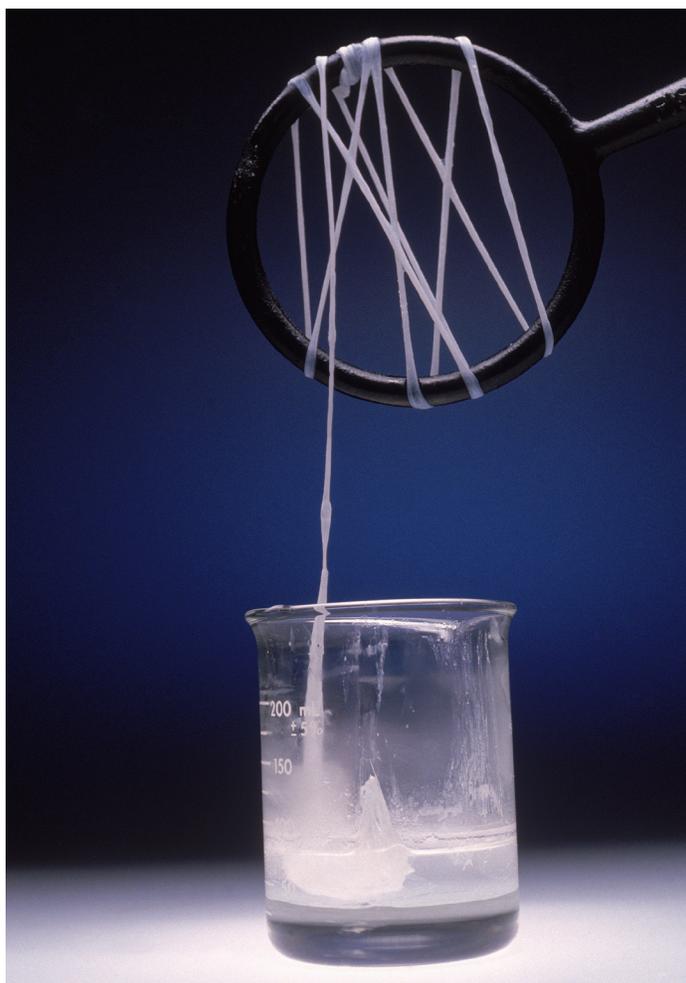
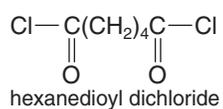


INTERCHAPTER 5

Synthetic Polymers



The formation of nylon by a condensation polymerization reaction at the interface of water and hexane, two immiscible solvents. The lower water layer contains the compound hexanedioyl dichloride,



The reaction produces nylon and $\text{HCl}(aq)$. The polymer forms at the interface between the two solutions and is drawn out as a continuous strand.

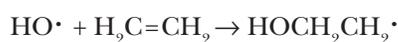
Some molecules contain so many atoms (up to tens of thousands) that understanding their structure would seem to be an impossible task. By recognizing that many of these macromolecules exhibit recurring structural motifs, however, chemists have come to understand how these molecules are constructed and, further, how to synthesize them. These molecules, called polymers, fall into two classes: natural and synthetic. Natural polymers include many of the biomolecules that are essential to life: proteins, nucleic acids, and carbohydrates among them. Synthetic polymers—most of which were developed in just the last 60 or so years—include plastics, synthetic rubbers, and synthetic fibers. We shall study synthetic polymers in this Interchapter and natural polymers in the next one.

Enormous industries have been built around synthetic polymer chemistry, which has profoundly changed the quality of life in the modern world. It is estimated that about half of all industrial research chemists are involved in some aspect of polymer chemistry. Few of us have not heard of nylon, rayon, polycarbonate, polyester, polyethylene, polystyrene, Teflon[®], Formican[®], and Saran, all of which are synthetic polymers. The technological impact of polymer chemistry is immense and continues to increase.

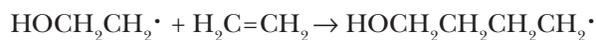
S-1. Polymers Are Composed of Many Molecular Subunits Joined End to End

The simplest very large molecule, or **macromolecule**, is polyethylene. Polyethylene is formed by joining many ethylene molecules, $\text{H}_2\text{C}=\text{CH}_2$, end to end. The repeated addition of small molecules to form a long, continuous chain is called **polymerization**, and the resulting chain is called a **polymer** (poly = many; mer = unit). The small molecules or units from which polymers are synthesized are called **monomers**.

