Biopolymers, Natural Polymers, and Fibers

Early efforts during the growth of the plastics industry focused on the development of synthetic materials having comparable or superior properties to those of natural polymers. The first important advance was the development of nylon (synthetic silk) by Wallace Carothers at DuPont in 1938. In the commercial fiber industry, natural polymers such as cotton and silk, some chemically modified natural polymers including regenerated (e.g., viscose) cellulose and acetate, and synthetic polymers such as nylon are all important. With recent achievements in the mapping of the human genome and the beginning of the immense task of identifying and studying the function of many thousands of cellular proteins, an understanding of the structure and function of proteins and polynucleotides is becoming increasingly desirable for many disciplines outside the life sciences. These include materials and chemical engineering and computer science. In addition, there has been significant recent interest in the use of renewable resources such as chitin, an amino polysaccharide, to compete with other commodity thermoplastics. This chapter focuses first

on biopolymers and other naturally occurring polymers including proteins, polynucleotides, and polysaccharides. This coverage is followed by a section on natural and synthetic fibers.
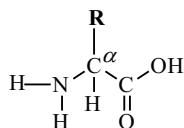
8.1   Biopolymers and Other Naturally Occurring Polymers

There are three main classes of biopolymers—proteins and polypeptides, polynucleotides, and polysaccharides. In biological systems, proteins have many roles including use as protective or supportive molecules in animals, as catalyst substrates, as oxygen-transporting molecules, and as regulators of chemical reactions in cells. Polynucleotides control such important functions as information storage and transfer, cell replication, and protein synthesis in living systems. The role of polysaccharides is primarily as skeletal reinforcement in plants and energy storage in both plants and animals.

Many naturally occurring polymers such as silk and cotton are utilized in their native form as textile fibers. Regenerated cellulose and cellulose derivatives are used in both fiber and film form as will be discussed in Section 8.2.2. Other naturally occurring polymers include keratin, collagen, elastin, fibronectin, and even polyisoprene (e.g., natural rubber). There are two other classes of naturally-occurring polymers that are important renewable resources and offer significant potential for commercial applications in many areas. These include agarose, made from seaweed, and chitin and its derivative, chitosan, which are obtained from the shells of shrimp and crabs.

8.1.1 Proteins

Proteins are heteropolymers containing up to 20 different types[*] of amino acids of the general structure

$$
\begin{array}{c}
\mathbf{R} \\
| \\
\mathrm{H\!-\!N}\underset{\underset{\mathrm{H}}{|}}{\overset{}{\diagup}}\overset{\alpha}{\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}}\underset{\mathrm{O}}{\overset{}{\underset{\|}{\mathrm{C}}}}\diagdown\mathrm{OH}
\end{array}
$$

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[*] The term *polypeptide* indicates a chain composed of a single amino acid while proteins contain two or more residues from any of the 20 genetically encoded amino acids in mammalial cells. A few organisms use 21 amino acids.
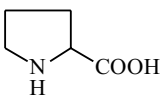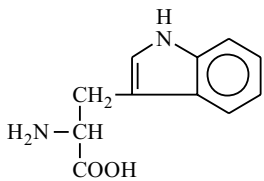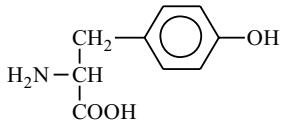
where R is a hydrogen atom in the case of the simplest amino acid glycine or any of a wide variety of substituent groups such as CH_3 (alanine) or an alkyl group as in the case of leucine. Identification of all 20 amino acids, including their common abbreviations, chemical structures, and characteristics, is are given in Table 8-1. With the sole exception of glycine, amino acids are optically active chiral molecules due to the asymmetric C^α as identified above. All naturally occurring proteins contain L-amino acids.

