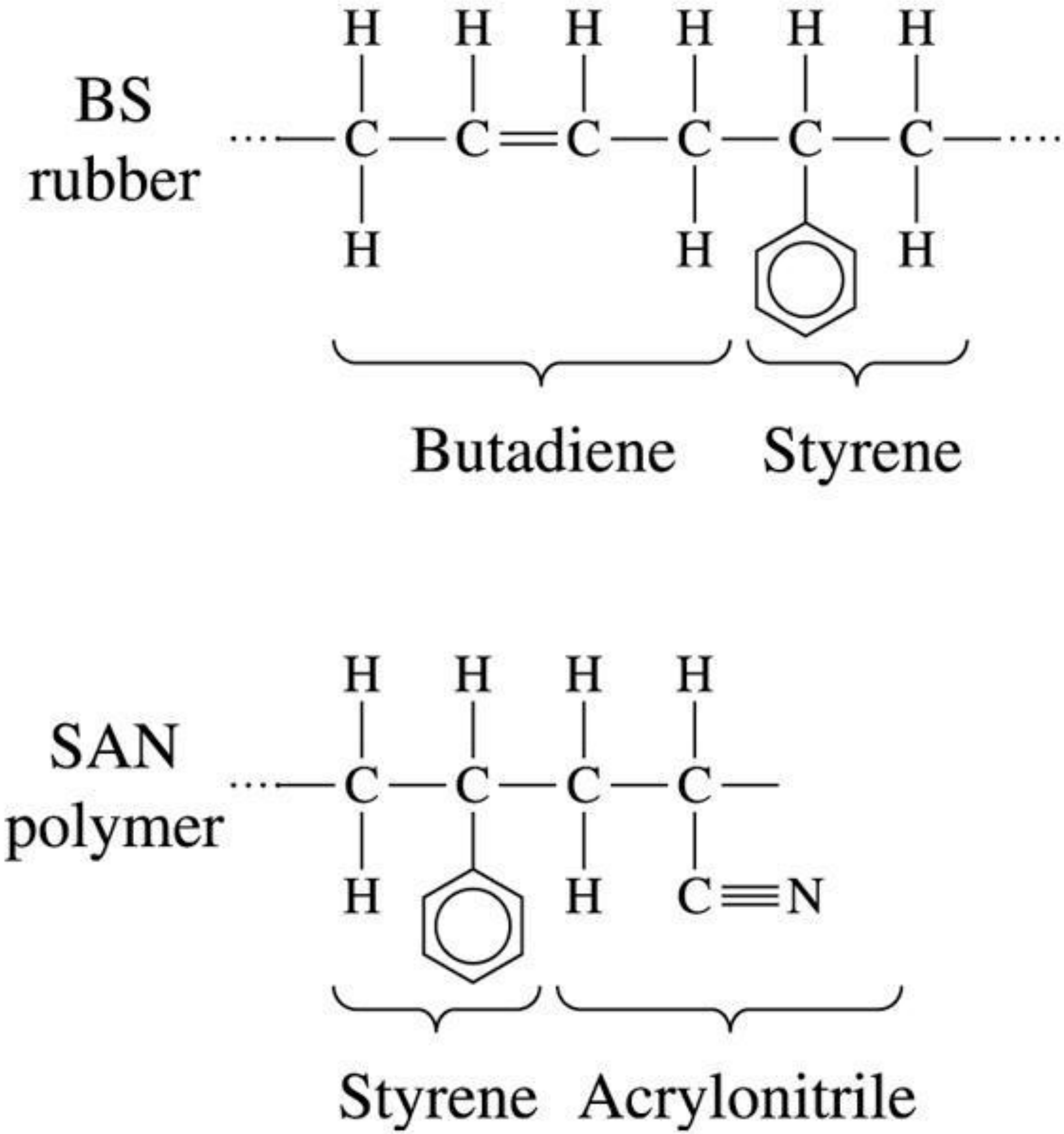
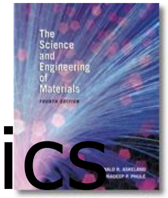


Figure 11 Copolymerization produces the polymer ABS, which is really made up of two copolymers, SAN and BS, grafted together.



Effect of Temperature on Thermoplastics

- Degradation temperature - The temperature above which a polymer burns, chars, or decomposes.
- Glass temperature - The temperature range below which the amorphous polymer assumes a rigid glassy structure.

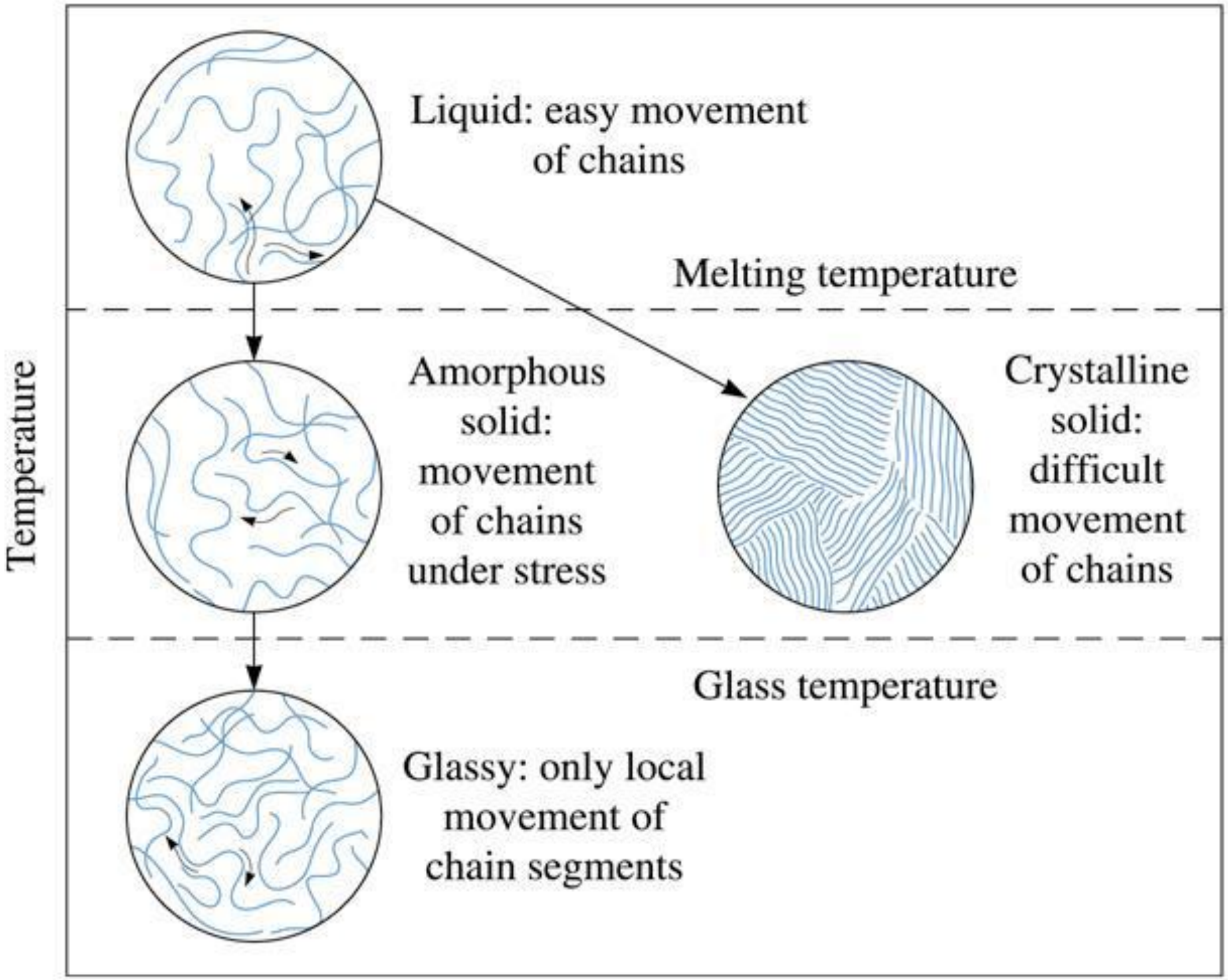
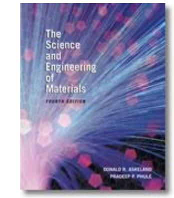


Figure 12 The effect of temperature on the structure and behavior of thermoplastics.



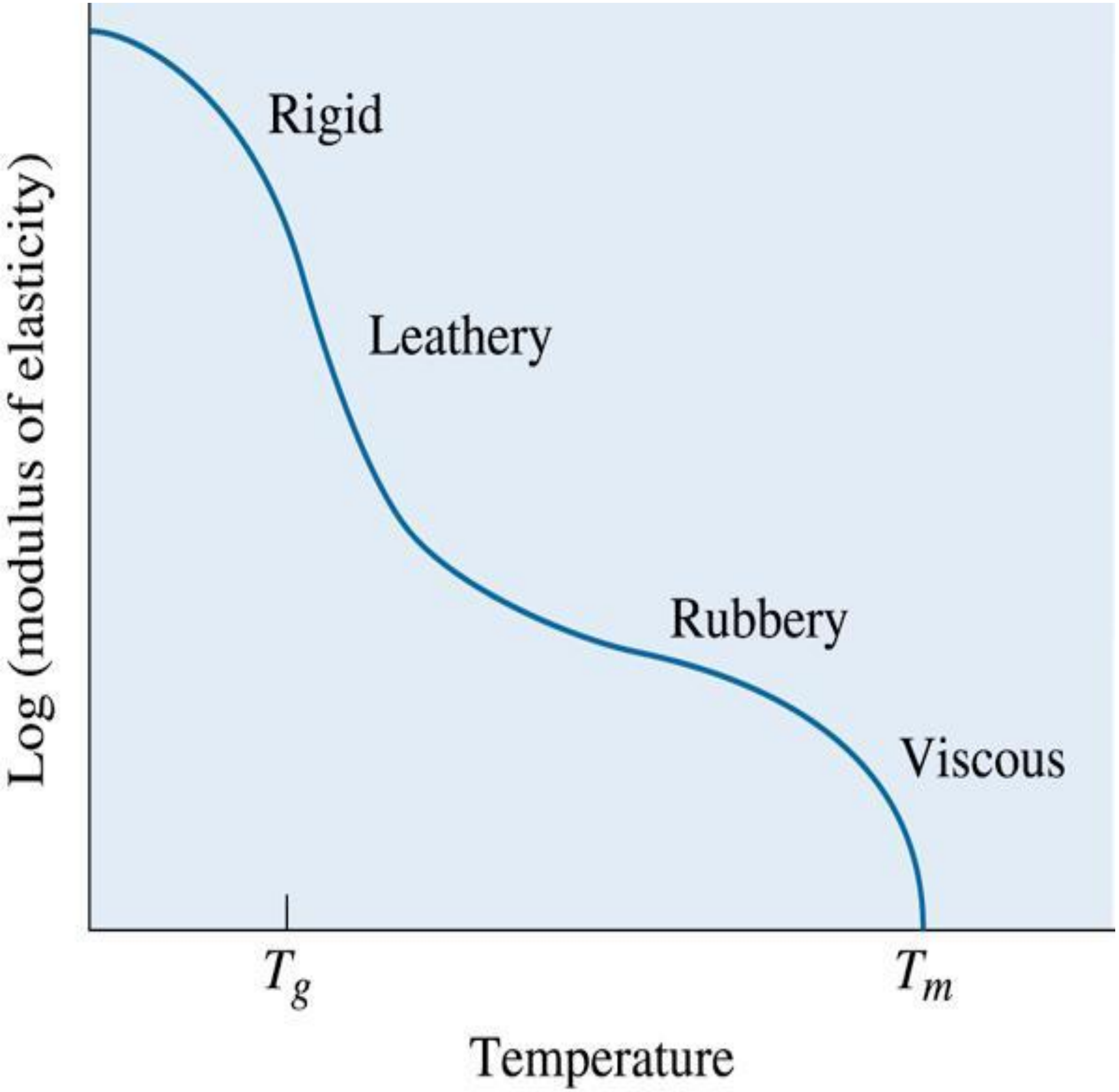
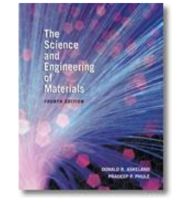


Figure 13 The effect of temperature on the modulus of elasticity for an amorphous thermoplastic. Note that T_g and T_m are not fixed.