The polymerization of the monomer ethylene can be initiated by a free radical, such as $\text{HO}\cdot$, the hydroxyl radical. (Recall from Section 7-7 that a free radical is a species having one or more unpaired electrons.) The first step in the polymerization of ethylene is the reaction described by



The product is a free radical that can react with another ethylene molecule to give

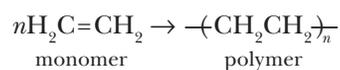


The product of this step is also a free radical that can react with another ethylene molecule according to



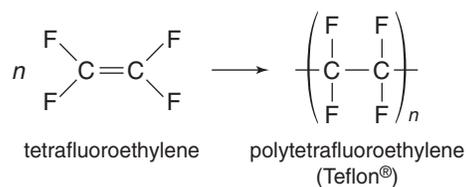
The product here is a reactive chain that can grow longer by the sequential addition of more ethylene molecules. The chain continues to grow until some **termination reaction**, such as the combination of two free radicals, occurs. The polyethylene molecules formed in this manner typically contain thousands of carbon atoms.

The polymerization of ethylene can be written schematically as



The notation $\text{-(CH}_2\text{CH}_2\text{)}_n\text{-}$ means that the group enclosed in the parentheses is repeated n times; it also serves to identify the monomer unit. The free radical that initiates the polymerization reaction is not indicated because n is large and thus the end group constitutes only a trivial fraction of the large polymer molecule. The precise number of monomer molecules incorporated into a polymer molecule is not important for typically large values of n . Polymer syntheses generally produce polymer molecules with a range of n values. The polymer properties are described in terms of the average value of n . It makes little difference whether a polyethylene molecule consists of 5000 or 5100 monomer units, for example.

Polyethylene is a tough, flexible plastic that is used in the manufacture of packaging films and sheets, wire and cable insulation, ice cube trays, refrigerator dishes, squeeze bottles, bags for foods and clothes, trash bags, and many other articles. Other well-known polymeric materials are made from other monomers. For example, polytetrafluoroethylene or Teflon[®] is produced from the monomer tetrafluoroethylene according to



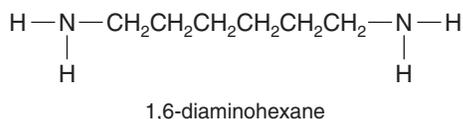
Teflon[®] is a tough, nonflammable, and exceptionally inert polymer with a slippery surface that is used for nonstick surfaces in pots and pans, and in electrical insulation, plastic pipes, and cryogenic bearings. Table S.1 lists some other common polymers made from substituted alkenes.