Table 8-1   Naturally Occurring Amino Acids

Amino Acid	Symbol	Structure	Character
Alanine	Ala	CH_3 $H_2N-CH-COOH$	Nonpolar, hydrophobic
Arginine	Arg	$CH_2(CH_2)_2NHC(NH)NH_2$ $H_2N-CH-COOH$	Basic
Asparagine	Asn	CH_2CONH_2 $H_2N-CH-COOH$	Polar, hydrophilic
Aspartic acid	Asp	CH_2COOH $H_2N-CH-COOH$	Acidic
Cysteine	Cys	CH_2SH $H_2N-CH-COOH$	Polar, hydrophilic
Glutamic acid	Glu	CH_2CH_2COOH $H_2N-CH-COOH$	Acidic
Glutamine	Gln	$CH_2CH_2CONH_2$ $H_2N-CH-COOH$	Polar, hydrophilic
Glycine	Gly	H $H_2N-CH-COOH$	Polar, hydrophilic
Histidine	His	H_2N-CH, CH_2- (imidazole ring with N, N—H) $COOH$	Polar, hydrophilic
Isoleucine	Ile	$CH(CH_3)CH_2CH_3$ $H_2N-CH-COOH$	Nonpolar, hydrophobic
Leucine	Leu	$CH_2CH(CH_3)_2$ $H_2N-CH-COOH$	Nonpolar, hydrophobic

(continues)

Table 8-1   Naturally Occurring Amino Acids (continued)

Amino Acid	Symbol	Structure	Character
Lysine	Lys	$CH_2(CH_2)_3NH_2$ $H_2N-CH-COOH$	Basic
Methionine	Met	$CH_2CH_2SCH_3$ $H_2N-CH-COOH$	Nonpolar, hydrophobic
Phenylalanine	Phe	CH_2- (benzene ring) H_2N-CH $COOH$	Nonpolar, hydrophobic
Proline	Pro	(pyrrolidine ring) N, H, COOH	Nonpolar, hydrophobic
Serine	Ser	CH_2OH $H_2N-CH-COOH$	Polar, hydrophilic
Threonine	Thr	$CH(CH_3)OH$ $H_2N-CH-COOH$	Polar, hydrophilic
Tryptophan	Trp	(indole ring) H–N CH_2 H_2N-CH $COOH$	Polar, hydrophilic
Tyrosine	Tyr	CH_2- (benzene ring) $-OH$ H_2N-CH $COOH$	Polar, hydrophilic
Valine	Val	$CH(CH_3)_2$ $H_2N-CH-COOH$	Nonpolar, hydrophobic

Proteins, folded to unique compact states called native structures, perform various biological functions. Molecular weights of proteins can be as low as 6000 and as high as 1 million. The number of possible conformations that a protein can take is nearly astronomical—more than 10^{100} for a protein of only 100 amino acid residues.

In the cell, proteins are produced by an aqueous-phase polycondensation of amino acids in the ribosome. The amino acid sequence within the chain defines the

primary structure of the protein. This sequence determines the conformation, the *secondary* structure of the protein. The shape of the protein, determined by internal crosslinks and mutually attractive residues, constitutes the *tertiary* structure. For example, cysteine residues can form internal disulfide (S–S) crosslinks. The aggregation of individual polypeptide chains into a supramolecular structure defines the final or *quaternary* structure. Certain amino acids provide binding sites for nonprotein or prosthetic groups such as iron porphyrins (e.g., as found in hemoglobin and myoglobin) that serve to bind oxygen. These important groups complex with the imidazole component of histidine.

   Fibrous proteins are tough, insoluble materials found in the protective and connective tissues of mammals, birds, and reptiles. Fibrous proteins include α-keratins, which are α-helix proteins found in hair, wool, horn, nails, feathers, and leather. Hydrogen bonding and disulfide bridges between cysteine residues provide strength and toughness. β-keratin collagens are found in animal connective tissue and tendons. Individual polypeptide chains form a loose helix that can hydrogen-bond with two other chains to create a triple-stranded rope.

   All proteins can be classified into two categories—fibrous and globular. Globular proteins include the important biological proteins that regulate chemical reactions in the body. Globular proteins that are soluble in aqueous media include enzymes, antibodies, myoglobin, cytochrome C, serum albumin, and some hormones. These proteins contain both an α-helix and non-helical segments. As mentioned above, myoglobin is an iron-containing protein. It is composed of only 153 amino acids (molecular weight of 17,000) and is important as an oxygen-storing protein that is present in all animal tissues, particularly in whales and seals. It consists of a single polypeptide chain to which is attached one Fe(II)-porphyrin (heme) unit. Due to its simple structure and biological importance, myoglobin was the first protein whose structure was completely determined by John Kendrew in 1957 after 22 years of effort [1]. Another important protein is hemoglobin, which contains four myoglobin-like molecules arranged in a supramolecular structure. Lysozyme is an enzyme present in mucus or egg white that kills bacteria by attacking the cell wall. Lysozyme consists of a single polypeptide chain of 129 amino acid residues. The chain possesses four intramolecular cysteine crosslinks and three α-helices. Today, the structures of thousands of important proteins are known and readily available from sources such as the Protein Data Bank [2].