TABLE 15-5 ■ ***Melting and glass temperature ranges (°C) for selected thermoplastics and elastomers***



Polymer	Melting Temperature	Glass Temperature (T_g)	Processing Temperature
Addition polymers			
Low-density (LD) polyethylene	98–115	−90 to −25	149–232
High-density (HD) polyethylene	130–137	−110	177–260
Polyvinyl chloride	175–212	87	
Polypropylene	160–180	−25 to −20	190–288
Polystyrene	240	85–125	
Polyacrylonitrile	320	107	
Polytetrafluoroethylene (Teflon)	327		
Polychlorotrifluoroethylene	220		
Polymethyl methacrylate (acrylic)		90–105	
Acrylonitrile butadiene styrene (ABS)	110–125	100	177–260
Condensation polymers			
Acetal	181	−85	
6,6-nylon	243–260	49	260–327
Cellulose acetate	230		
Polycarbonate	230	149	271–300
Polyester	255	75	
Polyethylene terephthalate (PET)	212–265	66–80	227–349
Elastomers			
Silicone		−123	
Polybutadiene	120	−90	
Polychloroprene	80	−50	
Polyisoprene	30	−73	

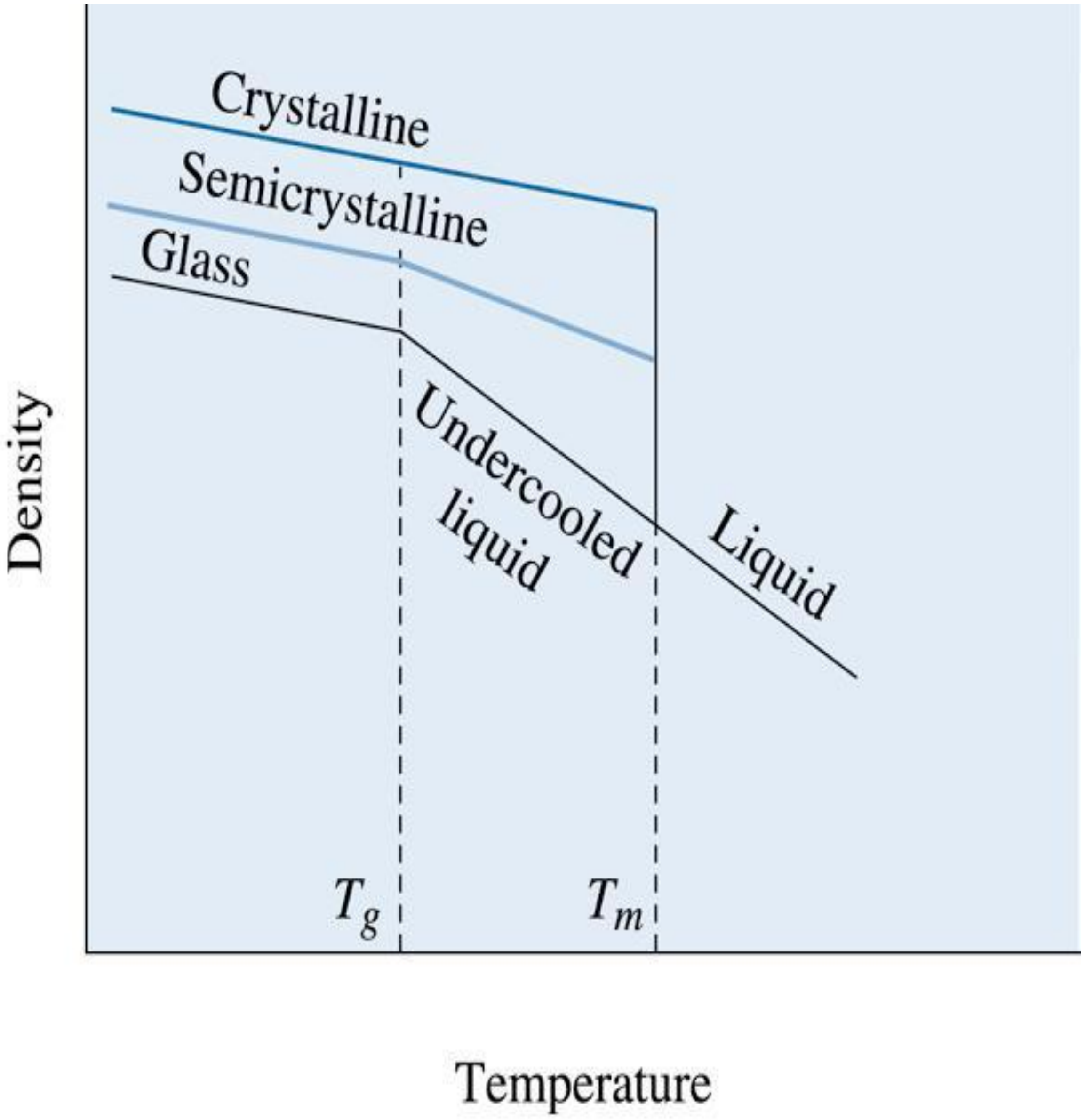


Figure 14 The relationship between the density and the temperature of the polymer shows the melting and lass temperatures. Note that T_g and T_m are not fixed; rather, they are ranges of temperatures.

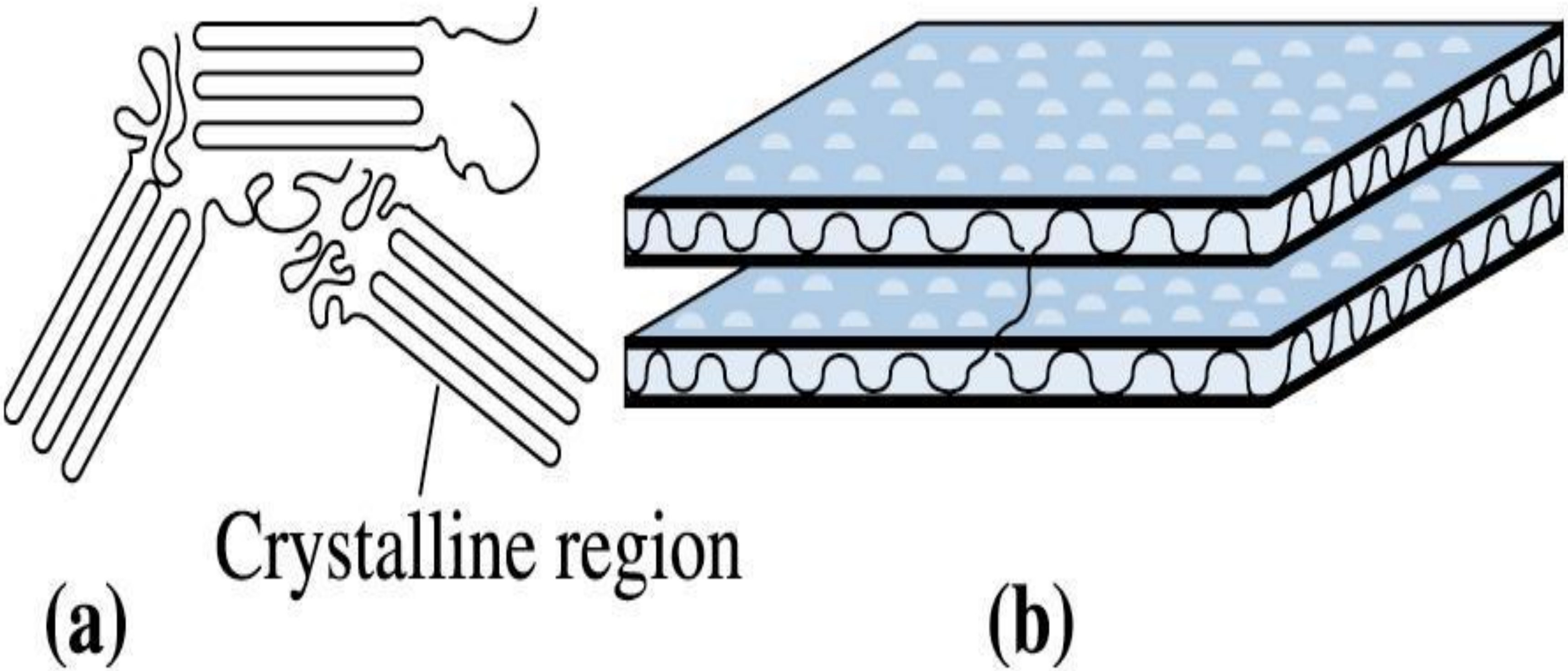


Figure 15 The folded chain ,model for crystallinity in polymers, shown in (a) two dimensions and (b) three dimensions.

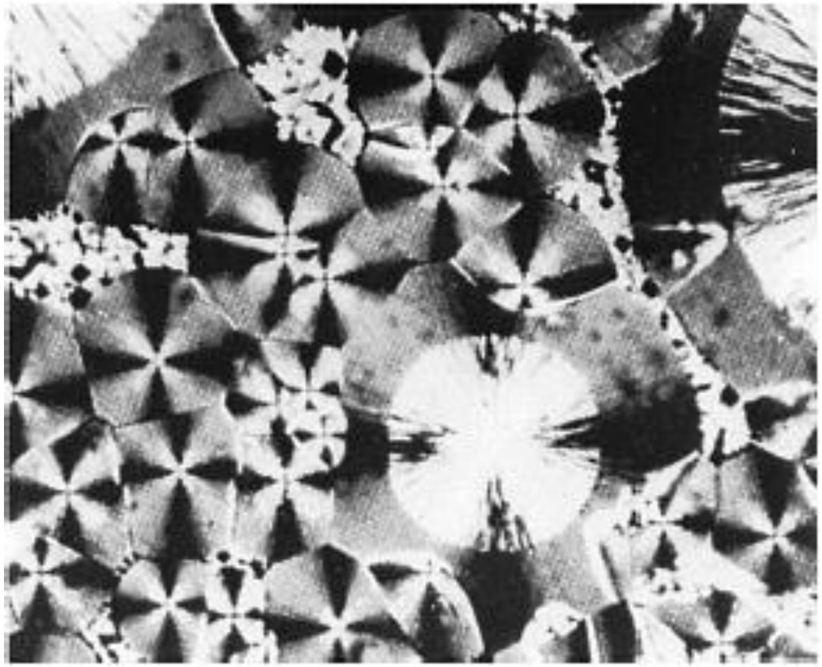


Figure 16 Photograph of spherulitic crystals in an amorphous matrix of nylon (× 200). (*From R. Brick, A. Pense and R. Gordon*, Structure and Properties of Engineering Materials, *4th Ed., McGraw-Hill, 1977*.)

TABLE 15-6 ■ ***Crystal structures of several polymers***

Polymer	Crystal Structure	Lattice Parameters (nm)
Polyethylene	Orthorhombic	$a_0 = 0.742$ $b_0 = 0.495$ $c_0 = 0.255$
Polypropylene	Orthorhombic	$a_0 = 1.450$ $b_0 = 0.569$ $c_0 = 0.740$
Polyvinyl chloride	Orthorhombic	$a_0 = 1.040$ $b_0 = 0.530$ $c_0 = 0.510$
Polyisoprene (cis)	Orthorhombic	$a_0 = 1.246$ $b_0 = 0.886$ $c_0 = 0.810$

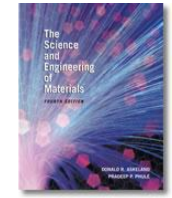
Example.6
Design of a Polymer Insulation Material

A storage tank for liquid hydrogen will be made of metal, but we wish to coat the metal with a 3-mm thickness of a polymer as an intermediate layer between the metal and additional insulation layers. The temperature of the intermediate layer may drop to 80°C. Design a material for this layer.

Example 6 SOLUTION

A material that has good ductility and/or can undergo large elastic strains is needed. We therefore would prefer either a thermoplastic that has a glass temperature below 80°C or an elastomer, also with a glass temperature below 80°C. Of the polymers listed in Table 15-2, thermoplastics such as polyethylene and acetal are satisfactory. Suitable elastomers include silicone and polybutadiene.