TABLE S.1 Common polymers prepared from substituted alkenes

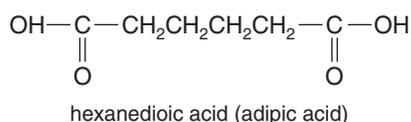
Names	Monomer	Applications	Structural unit
polyethylene	$\text{H}_2\text{C}=\text{CH}_2$ ethylene	machine parts, toys, buckets, containers, shrink wrap, bags, films, pipes, electrical insulation	$\left(\text{CH}_2-\text{CH}_2 \right)_n$
polypropylene	$\begin{array}{c} \text{HC}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ propylene	food packaging, ropes, clothing, carpeting, molded plastic parts, labware, pipes, valves	$\left(\begin{array}{c} \text{CH}-\text{CH}_2 \\ \\ \text{CH}_3 \end{array} \right)_n$
polychloroethylene, polyvinylchloride, PVC, or vinyl	$\begin{array}{c} \text{HC}=\text{CH}_2 \\ \\ \text{Cl} \end{array}$ vinyl chloride	building materials, pipes, tubing, electrical insulation, signs, toys	$\left(\begin{array}{c} \text{CH}-\text{CH}_2 \\ \\ \text{Cl} \end{array} \right)_n$
polychloroprene, Neoprene	$\begin{array}{c} \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \\ \quad \\ \text{Cl} \quad \text{H} \end{array}$ chloroprene	high-quality automobile and garden hoses, wet suits, gaskets	$\left(\begin{array}{c} \text{H}_2 \\ \\ \text{C} \\ \\ \text{Cl} \end{array} = \begin{array}{c} \text{C} \\ \\ \text{H} \end{array} \begin{array}{c} \text{H}_2 \\ \\ \text{C} \\ \\ \text{H} \end{array} \right)_n$
Plexiglas [®] , Lucite [®] , acrylic glass, polymethyl methacrylate	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{H}_3\text{C}-\text{O}-\text{C}=\text{O} \end{array}$ methyl methacrylate	helmet visors, aquariums, hard contact lenses, dentures, office furniture, artificial fingernails	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{C} \\ \\ \text{H}_3\text{C}-\text{O}-\text{C}=\text{O} \end{array} \right)_n$
Teflon [®] , polytetrafluoroethylene, or PTFE	$\text{F}_2\text{C}=\text{CF}_2$ tetrafluoroethylene	nonstick coatings; lubricant coatings on certain mechanical parts	$\left(\begin{array}{c} \text{F} \quad \text{F} \\ \quad \\ \text{C}-\text{C} \\ \quad \\ \text{F} \quad \text{F} \end{array} \right)_n$
polyacrylonitrile, Orlon [®] , Acrilan [®] , or acrylic fibers	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{CN} \end{array}$ acrylonitrile	acrylic fabrics, tents, awnings, sails, carpet, carbon fibers (for bikes, tennis rackets, auto bodies, etc.)	$\left(\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{CN} \end{array} \right)_n$
polystyrene or expanded polystyrene (Styrofoam [™])	$\begin{array}{c} \text{H}_2\text{C}=\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array}$ styrene	packaging, insulation, modeling, biological labware, toys	$\left(\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array} \right)_n$

S-2. Nylon and Dacron Are Made by Condensation Reactions

The polymerization reaction of ethylene is an **addition polymerization reaction** because it involves the direct addition of monomer molecules. Another type of polymerization reaction is a **condensation polymerization reaction**. In such a reaction, a small molecule, such as water, is split out as each monomer is added to the polymer chain. The polymerization product is called a **condensation polymer**. The synthesis of nylon is an example of a condensation polymerization reaction. Nylon is formed by the reaction of a diamino compound, such as 1,6-diaminohexane,

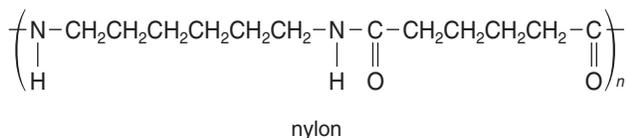


and a dicarboxylic acid, such as hexanedioic acid (adipic acid),



These two molecules can be linked by the reaction described by the equation shown in the box below.

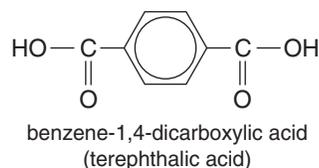
The product in this reaction is called a **dimer** (di = two; mer = unit). Observe that one end of the dimer is an amino group, $-\text{NH}_2$, and the other end is a carboxyl group, $-\text{COOH}$. The dimer can grow by the reaction of its amino end with a dicarboxylic acid monomer or by the reaction of its carboxyl end with a diamine monomer. Repetition of this process yields nylon (Frontispiece), whose general formula is



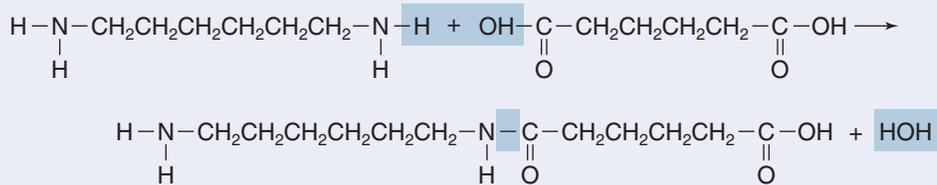
The two monomers of nylon are linked together by an **amide bond**, $\begin{array}{c} -\text{N}-\text{C}- \\ | \qquad || \\ \text{H} \qquad \text{O} \end{array}$. A condensation polymerization reaction, such as the synthesis of nylon, generally involves two different monomers that combine to form the basic repeating unit of the polymer. A polymer made from more than one type of monomer is known as a **copolymer**, whereas one made from just one type of monomer is called a **monopolymer**.