   The importance of proteins in the understanding and treatment of human diseases has led to the growth of a newly defined field of investigation, *proteomics*. Proteomics is the study of protein function and the interactions of proteins with small molecules and other proteins. Following the completion of the Human Genome Project in 2000, proteomics has become the new frontier. There may be as many as 200,000 proteins in the human genome. The total deciphering of the human proteome will be a more demanding task than mapping the human genome. Proteomics will focus on an understanding of where proteins are located in the cell, when they are present during the life of a cell, at what concentration, for how long, and

what other proteins they functionally interact with. Since most diseases are a result of protein malfunction, proteomics should lead to new advances in medical science.

Protein Synthesis. In the laboratory, proteins can be synthesized by a sequential addition of amino acids to crosslinked, chloromethylated polystyrene beads (see Section 2.4.1) by a procedure developed by Bruce Merrifield in the 1960s [3]. As discussed in Section 2.5.4, proteins can also be synthesized through a process involving gene-splicing of bacterial DNA. Synthetic human insulin can also be made in this way. Some synthetic polypeptides can be synthesized by a condensation reaction of some simple amino acids such as glycine, alanine, or phenylalanine. In a living cell, proteins are synthesized at ribosomal sites by the RNA-initiated process described in the following section.

8.1.2 Polynucleotides

Two main types of polynucleotides, or nucleic acids, occur in nature—deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). DNA provides the storage sites for genetic information within the chromosomes of the cell nucleus. RNA molecules transmit information coded into their structure to the ribosomes where protein synthesis occurs. A single nucleotide, the monomer with which polynucleotides are built, consists of three parts—a phosphoric acid residue, a cyclic five-carbon (pentose) sugar, and a heterocyclic organic base, either a purine or pyrimidine, as illustrated below.
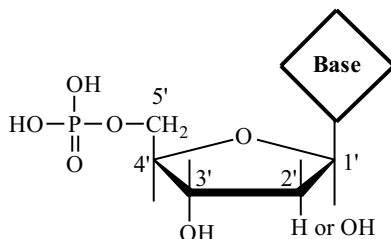
One of two types of sugar molecules, ribose or deoxyribose, is found in polynucleotides. The central difference between ribose and deoxyribose is the type of substituent group at the 2' carbon position. As shown next, ribose has a hydroxyl group at the 2' position; both substituents at the 2' position in deoxyribose are hydrogen atoms.[*]

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[*] For simplicity, hydrogen atoms are not explicitly shown but are understood to be present at all open positions.

ribose   deoxyribose
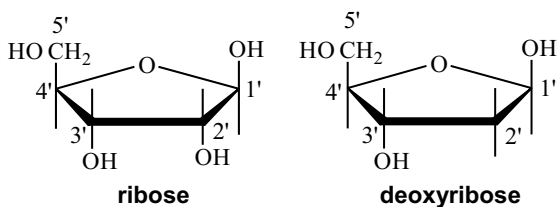
Only D-ribose is found in RNA while deoxy-D-ribose is unique for DNA.

The heterocyclic bases include two purines—adenine (A) and guanine (G)— and three pyrimidines—thymine (T), cytosine (C), and uracil (U). Structures of the five bases are shown in Table 8-2. Thymine, adenine, guanine, and cytosine are found in DNA; adenine, guanine, cytosine, and uracil are present in RNA. Thymine is, therefore, unique to DNA while uracil is unique to RNA. Sugar units of different nucleotides are joined by phosphate–hydroxyl linkages between the 3' and 5' carbons to form the polynucleotide. Representative skeletal chains for RNA and DNA are illustrated in Figure 8-1.