TABLE 15-2 ■ ***Properties of selected thermoplastics***



	Tensile Strength (psi)	% Elongation	Elastic Modulus (psi)	Density (g/cm^3)	Izod Impact (ft lb/in.)
Polyethylene (PE):					
Low-density	3,000	800	40,000	0.92	9.0
High-density	5,500	130	180,000	0.96	4.0
Ultrahigh molecular weight	7,000	350	100,000	0.934	30.0
Polyvinyl chloride (PVC)	9,000	100	600,000	1.40	
Polypropylene (PP)	6,000	700	220,000	0.90	1.0
Polystyrene (PS)	8,000	60	450,000	1.06	0.4
Polyacrylonitrile (PAN)	9,000	4	580,000	1.15	4.8
Polymethyl methacrylate (PMMA) (acrylic, Plexiglas)	12,000	5	450,000	1.22	0.5
Polychlorotrifluoroethylene	6,000	250	300,000	2.15	2.6
Polytetrafluoroethylene (PTFE, Teflon)	7,000	400	80,000	2.17	3.0
Polyoxymethylene (POM) (acetal)	12,000	75	520,000	1.42	2.3
Polyamide (PA) (nylon)	12,000	300	500,000	1.14	2.1
Polyester (PET)	10,500	300	600,000	1.36	0.6
Polycarbonate (PC)	11,000	130	400,000	1.20	16.0
Polyimide (PI)	17,000	10	300,000	1.39	1.5
Polyetheretherketone (PEEK)	10,200	150	550,000	1.31	1.6
Polyphenylene sulfide (PPS)	9,500	2	480,000	1.30	0.5
Polyether sulfone (PES)	12,200	80	350,000	1.37	1.6
Polyamide-imide (PAI)	27,000	15	730,000	1.39	4.0

Example 7
Impact-Resistant Polyethylene

A new grade of flexible, impact-resistant polyethylene for use as a thin film requires a density of 0.88 to 0.915 g/cm^3. Design the polyethylene required to produce these properties. The density of amorphous polyethylene is about 0.87 g/cm^3.

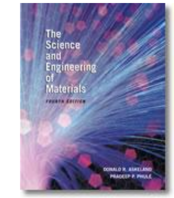
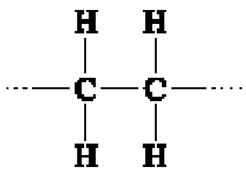
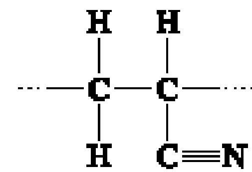
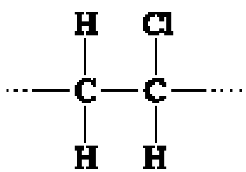
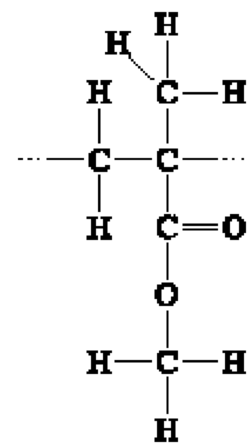


TABLE 15-3 ■ ***Repeat units and applications for selected addition thermoplastics***

Polymer	Repeat Unit	Application	Polymer	Repeat Unit	Application
Polyethylene (PE)		Packing films, wire insulation, squeeze bottles, tubing, household items	Polyacrylonitrile (PAN)		Textile fibers, precursor for carbon fibers, food container
Polyvinyl chloride (PVC)		Pipe, valves, fittings, floor tile, wire insulation, vinyl automobile roofs	Polymethyl methacrylate (PMMA) (acrylic-Plexiglas)		Windows, windshields, coatings, hard contact lenses, lighted signs

Example 7 SOLUTION

We can use the data in Table 15-3 to calculate this density if we recognize that there are two polyethylene repeat units in each unit cell (see Example 3.16):

$$\rho_c = \frac{(4C)(12)+(8H)(1)}{(7.42)(4.95)(2.55)(10^{-24})(6.02\times 10^{23})} = 0.9932 \ g/cm^3$$

Example 7 SOLUTION (Continued)

We know that ρ_a = 0.87 g/cm^3 and that ρ varies from 0.88 to 0.915 g/cm^3. The required crystallinity then varies from:

$$\%\,\text{Crystalline} = \frac{(0.9932)(0.88-0.87)}{(0.88)(0.9932-0.87)} \times 100 = 9.2$$

$$\%\,\text{Crystalline} = \frac{(0.9932)(0.915-0.87)}{(0.915)(0.9932-0.87)} \times 100 = 39.6$$

Therefore, we must be able to process the polyethylene to produce a range of crystallinity between 9.2 and 39.6%.

Section 8
Mechanical Properties of Thermoplastics

- Viscoelasticity - The deformation of a material by elastic deformation and viscous flow of the material when stress is applied.
- Relaxation time - A property of a polymer that is related to the rate at which stress relaxation occurs.

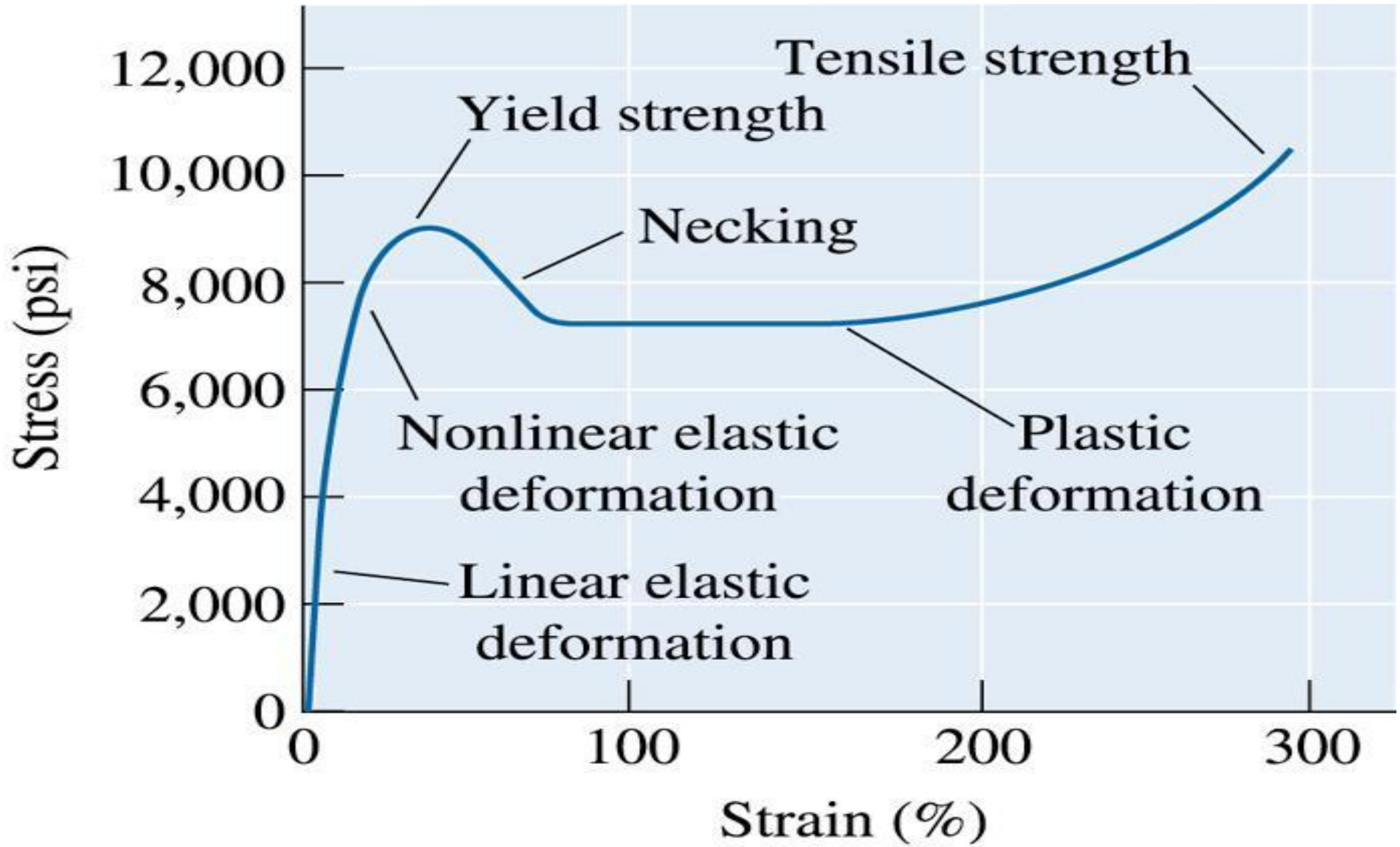


Figure 17 The stress-strain curve for 6,6-nylon, a typical thermoplastic polymer.

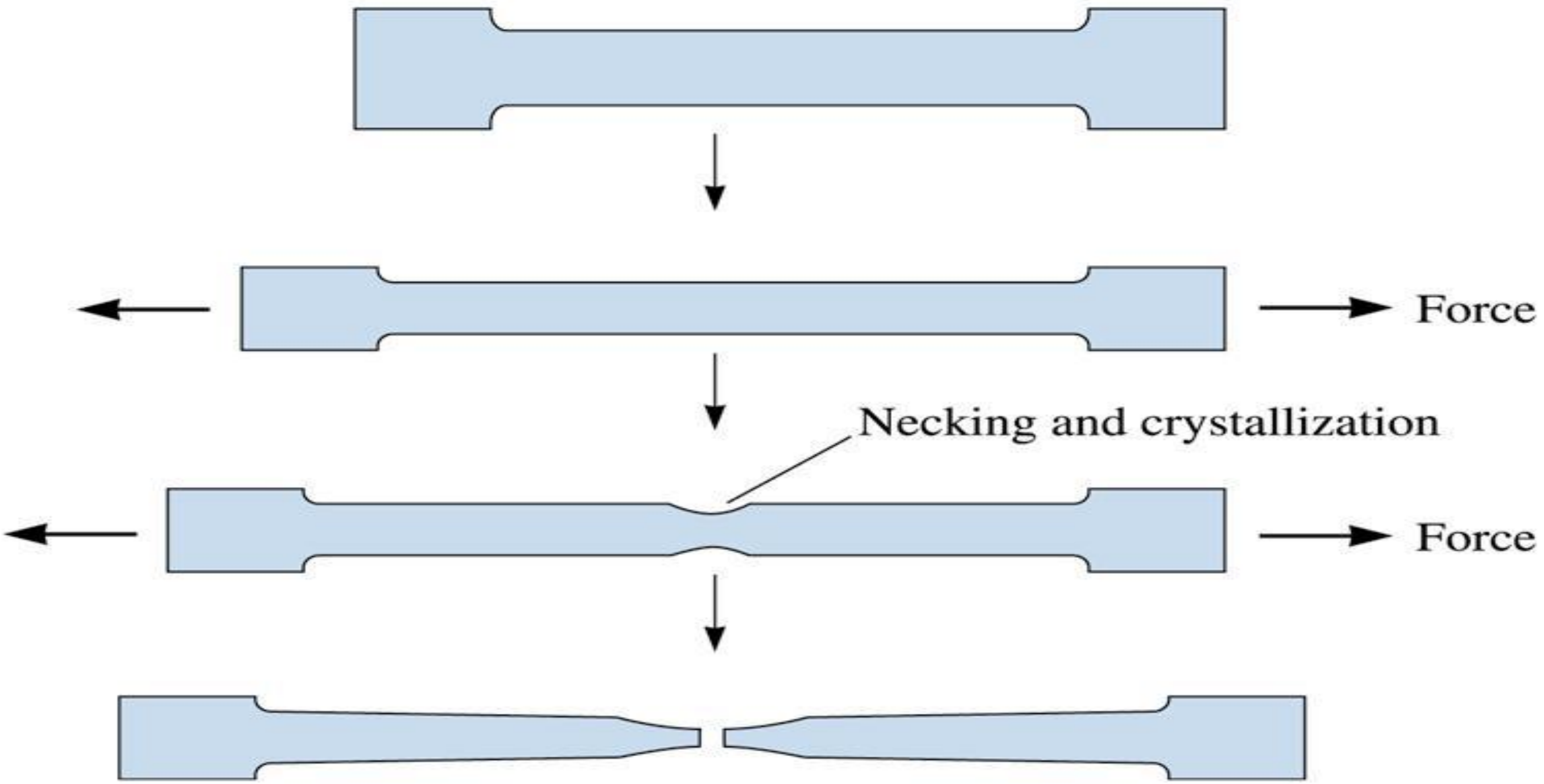


Figure 18 Necks are not stable in amorphous polymers, because local alignment strengthens the necked region and reduces its rate of deformation.

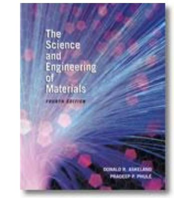
Example 8
Comparing Mechanical Properties of Thermoplastics

Compare the mechanical properties of LD polyethylene, HD polyethylene, polyvinyl chloride, polypropylene, and polystyrene, and explain their differences in terms of their structures.