Nylon was first synthesized by W. H. Carothers of the Dupont Chemical Company in 1931. His work was carried on by his colleague Paul J. Flory, who was awarded the 1974 Nobel Prize in Chemistry for his research on the dynamics and physical properties of polymers (Figure S.1). Their research played a major role in launching the U.S. polymer chemical industry. Over one thousand metric tons of nylon fiber are produced annually in the United States. It is used to make strong, long-wearing fibers that find extensive use in rugs as well as hosiery, sweaters, and other clothing. Nylon resembles silk in many of its properties but is cheaper to produce. This resemblance to silk is not at all coincidental. Silk is a protein, and, as we shall learn in Interchapter T, proteins are polymers in which the monomers are linked together by amide bonds as in nylon.

Polyethylene terephthalate, commonly known as Dacron[®], is a condensation polymer typically formed from the monomers ethane-1,2-diol (commonly called ethylene glycol), $\text{HOCH}_2\text{CH}_2\text{OH}$, a dialcohol, and benzene-1,4-dicarboxylic acid (or terephthalic acid),



a dicarboxylic acid. The reaction proceeds by the formation of an ester linkage between a carboxyl group on the dicarboxylic acid and an $-\text{OH}$ group of the dialcohol. The basic polymer unit in Dacron[®] is



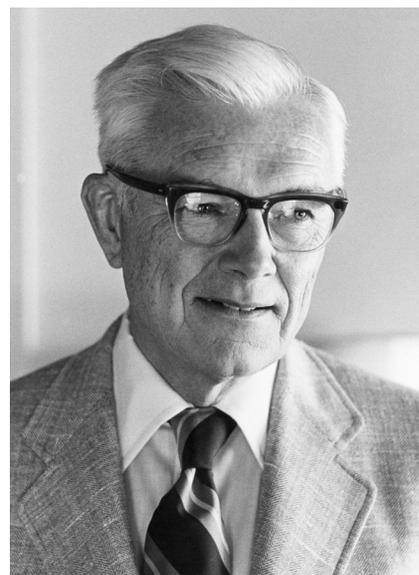
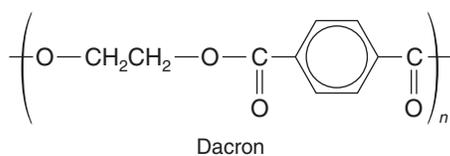


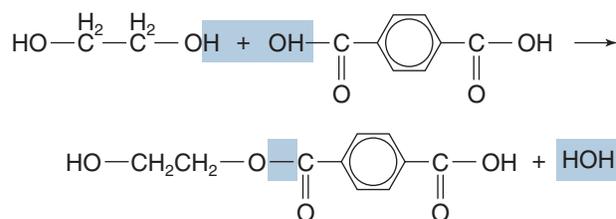
Figure S.1 Wallace H. Carothers (1896–1937) (*left*). Carothers discovered nylon in 1931 while working at Dupont. His work was carried on by his colleague Paul J. Flory (1910–1985) (*right*), who was awarded the 1974 Nobel Prize in Chemistry for his research on the dynamics and physical properties of polymers. Their research played a major role in launching the U.S. polymer chemical industry. Carothers and Flory were members of a research group at Dupont that was given freedom to pursue research problems that were of interest to them without regard to the potential practical applications of their work. This approach was a novel one in industrial research at that time. The many practical applications that sprang from their work led to the establishment of numerous industrial research laboratories. The discoveries made in these chemical research laboratories have impacted almost every aspect of our modern lives; one look around almost any room reveals the ubiquity of items incorporating synthetic polymers.



Dacron[®] is called a **polyester** because the monomers

are joined together through ester linkages, $\text{—O—C}(=\text{O})\text{—}$.