Table 8-2   Purine and Pyrimidine Bases Found in Nucleic Acids

DNA Only	DNA and RNA			RNA Only
Thymine	Adenine	Guanine	Cytosine	Uracil

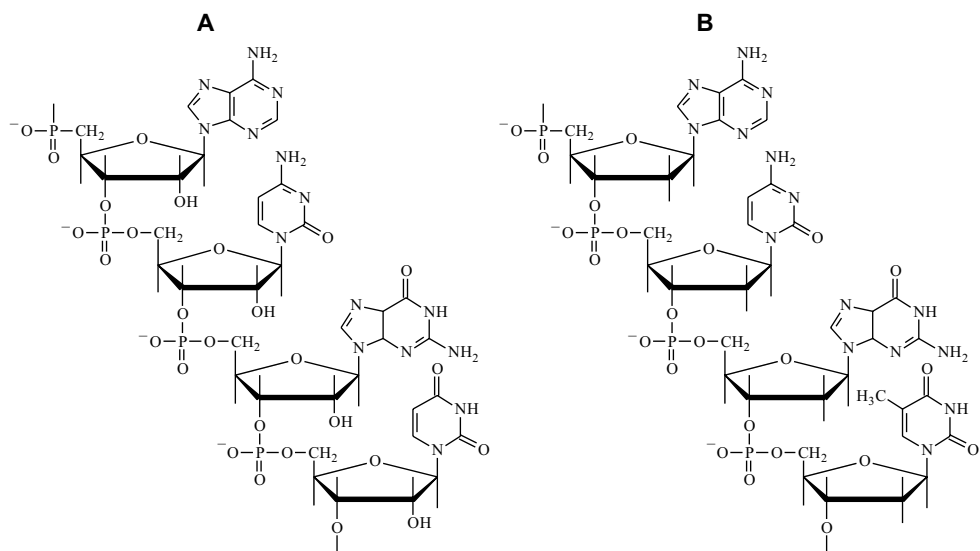**Figure 8-1**   (**A**) A representative four-nucleotide segment of RNA with an A–C–G–U base sequence. (**B**) A four-nucleotide segment of DNA with an A–C–G–T sequence segment.
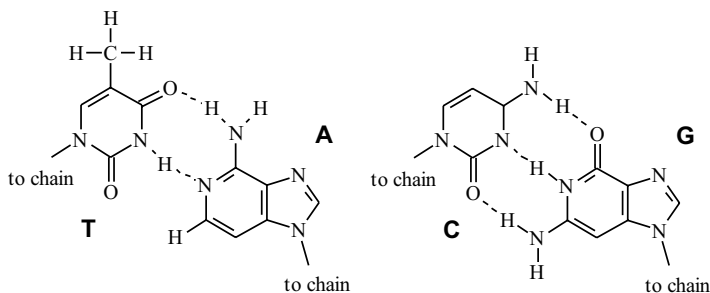
Figure 8-2   Hydrogen bonding between complementary base pairs in DNA.

A typical DNA molecule is extremely large. Molecular weights can range from several million to more than several hundred million corresponding to several thousand to hundreds of thousands of nucleotides. Within a cell, a DNA molecule exists in a very compact conformation, but when stretched out, a typical DNA molecule can form a thread several feet in length. As deduced by Watson and Crick from an analysis of the X-ray diffraction patterns of highly oriented DNA fibers obtained by Maurice Wilkins in 1953 [4, 5], DNA exists in the form of a right-handed helix with two complementary chains running in opposite directions. The helix undergoes one complete turn every 34 Å. The helical structure is stabilized by

the formation of hydrogen bonds between two complementary base pairs along the chain—either an A–T or a C–G combination as illustrated in Figure 8-2. As shown, two hydrogen bonds link adenine to thymine while three hydrogen bonds links guanine to cytosine. An illustration of a DNA double helix is shown in Figure 8-3.
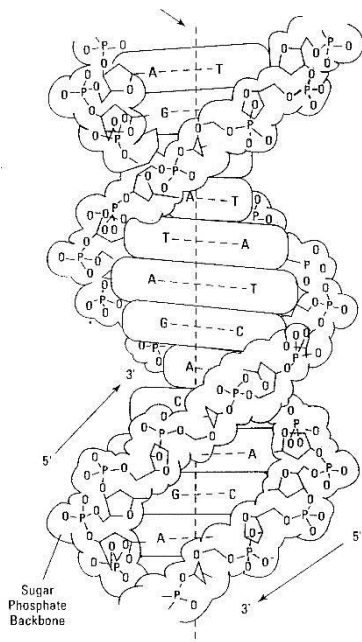

Figure 8-3   Structure of a DNA double helix. Arrows show the direction of phosphate linkages connecting 3' to 5' carbons on contiguous deoxyribose sugar residues. Adenine, thymine, guanine, and cytosine are hydrogen bonded to their complementary base pairs (see Figure 8-2) and stacked at right angles to the axis of the helix (top arrow). Reproduced from J. Yin, *Chemical Engineering Progress*, November 1999, p. 65–74, with permission from the American Institute of Chemical Engineers.