Example 8 SOLUTION

Let us look at the maximum tensile strength and modulus of elasticity for each polymer.

Example 8 SOLUTION (Continued)



Polymer	Tensile Strength (psi)	Modulus of Elasticity (ksi)	Structure
LD polyethylene	3000	40	Highly branched, amorphous structure with symmetrical monomers
HD polyethylene	5500	180	Amorphous structure with symmetrical monomers but little branching
Polypropylene	6000	220	Amorphous structure with small methyl side groups
Polystyrene	8000	450	Amorphous structure with benzene side groups
Polyvinyl chloride	9000	600	Amorphous structure with large chlorine atoms as side groups

We can conclude that:

1. Branching, which reduces the density and close packing of chains, reduces the mechanical properties of polyethylene.

2. Adding atoms or atom groups other than hydrogen to the chain increases strength and stiffness. The methyl group in polypropylene provides some improvement, the benzene ring of styrene provides higher properties, and the chlorine atom in polyvinyl chloride provides a large increase in properties.

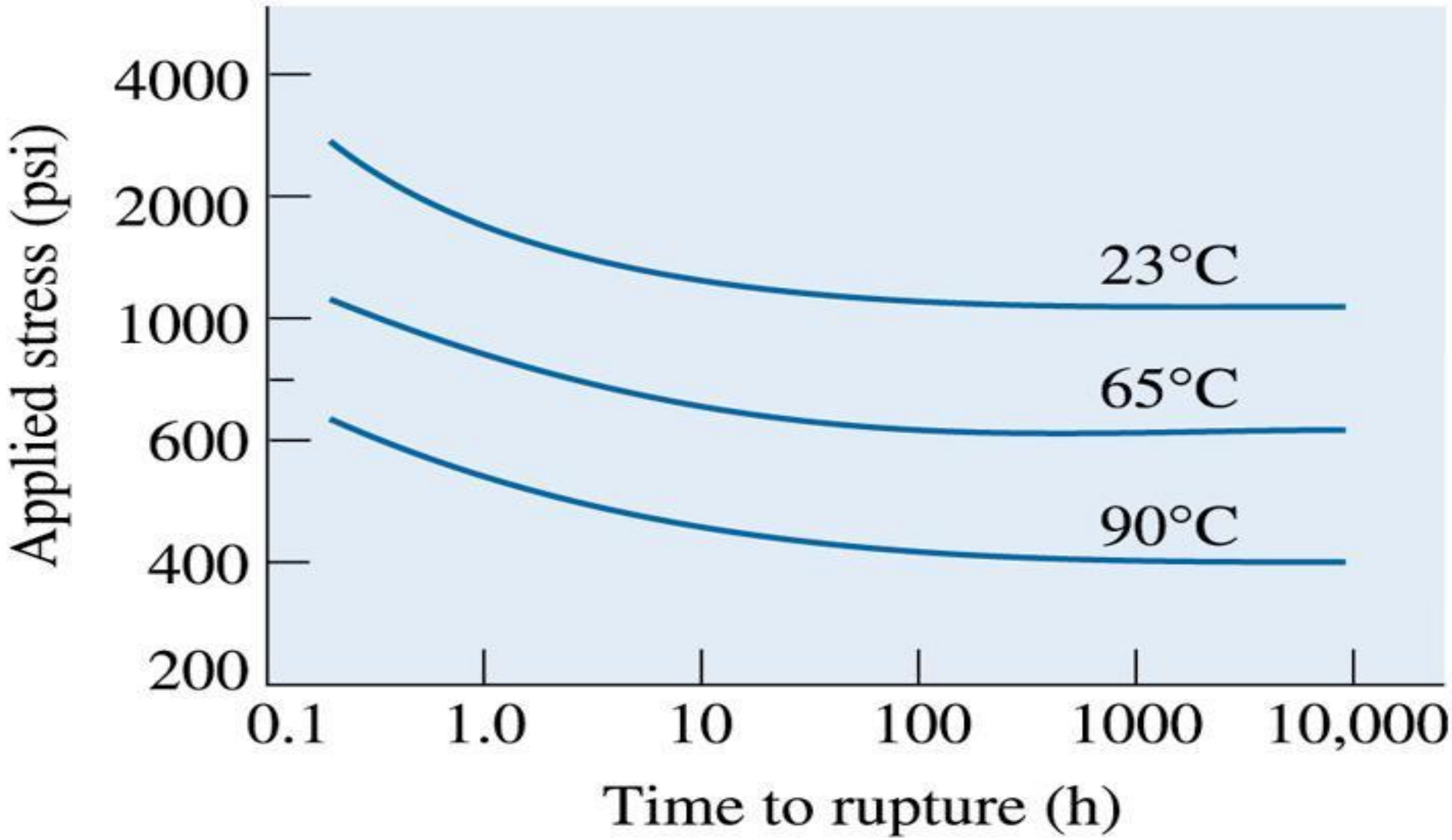


Figure 19 The effect of temperature on the stress-rupture behavior of high-density polyethylene.

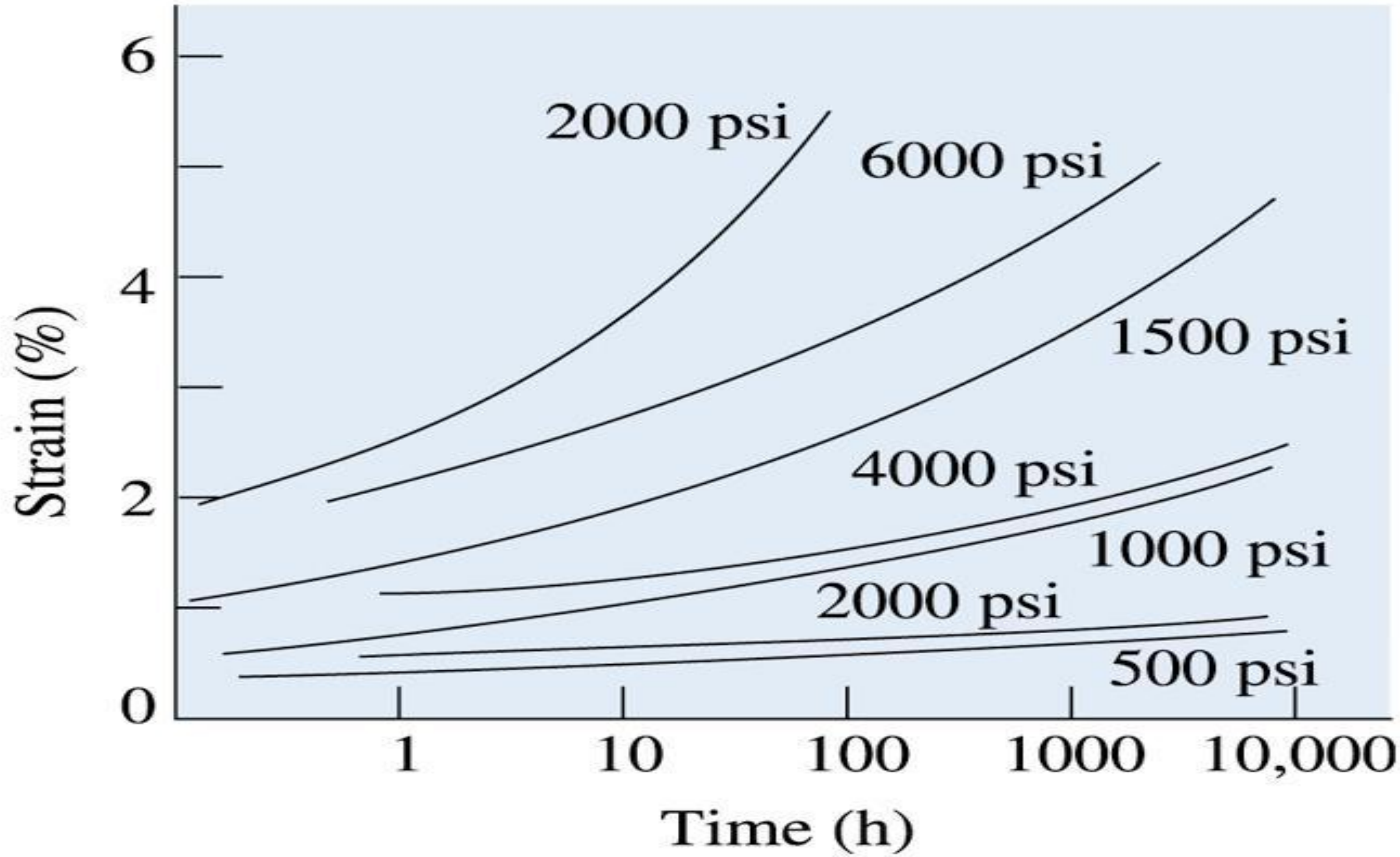


Figure 20 Creep curves for acrylic (PMMA) (colored lines) and polypropylene (black lines) at 20°C and several applied stresses.

Example 9
Design of Initial Stress in a Polymer

A band of polyisoprene is to hold together a bundle of steel rods for up to one year. If the stress on the band is less than 1500 psi, the band will not hold the rods tightly. Design the initial stress that must be applied to a polyisoprene band when it is slipped over the steel. A series of tests showed that an initial stress of 1000 psi decreased to 980 psi after six weeks.

Example 9 SOLUTION

We can use Equation 15-5 and our initial tests to determine the relaxation time for the polymer:

$$\sigma = \sigma_0 \exp\left(-\frac{t}{\lambda}\right)$$

$$980 = 1000 \exp\left(-\frac{6}{\lambda}\right), \qquad \lambda = \frac{6}{0.0202} = 297 \text{ weeks}$$

Example 9 SOLUTION (Continued)

Now that we know the relaxation time, we can determine the stress that must be initially placed onto the band in order that it still be stressed to 1500 psi after 1 year (52 weeks).

$$1500 = \sigma_o \exp(-52/297) = \sigma_o \exp(-0.175) = 0.839\sigma_o$$

$$\sigma_o = \frac{1500}{0.839} = 1788 \text{ psi}$$

The polyisoprene band must be made significantly undersized so it can slip over the materials it is holding together with a tension of 1788 psi. After one year, the stress will still be 1500 psi.

TABLE 15-7 ■ ***Deflection temperatures for selected polymers for a 264-psi load***

Polymer	Deflection Temperature (°C)
Polyester	40
Polyethylene (ultra-high density)	40
Polypropylene	60
Phenolic	80
Polyamide (6,6-nylon)	90
Polystyrene	100
Polyoxymethylene (acetal)	130
Polyamide-imide	280
Epoxy	290

Section 9
Elastomers (Rubbers)

- Geometric isomer - A molecule that has the same composition as, but a structure different from, a second molecule.
- Diene - A group of monomers that contain two double-covalent bonds. These monomers are often used in producing elastomers.
- Cross-linking - Attaching chains of polymers together to produce a three-dimensional network polymer.
- Vulcanization - Cross-linking elastomer chains by introducing sulfur or other chemicals.