The ester linkage results from an esterification reaction (Interchapter R) of one of the alcohol groups of ethylene glycol with one of the carboxyl groups of terephthalic acid according to



This dimer can grow through the reaction of its left-hand end with another terephthalic acid molecule and the reaction of its right-hand end with another ethylene glycol molecule.

Dacron[®] is a light and durable polymer that is used to make clear films, skis, boat and aircraft components,

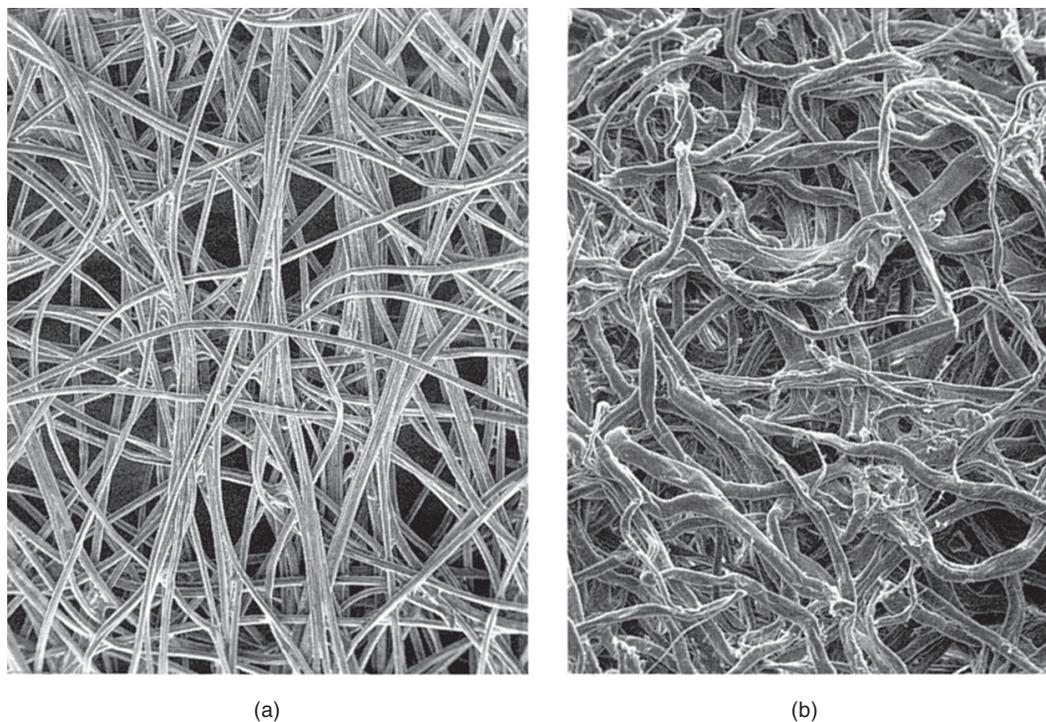
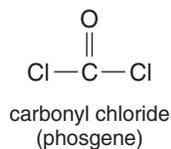


Figure S.2
 (a) Synthetic Dacron fibers and (b) natural cotton fibers. A blend of these two fibers produces permanent-press clothing.

surgical components, and permanent-press clothing. When used for clothing, it is usually blended in a roughly two-to-one ratio with cotton because the resulting blended fibers are softer and pass moisture more readily than pure Dacron® (Figure S.2).

Another example of a condensation polymer is polycarbonate or Lexan (Figure S.3). Lexan is a transparent, shatter-resistant polymer that is used to fabricate safety glasses, safety helmets, electrical components, and optical media such as DVDs. Nalgene products are made of Lexan. Lexan is formed from the reaction of carbonyl chloride (phosgene),



and the compound bisphenol A:

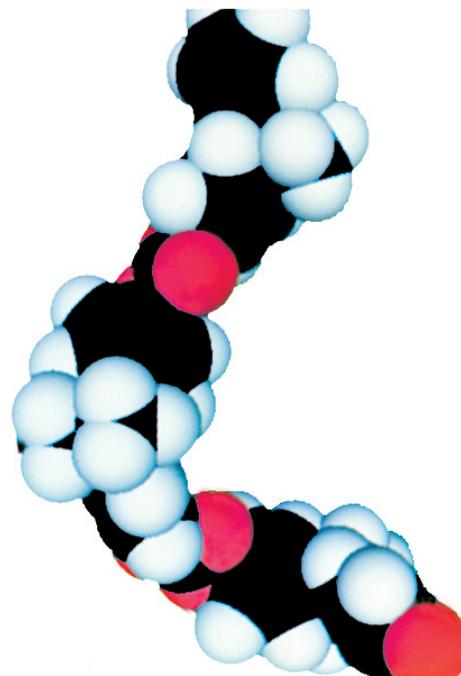
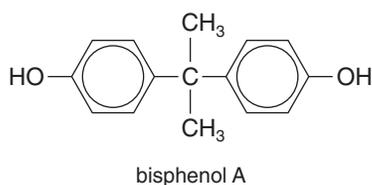
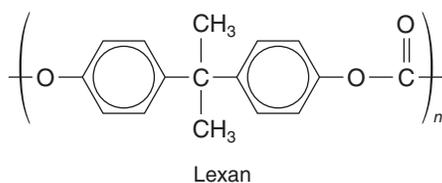


Figure S.3 A computer-generated three-dimensional space-filling model of a section of the polymer chain of polycarbonate or Lexan. The black spheres represent the carbon “backbone” of a Lexan polycarbonate polymer chain; the white spheres indicate the hydrogen atoms; and the red spheres indicate oxygen atoms.

The reaction proceeds in the presence of pyridine by splitting out two molecules of HCl per polymer unit to give



There are many other condensation polymers, including polyurethanes (insulation and furniture) and phenolics (brake linings and structural components). The essential feature in the synthesis of condensation polymers is the presence of reactive groups at both ends of the monomers. Table S.2 lists some industrially important polymers and their annual production by region.

One of the most significant developments in polymer chemistry is the recent production of conducting polymers: plastics that can conduct an electrical current (Figure S.4). Conducting polymers are currently used to produce low-energy LED lighting, solar cells, smart windows, and the small flat-screen displays found in most cellular phones and handheld devices. In the future, conducting polymers may make it possible to synthesize transistors made of individual mol-

ecules—allowing the entire contents of a modern desktop computer to fit into a wristwatch. Panels of low-energy LED lighting based on conducting polymers may replace incandescent and fluorescent light bulbs, yielding great energy savings and integrating lighting seamlessly into home building materials, allowing for a wide range of creative and artistic lighting options. Conducting polymers may also lead to a new generation of microsized medical implants and sensors, inexpensive flexible solar paneling, and a wide range of new and smaller electronic devices.

S-3. Polymers with Cross-Linked Chains Are Elastic

Depending on the length of the polymer chains and on the temperature, a particular type of polymer may exist as a viscous liquid, a rubbery solid, a glass, or a partially crystalline solid. Generally, the longer the average length of the polymer chains, the less liquid-like the polymer at a given temperature. For chain lengths involving more than 10 000 bonds, liquid flow is negligible at normal temperatures, but elastic-like deformations are possible.

The elasticity of polymers can be explained in terms of structure. Although we write the formulas for polymers as straight lines across a page, the

TABLE S.2 2006 Annual production data for some commercially important polymers*

Polymer	Annual production/thousands of metric tons		
	United States and Canada	Europe, Russia, and Turkey	Japan, Korea, and Taiwan
polyethylene	19 244	14 500	7 943
polypropylene	8 301	9 050	7 263
polyvinylchloride (PVC)	6 767	6 600	3 349
polystyrene	3 039	1 860	3 467
other styrene polymers	1 411	900	2 351
synthetic rubber	1 960	4 300	1 759
polyesters	1 334	975	645
polyamides	576	2 119	
Epoxy resins	283	690	229

*Most data from “Facts and Figures,” *C&E News*, July 2007, pp. 55–64. Blank space indicates no data available for entry but not necessarily a lack of production.