As discussed, RNA differs from DNA in the type of sugar (i.e., ribose in RNA and deoxyribose in DNA) and in the uniqueness of one pyrimidine base (i.e., thymine in DNA and uracil in RNA). Unlike DNA, RNA exists as a single helix and, therefore, does not possess the complementary base-pairing characteristic of DNA. RNA molecules are also significantly lower in molecular weight. Three forms of RNA are involved in protein synthesis. These are transfer RNA (t-RNA), messenger RNA (m-RNA), and ribosomal RNA (r-RNA). Messenger RNA accounts for about 5% to 10% of the cell's total RNA. The function of m-RNA is to receive genetic code from the DNA in the genes (the transcription process) and to transmit that in-

formation to the ribosomes where protein synthesis occurs.[*] The sequence of bases of the m-RNA is complementary to a portion of one DNA strand unwound from a DNA pair in the cell nucleus. For example, an A–T–C–G–T sequence in DNA will be transcribed to a U–A–G–C–U sequence in m-RNA. Transfer RNA molecules are relatively small, only about 70 to 80 repeating units in length.

Protein synthesis in the ribosome is a rapid process whereby as many as 150 amino acid residues can be assembled in a matter of seconds. The ribosomes are nearly spherical particles, about 200 Å in diameter, that are scattered through the cell protoplasm. These are formed from certain proteins and high-molecular-weight ribosome-RNA (r-RNA). The synthesis process involves four steps. Initially, amino acid molecules become enzymatically bound to t-RNA by an esterification reaction. There is at least one t-RNA for each amino acid; however, several different t-RNA molecules can attach to the same amino acid. Then an initiation complex is formed between the t-RNA ester and the m-RNA, whose code directs the sequential linkage of amino acids in the ribosome. Construction of the protein begins with a reaction between the carboxylic acid end of the first amino acid and the amino residue of the second amino acid that is coded by the m-RNA. Both m-RNA– and t-RNA–peptide chains are moved along the ribosome to position the next coded site. Finally, when the last coded instruction from the m-RNA has been followed, the completed protein separates from the ribosome.

It is clear that only four bases—adenine, uracil, guanine, and cytosine—must code for at least 20 different amino acids (see Section 8.1.1). This means that a sequence of at least three nucleotides, the codon, must provide the minimal code for a single amino acid. Such a three-base or triplet sequence represents 64 (4^3) combinations. Since there are only 20 genetically coded amino acids, some redundancy must be built into the coding process. This is a helpful protection against harmful mutations. As shown in Table 8-3, some amino acids (arginine, leucine, and serine) are coded for as many as six different triplet combinations while tryptophan and methionine are each coded by a single triplet (A–U–G and U–G–G, respectively). As also illustrated by Table 8-3, some codons provide a start or stop instruction to the protein synthesis process.

---

[*] A gene is a sequence in DNA that codes for a protein. In the human, there can be as many as 100,000 to 150,000 genes.

**Table 8-3   Codon Assignments for Individual Amino Acids in Protein Synthesis**

S E C O N D   P O S I T I O N

		U	C	A	G		
F	**U**	Phenylalanine	Serine	Tryosine	Cysteine	**U**	**T**
I						**C**	**H**
R		Leucine		STOP	STOP	**A**	**I**
S				STOP	Tryptophan	**G**	**R**
T	**C**	Leucine	Proline	Histidine	Arginine	**U**	**D**
						C	
P				Glutamine		**A**	**P**
O						**G**	**O**
S	**A**	Isoleucine	Threonine	Asparagine	Serine	**U**	**S**
I						**C**	**I**
T				Lysine	Arginine	**A**	**T**
I		Methionine[a]				**G**	**I**
O	**G**	Valine	Alanine	Aspartic acid	Glycine	**U**	**O**
N						**C**	**N**
				Glutamic acid		**A**	
						G	

[a] And START.