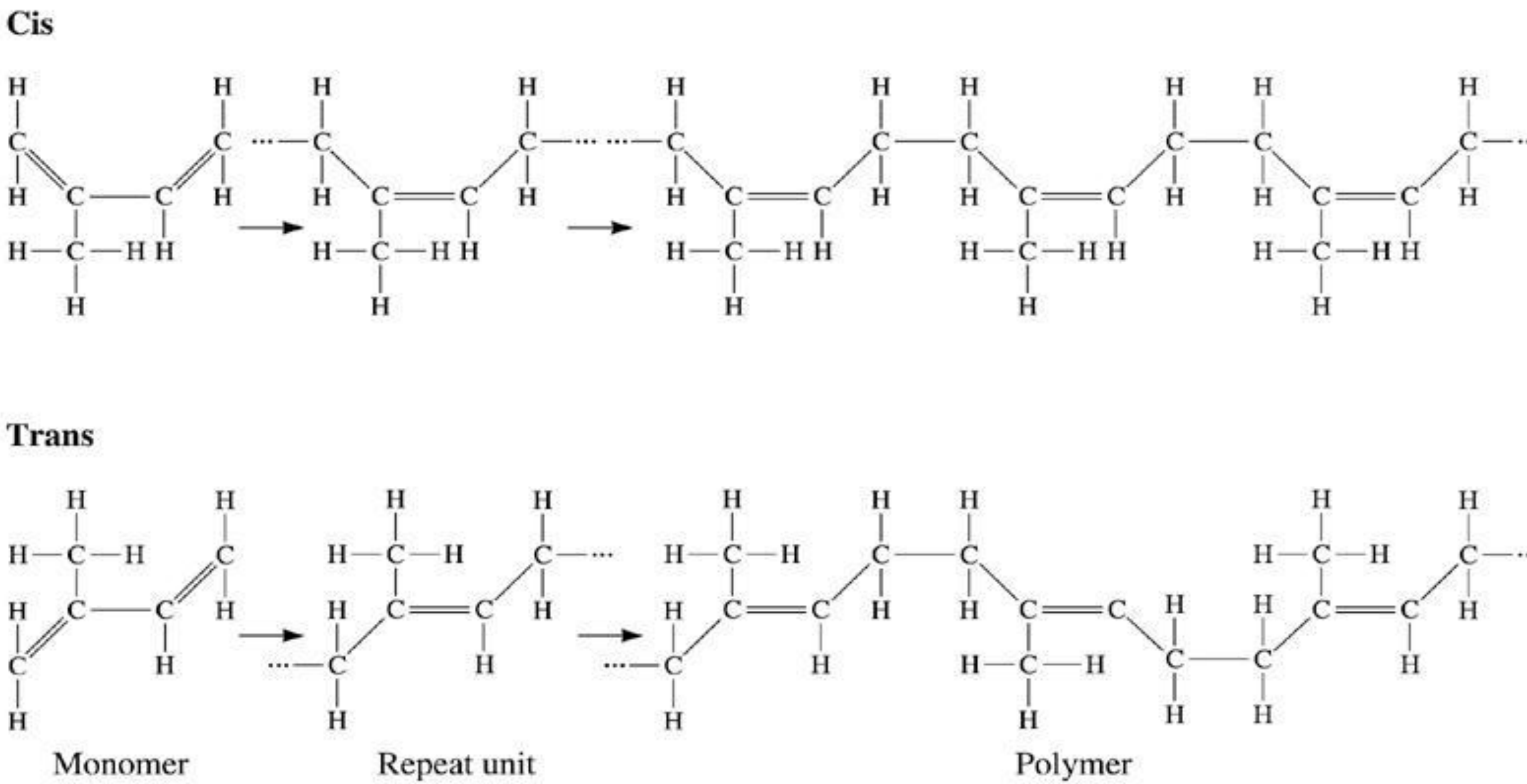


Figure 21 The cis and trans structures of isoprene. The cis form is useful for producing the isoprene elastomer.

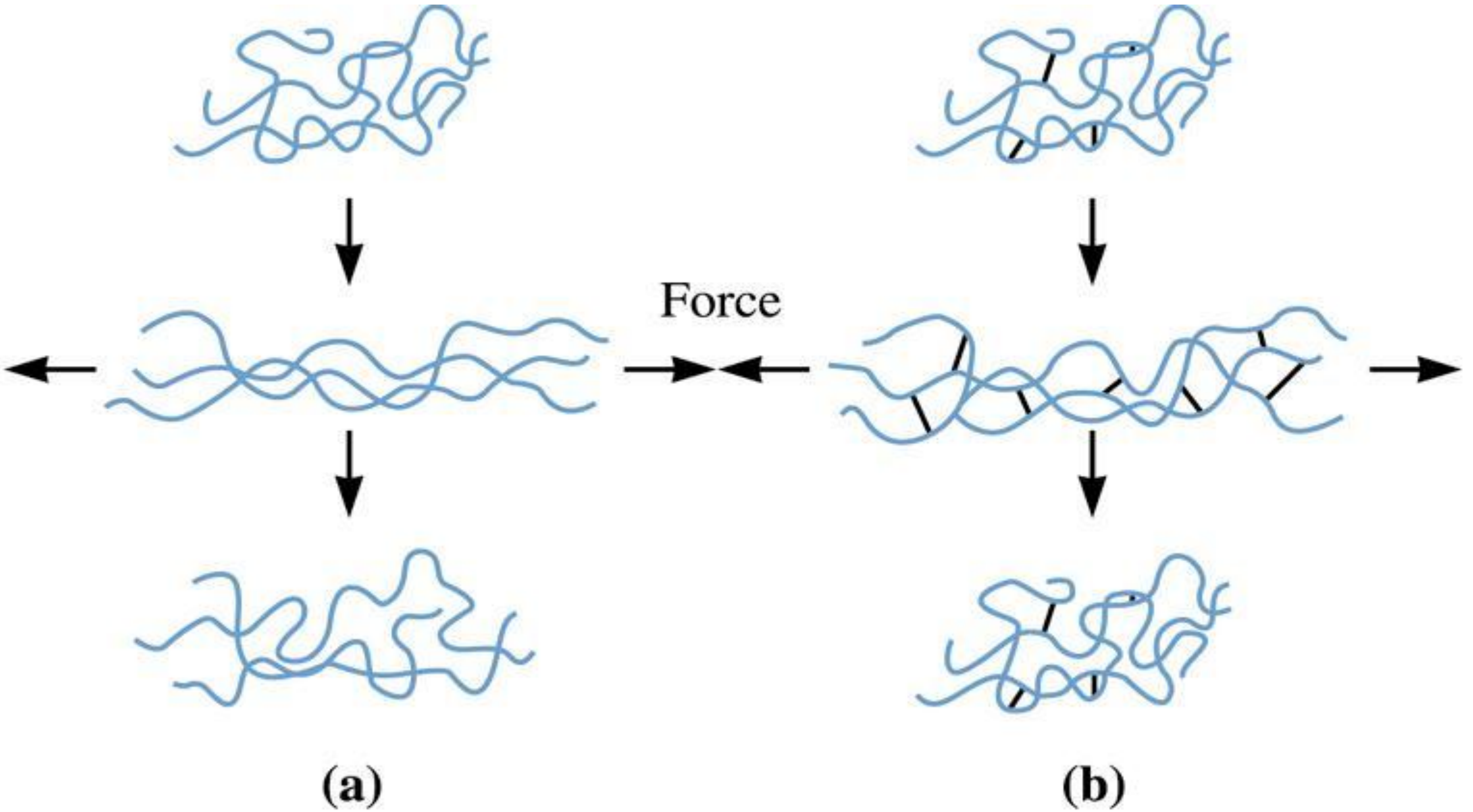


Figure 22 (a) When the elastomer contains no cross-links, the application of a force causes both elastic and plastic deformation; after the load is removed, the elastomer is permanently deformed. (b) When cross-linking occurs, the elastomer still may undergo large elastic deformation; however, when the load is removed, the elastomer returns to its original shape.

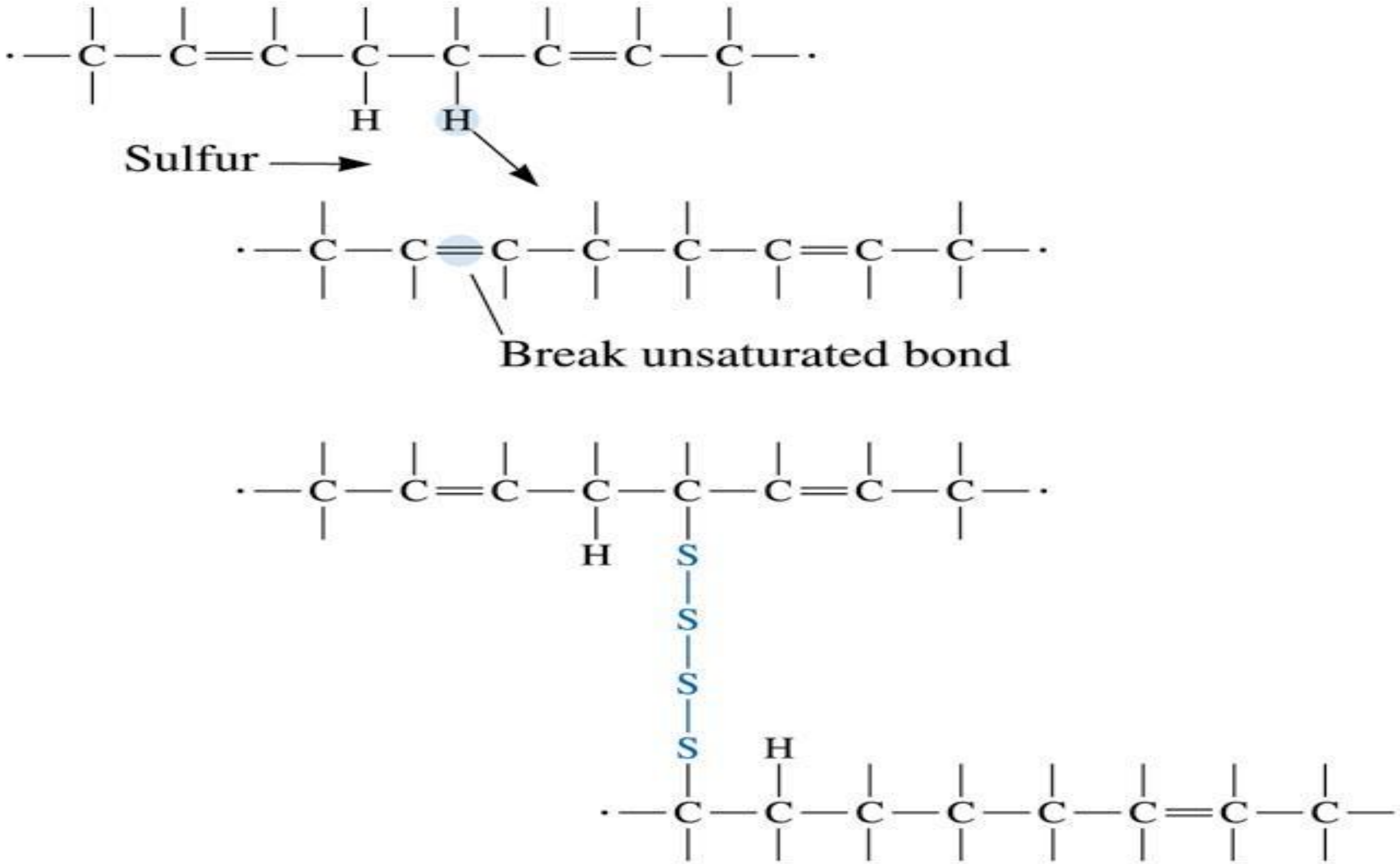


Figure 23 Cross-linking of polyisoprene chains may occur introducing strands of sulfur atoms. Sites for attachment of the sulfur strands occur by rearrangement or loss of a hydrogen atom and the breaking of an unsaturated bond.