Figure S.4 Alan G. MacDiarmid of the University of Pennsylvania (*left*), Hideki Shirakawa of the University of Tsukuba, Japan (*center*), and Alan J. Heeger of the University of California at Santa Barbara (*right*), shared the 2000 Nobel Prize in Chemistry “for the discovery and development of conducting polymers.”

tendency of individual polymer chains is to coil into the shape of a ball, as shown in Figure S.5a. If we were to grab the polymer at two points and stretch it, it would rebound into the coiled configuration upon release. Thus, individual polymer chains show a property of elasticity. In a sample of a polymer, not only are the individual chains coiled, but they are intertangled with one another. If the polymer is stretched, then the chains slowly untangle and the sample appears to flow. The relative movement of polymer chains that occurs when the sample is stretched can be decreased by connecting the polymer chains to one another through chemical bonds called **cross-links** (Figure S.5a). When the cross-linked network is stretched, the coils become elongated (Figure S.5b); but when the stress is released, the polymer network returns to its original coiled state. A cross-linked polymer that exhibits elastic behavior is called an **elastomer**. If the cross-links occur at average intervals of about 100 to 1000 bonds along the chain, then the polymer may be stretched to several times its unstretched length without breaking. The stretched polymer returns to its initial length when the force is

released. The resistance of an elastomer to stretching can be increased by increasing the number of cross-links between chains. High elasticity is found in substances composed of long polymer chains joined by sparsely distributed cross-links, such as the polymer chains found in rubber bands.

Natural rubber is composed of chains of *cis*-1,4-isoprene units with an average chain length of 5000 isoprene units (Figure S.6a). The major problem associated with natural rubber is tackiness, which causes particles of material to stick to the surface of the rubber. This problem was solved in 1839 by Charles Goodyear, who discovered that if sulfur is added to natural rubber and the mixture is heated (a process called **vulcanization**), then the rubber remains elastic but is much stronger and no longer tacky. The vulcanization of natural rubber involves the formation of $-S-S-$ cross-links between the polyisoprene chains (Figure S.6b). Interestingly, the ancient Aztecs had also developed a method of cross-linking natural latex from tree sap to produce rubber, probably by boiling the sap in a solution of juice from a species of morning glory vine that promotes cross-linking of the

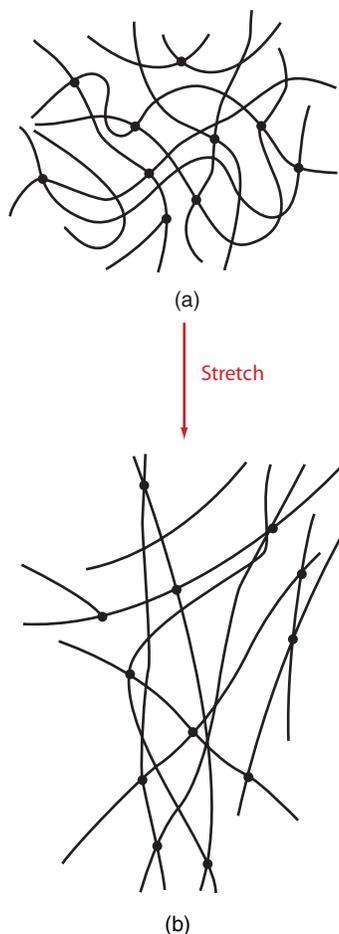
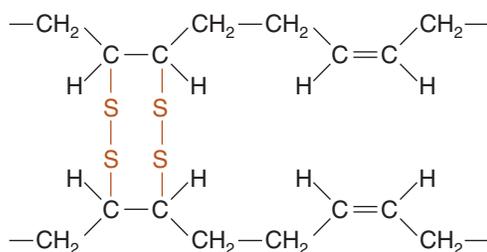


Figure S.5 Schematic representation of a cross-linked polymer network. The cross-links between chains are represented by dots. (a) In the natural (unstretched) state, the polymer chains are coiled. (b) When the polymer is stretched, the chains become elongated.

polymer. The Aztecs used the procedure to produce large rubber balls for sporting events, lip balm, bands to bind axe heads to shafts, and even latex paints.