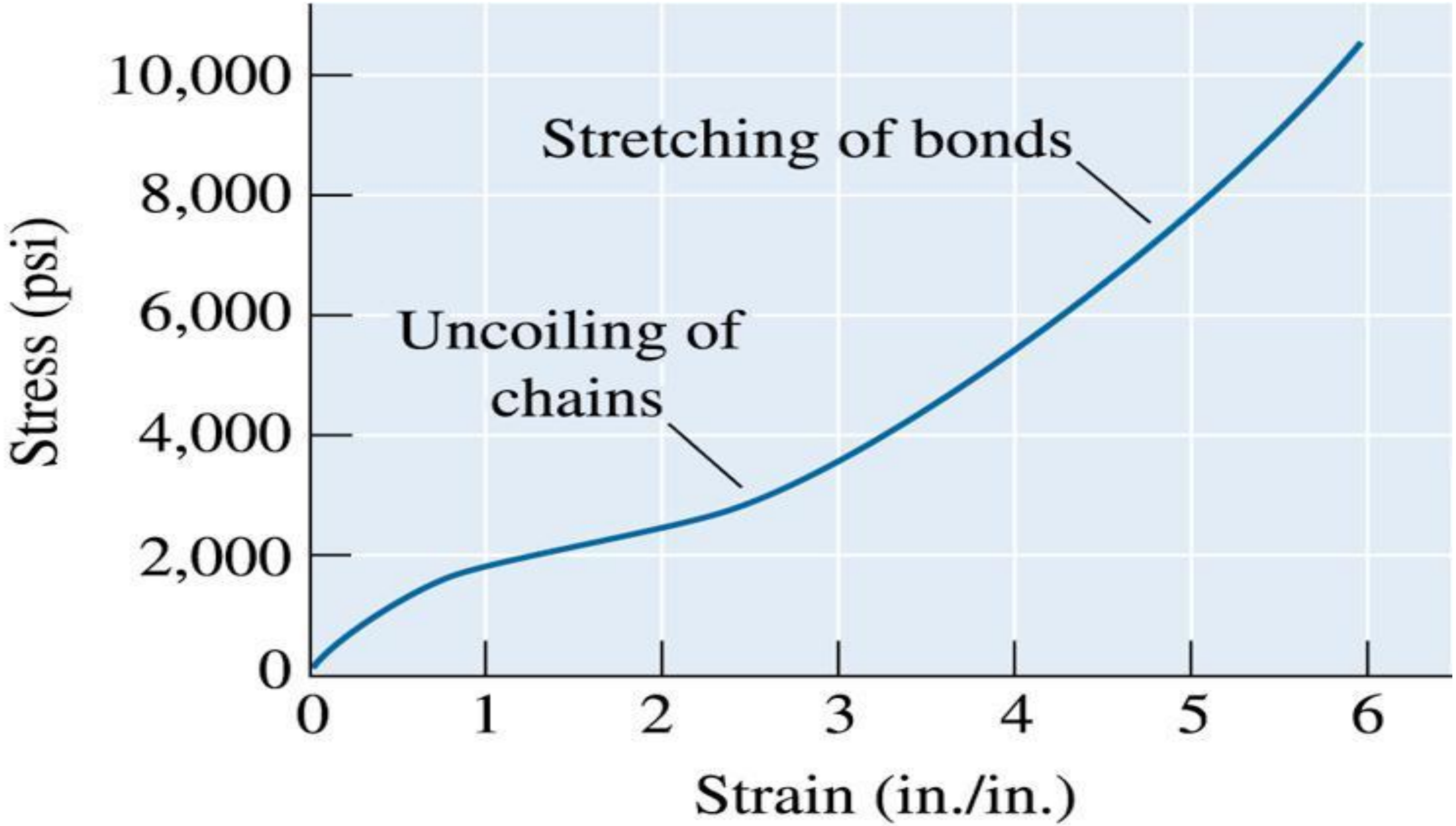


Figure 24 The stress-strain curve for an elastomer. Virtually all of the deformation is elastic; therefore, the modulus of elasticity varies as the strain changes.

TABLE 15-8 *Repeat units and applications for selected elastomers*

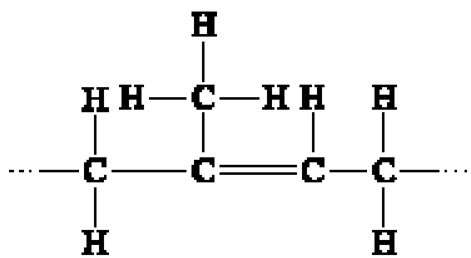
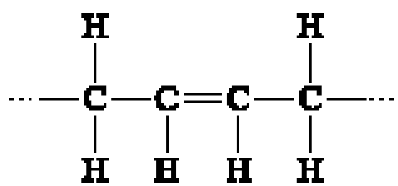
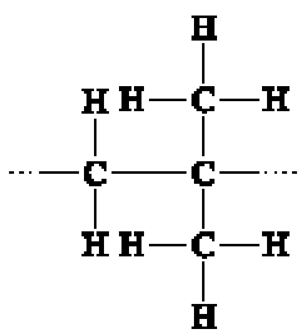
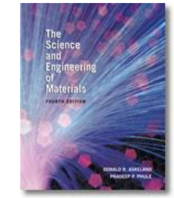
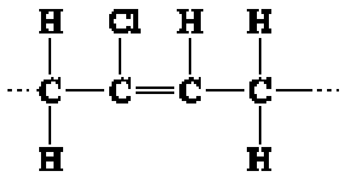
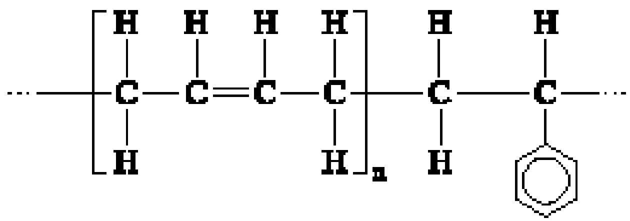
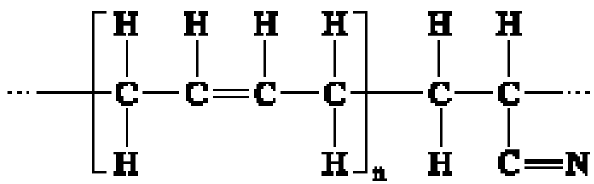
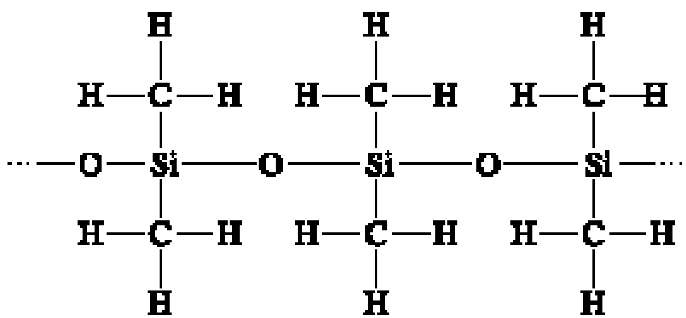
Polymer	Repeat Unit	Applications
Polyisoprene		Tires, golf balls, shoe soles
Polybutadiene (or butadiene rubber or Buna-S)		Industrial tires, toughening other elastomers, inner tubes of tires, weatherstripping, steam hoses
Polyisobutylene (or butyl rubber)		

Table 8 (Continued)



Polychloroprene (Neoprene)		Hoses, cable sheathing
Butadiene-styrene (BS or SBR rubber)		Tires
Butadiene-acrylonitrile (Buna-N)		Gaskets, fuel hoses
Silicones		Gaskets, seals

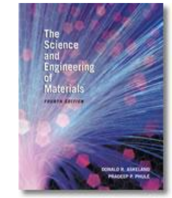


TABLE 15-9 ■ *Properties of selected elastomers*

	Tensile Strength (psi)	% Elongation	Density (g/cm^3)
Polyisoprene	3000	800	0.93
Polybutadiene	3500		0.94
Polyisobutylene	4000	350	0.92
Polychloroprene (Neoprene)	3500	800	1.24
Butadiene-styrene (BS or SBR rubber)	3000	2000	1.0
Butadiene-acrylonitrile	700	400	1.0
Silicones	1000	700	1.5
Thermoplastic elastomers	5000	1300	1.06

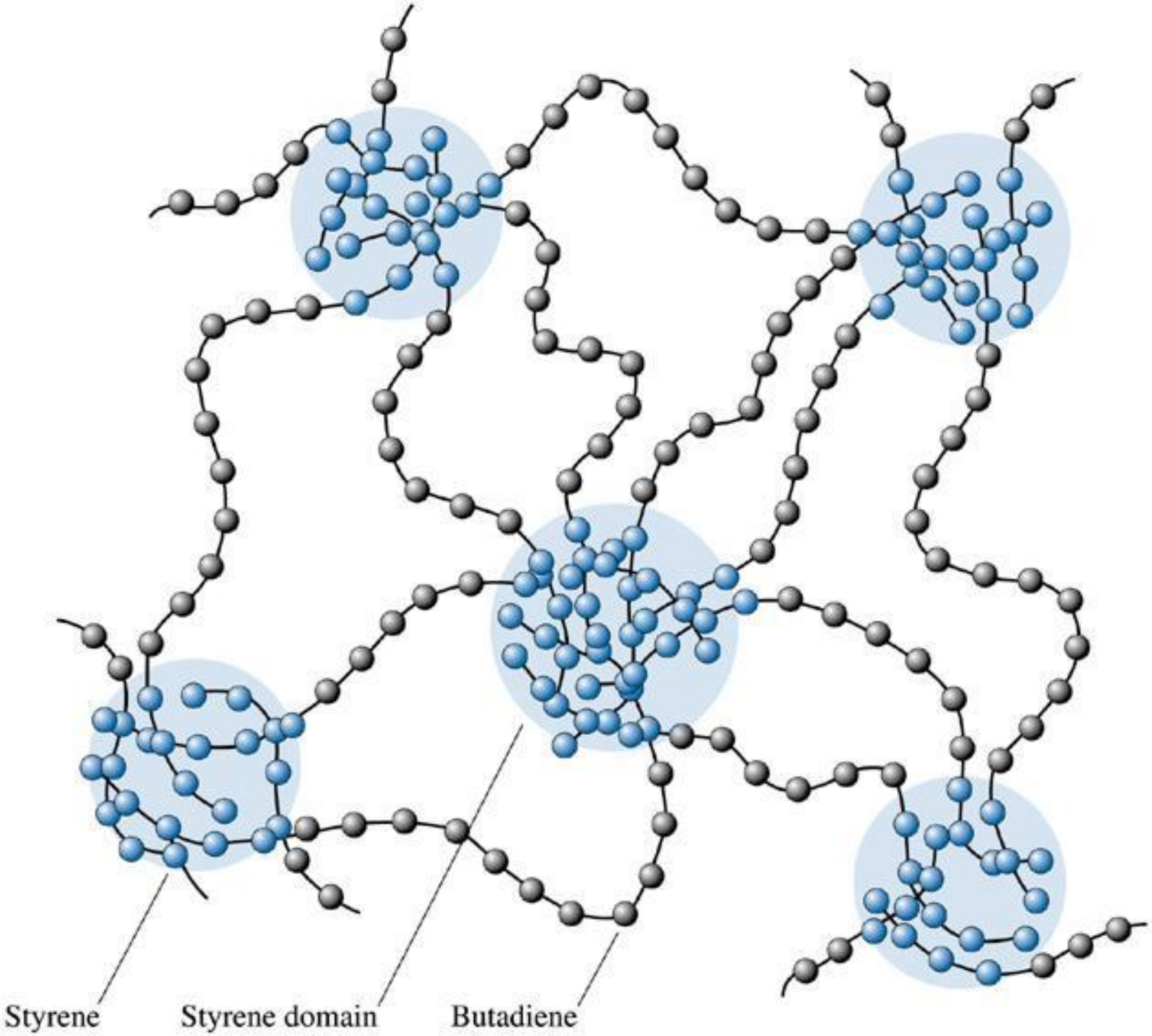


Figure 25 The structure of the styrene-butadiene (SB) copolymer in a thermoplastic elastomer. The glassy nature of the styrene domains provides elastic behavior without cross-linking of the butadiene.

Section 10
Thermosetting Polymers

- Phenolics
- Amines
- Urethanes
- Polyesters
- Epoxies
- Polyimides
- Interpenetrating Polymer Networks

TABLE 15-10 ■ ***Functional units and applications for selected thermosets***

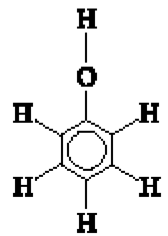
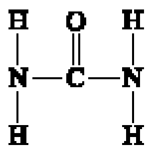
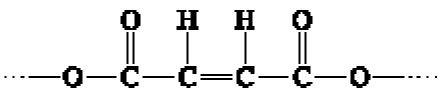
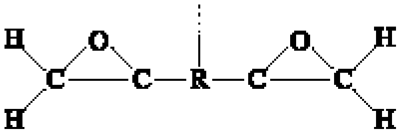
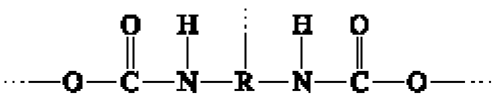
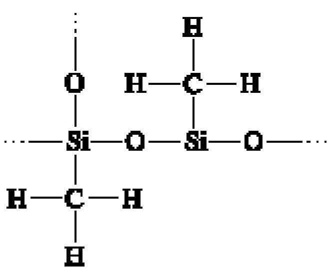
Polymer	Functional Units	Typical Applications
Phenolics		Adhesives, coatings, laminates
Amines		Adhesives, cookware, electrical moldings
Polyesters		Electrical moldings, decorative laminates, polymer matrix in fiberglass
Epoxies		Adhesives, electrical moldings, matrix for composites
Urethanes		Fibers, coatings, foams, insulation
Silicone		Adhesives, gaskets, sealants

TABLE 15-11 ■ ***Properties of typical thermosetting polymers***

	Tensile Strength (psi)	% Elongation	Elastic Modulus (psi)	Density (g/cm^3)
Phenolics	9,000	2	1300	1.27
Amines	10,000	1	1600	1.50
Polyesters	13,000	3	650	1.28
Epoxies	15,000	6	500	1.25
Urethanes	10,000	6		1.30
Silicone	4,000	0	1200	1.55