The U.S. sources of natural rubber in Southeast Asia were cut off by Japanese territorial expansions in 1941. As a result, research in the United States directed toward the production of synthetic rubber underwent a major expansion that culminated in the development of several varieties of synthetic rubber, including a product essentially identical to natural rubber. As with all rubbers, vulcanization is used to produce the cross-links that give rise to the desired degree of elasticity. The United States produces about 2 million metric tons of synthetic rubber annually (Table S.2). The total world consumption of synthetic rubber in 2006 was 17.5 million metric tons.

An example of a synthetic rubber is polybutadiene, which is formed from the monomer butadiene, $\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$.



As in the case of the vulcanization of isoprene (Figure S.6), the $-\text{S}-\text{S}-$ cross-links result from the reaction of sulfur with carbon-carbon double bonds on adjacent polymer chains, as shown above.

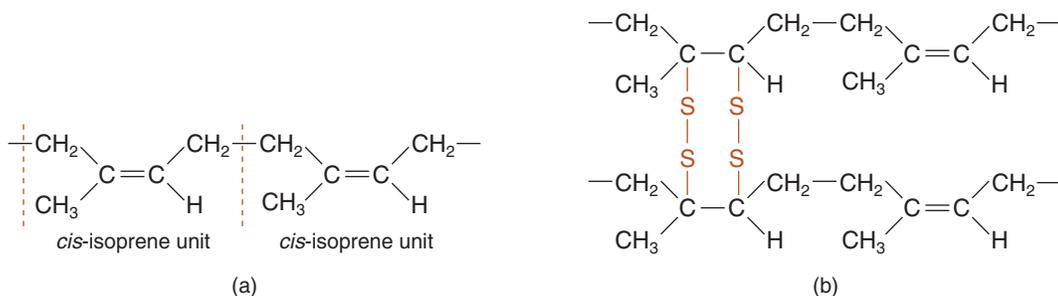


Figure S.6 The vulcanization of rubber involves the formation of disulfide ($-\text{S}-\text{S}-$) cross-links between chains.

TERMS YOU SHOULD KNOW

macromolecule S1
 polymerization S1
 polymer S1
 monomer S1
 termination reaction S1
 addition polymerization reaction S3
 condensation polymerization reaction S3
 condensation polymer S3
 dimer S3
 amide bond S3
 copolymer S3
 monopolymer S3
 polyester S4
 cross-links S7
 elastomer S7
 vulcanization S7

QUESTIONS

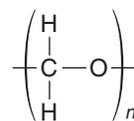
S-1. What is the difference between an addition polymerization reaction and a condensation polymerization reaction? Give an example of each.

S-2. How does cross-linking change the physical properties of polymers?

S-3. Write the chemical equation describing the reaction in which neoprene is produced. Is it an addition polymerization reaction or a condensation polymerization reaction?

S-4. Why do you think the nylon discussed in Section S-2 is called nylon-66?

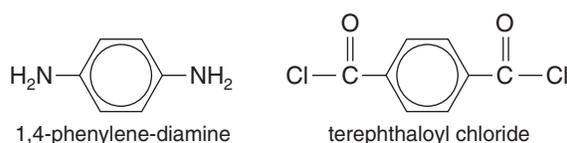
S-5. Polyoxymethylene (POM), an engineering plastic used to make bolts, bearings, handles, guitar picks, and other durable items, has the formula



Write the formula for the monomer. What is the common name of the monomer?

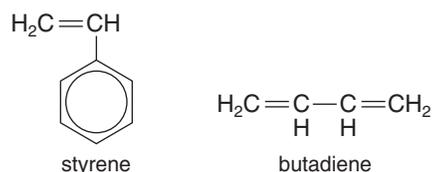
S-6. Write out the equations for the steps that describe the addition reactions between the chloroethylene (vinyl chloride) monomers that result in the formation of polychloroethylene (polyvinyl chloride or PVC).

S-7. Kevlar® is a strong synthetic fiber used in bulletproof vests and body armor. Kevlar® is made by the condensation reaction between 1,4-phenylenediamine and terephthaloyl chloride,



Write the equation for the condensation reaction that describes the formation of the copolymer in Kevlar®.

S-8. One form of synthetic rubber can be made from a styrene-butadiene copolymer.



Write the formula of the polymer.