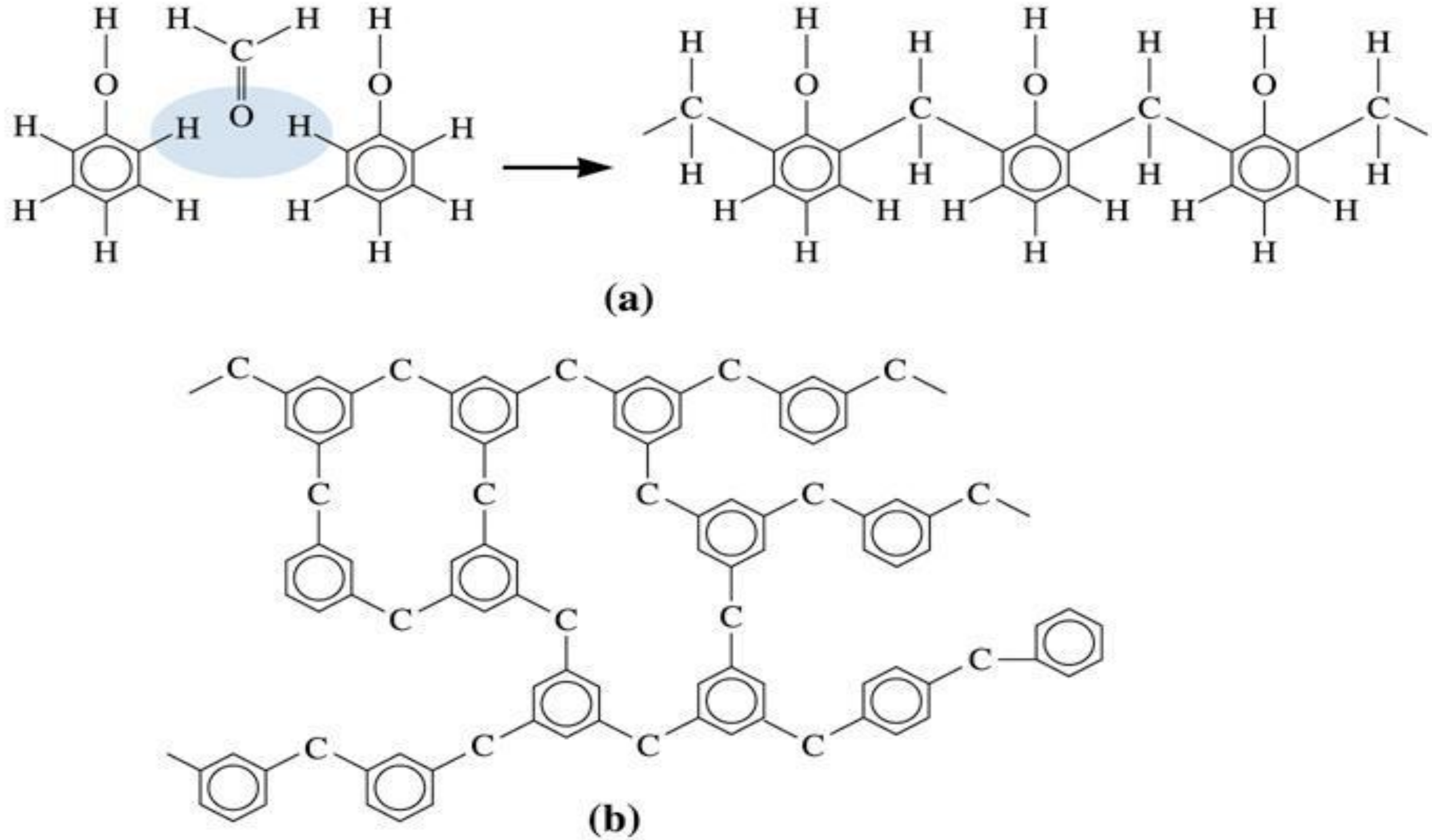


Figure 26 Structure of a phenolic. In (a) two phenol rings are joined by a condensation reaction through a formaldehyde molecule. Eventually, a linear chain forms. In (b), excess formaldehyde serves as the cross-linking agent, producing a network, thermosetting polymer.

Section 11
Adhesives

- Chemically Reactive Adhesives
- Evaporation or Diffusion Adhesives
- Hot-Melt Adhesives
- Pressure-Sensitive Adhesives
- Conductive Adhesives

Section 12
Additives for Plastics

- Fillers
- Pigments
- Stabilizers
- Antistatic Agents
- Flame Retardants
- Plasticizers
- Reinforcements
- Catalysts

Section 13
Polymer Processing and Recycling

Forming Processes for Thermoplastics:

- Extrusion
- Blow Molding
- Injection Molding
- Thermoforming

Forming Processes for Thermosetting polymers:

- Calendaring
- Spinning
- Compression Molding
- Transfer Molding

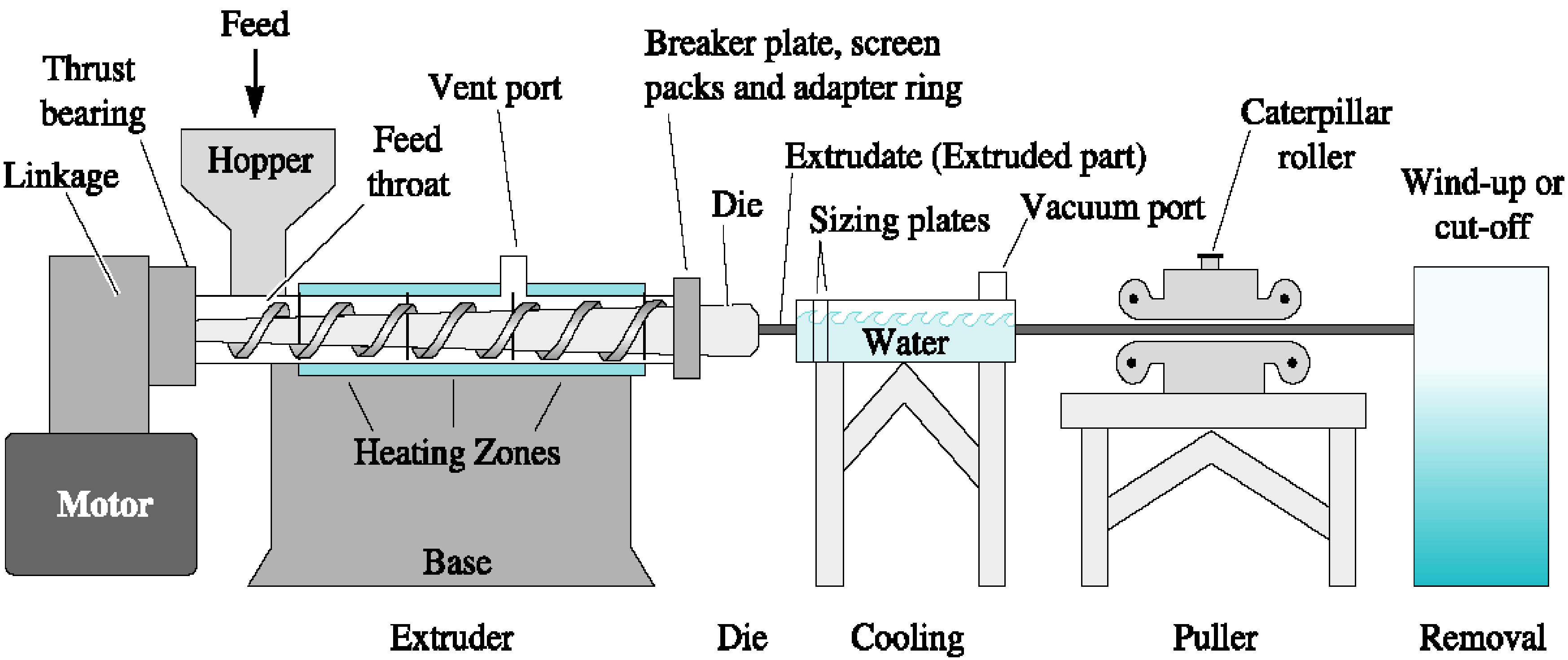


Figure 27 Schematic of an extruder used for polymer processing. (*Source: Adapted from* Plastics: Materials and Processing, *Second Edition, by A. Brent Strong, p. 382, Fig. 11-1. Copyright © 2000 Prentice Hall. Adapted with permission of Pearson Education, Inc., Upper Saddle River, NJ.*)

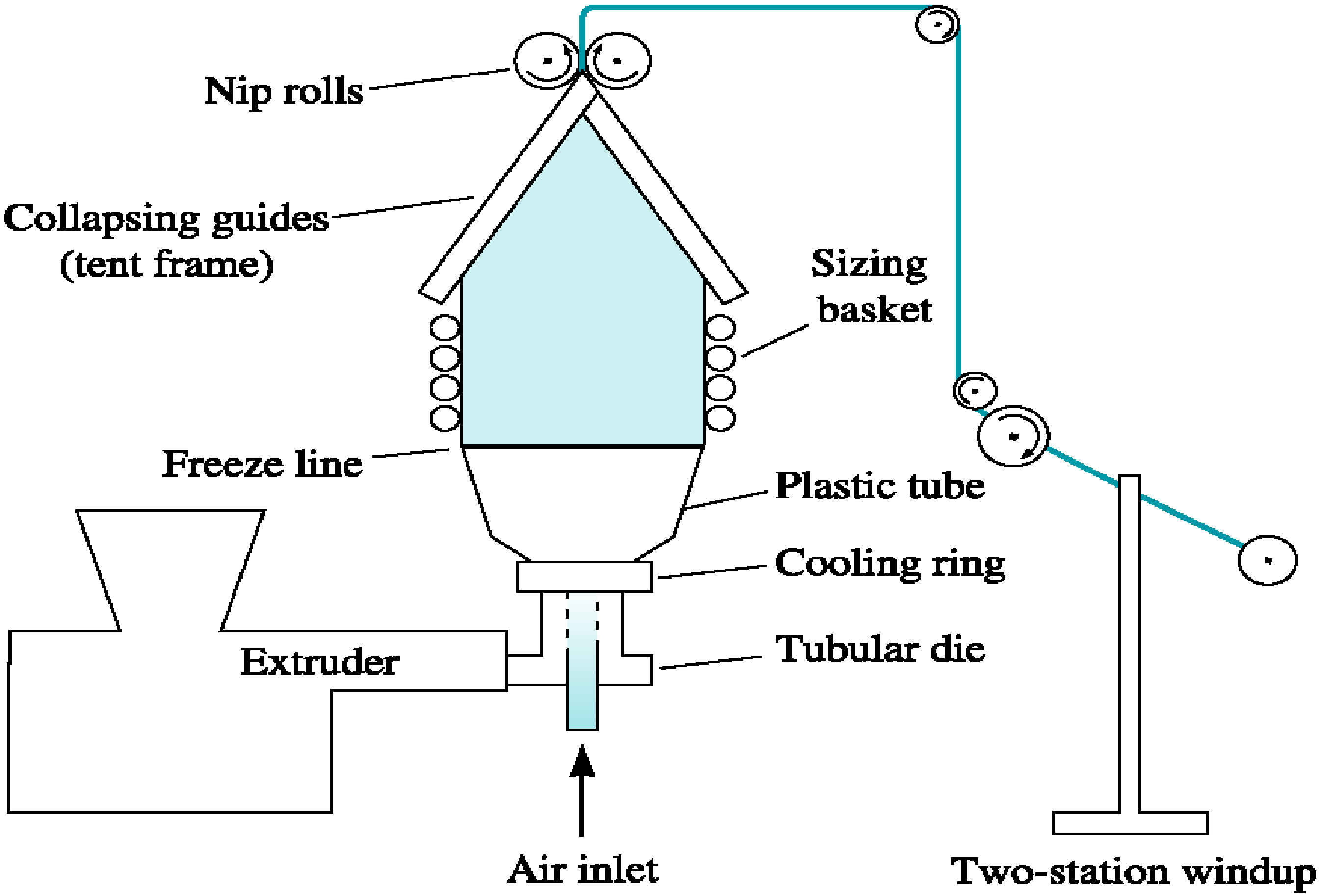


Figure 28 One technique by which polymer films (used in the manufacture of garbage bags, for example) can be produced. The film is extruded in the form of a bag, which is separated by air pressure until the polymer cools. (*Source: Adapted from* Plastics: Materials and Processing, *Second Edition, by A. Brent Strong, p. 397, Fig. 11-8. Copyright © 2000 Prentice Hall. Adapted with permission of Pearson Education, Inc., Upper Saddle River, NJ.*)

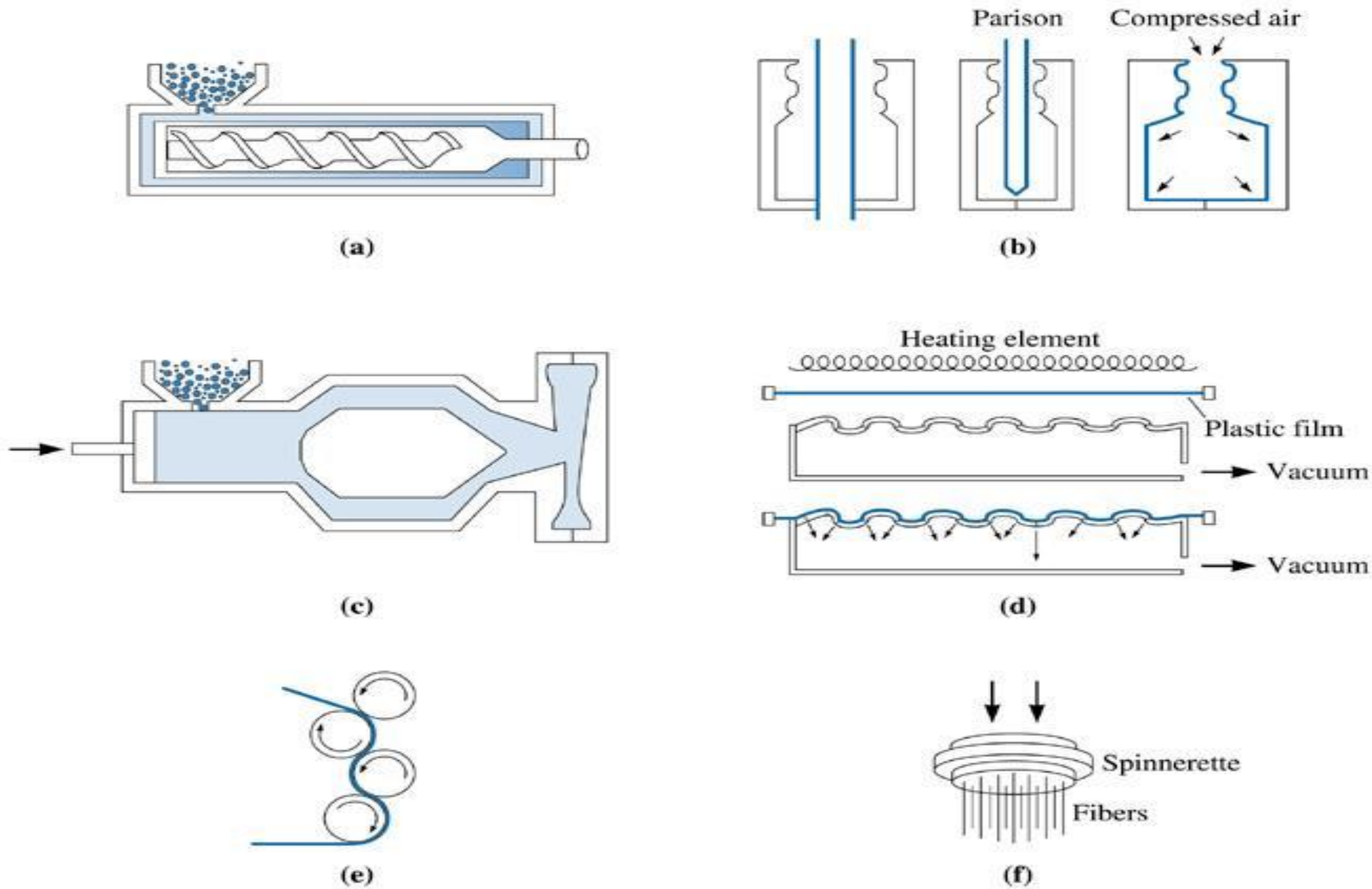


Figure 29 Typical forming processes for thermoplastic: (a) extrusion, (b) blow molding, (c) injection molding, (d) thermoforming, (e) calendaring, and (f) spinning.

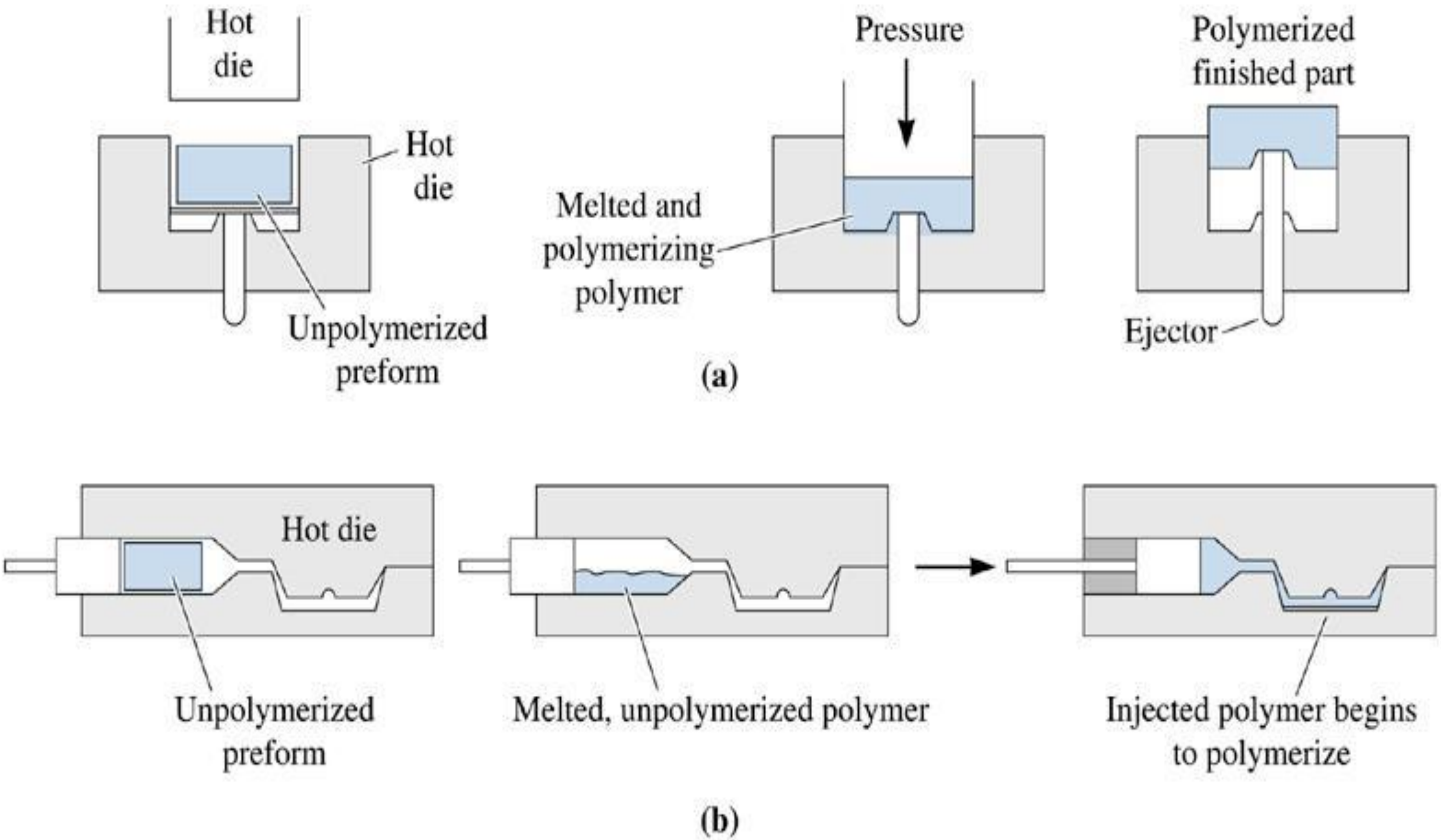


Figure 30 Typical forming processes for thermosetting polymers: (a) compression molding and (b) transfer molding.

Example 10
Insulation Boards for Houses

You want to design a material that can be used for making insulation boards that are approximately 4 ft wide and 8 ft tall. The material must provide good thermal insulation. What material would you choose?

Example 10 SOLUTION

Glasses tend to be good insulators of heat. However, they will be heavy, more expensive, and prone to fracture. Polymers are lightweight, can be produced inexpensively, and they can be good thermal insulators. We can use foamed polystyrene since the air contained in the pores adds significantly to their effectiveness as thermal insulators.

Finally, from a safety viewpoint, we want to be sure that some fire and flame retardants are added to the foams. Such panels are made using expanded polystyrene beads containing pentane.

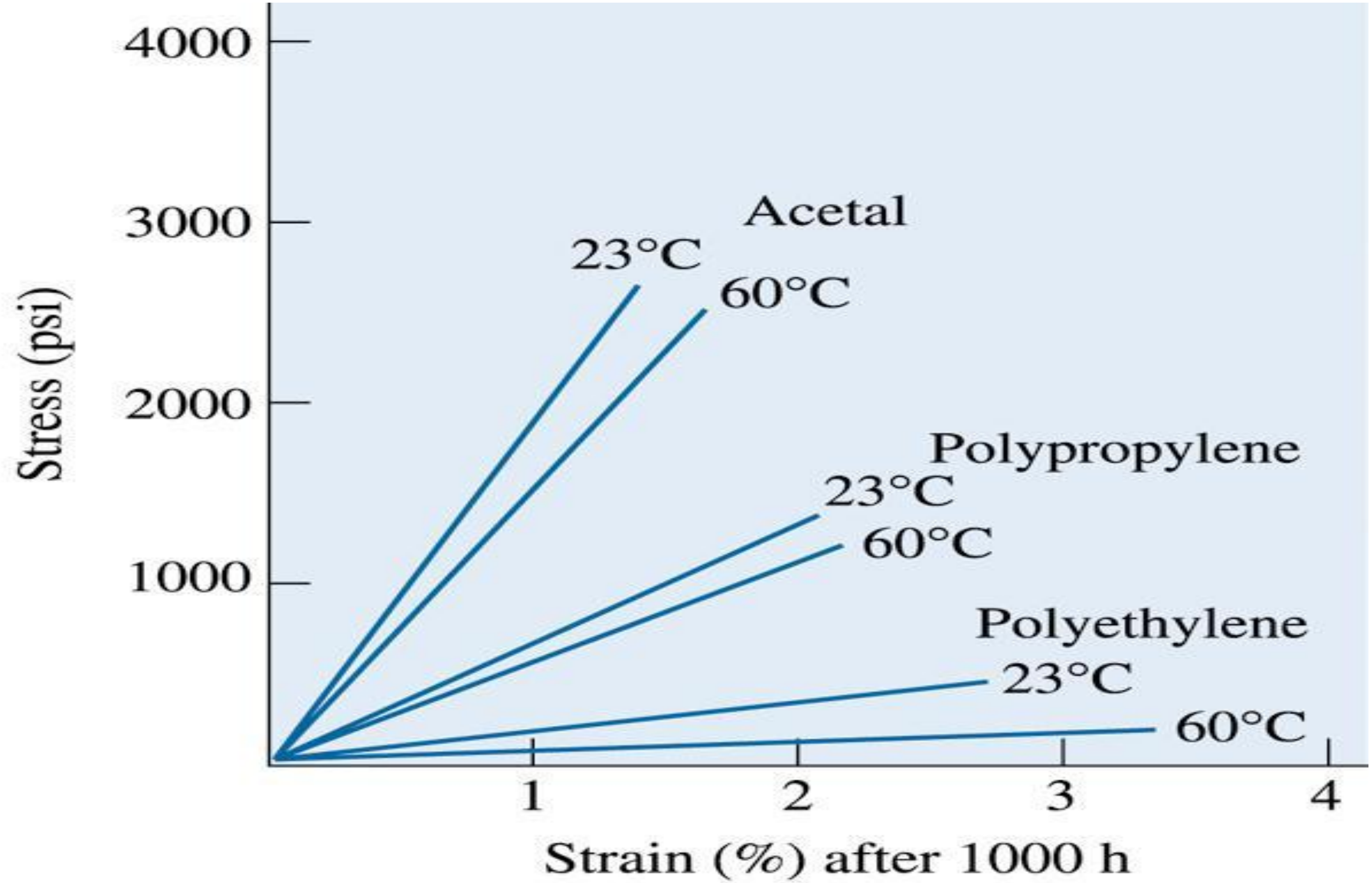


Figure 31 The effect of applied stress on the percent creep strain for three polymers (for Problem 15.62)