8.1.3 Polysaccharides

Polysaccharides, which include cellulose, starch, and glycogen, are cyclolinear polyethers formed by the condensation of sugar molecules. Degrees of polymerization can range from 30 to 100,000. Common types of sugar molecules found in cellulose and starch include two cyclic forms of glucose, or glucopyranoses. These are α-D-glucose (α-D-glucopyranose) and β-D-glucose (β-D-glucopyranose), whose chemical structures are shown in Figure 8-4. In cellulose, starch, and glycogen, the glucose residues are condensed via the hydroxyl groups at the 1 and 4 positions on adjacent molecules. Another important polysaccharide, chitin, an amino polysaccharide found in insect and some shellfish exoskeletons, is formed from 2-acetamido-2-deoxy-D-glucose (N-acetyl-D–glucosamine). Chitin differs from cellu-

lose only in the substitution of the hydroxyl group on the 2-carbon with the *N*-acetyl group

$$-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \,.$$
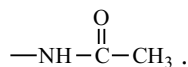
Cellulose and chitin are the most important naturally occurring polymeric materials due to their abundance, accessibility, low cost, and nontoxic, attractive properties including biodegradability and biocompatibility.
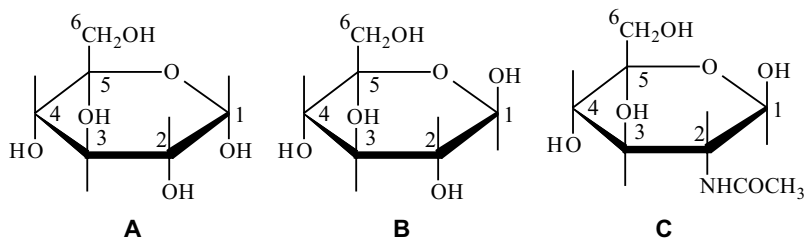

Figure 8-4   Sugars found in common polysaccharides. **A**. α-D-glucose; **B**. β-D-glucose; **C**. 2-acetamido-2-deoxy-D-glucose.

Cellulose. Cellulose is one of the most abundant organic materials found in nature. Cotton, in its purified form, is 94% cellulose with only small amounts of related products (e.g., hemicellulose and pectin). Wood contains about 50% cellulose. Plant cell walls and fibers are all made from cellulose. Cellulose is formed through the 1,4-β-linkage of glucose units. A typical chain of cellulose is composed of 200 to 6000 anhydroglucose units, each of which contains three hydroxyl groups and are linked by an acetal bridge (see Figure 8-5). Corresponding molecular weights are 300,000 to 1,000,000. Cellulose consists of fully extended chains that are strongly hydrogen bonded into sheets of a highly crystalline matrix. Cellulose is, therefore, an insoluble, infusible (i.e., degrades before melting) polymer and fibers and films are obtained only by chemically modifying cellulose, as discussed in Section 8.2.2.

Starch. Starch is the principal energy storage polysaccharide in photosynthetic plants. Most starches have two structurally different forms—amylose, a linear polymer having degrees of polymerization between 100 and 6000, and a high concentration of amylopectin, a highly branched fraction. Branches in amylopectin are 12 to 15 glucose residues in length and occur at every sixth to twelfth backbone residue. Amylose consists of 1,4-α linked glucose units compared to the 1,4-β linked glucose in cellulose. In water, amylose forms a helical conformation. Glycogen, which is more heavily branched than amylopectin, is used as an energy-storage mechanism in animal tissues.
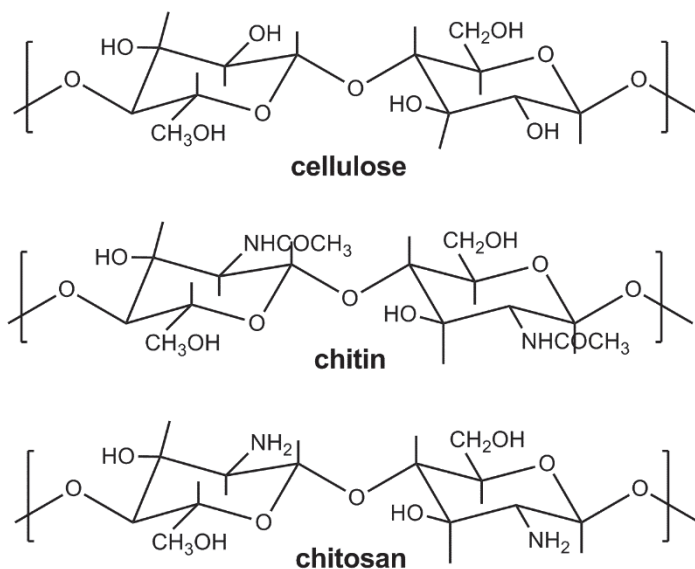
Figure 8-5   Chemical structures of cellulose, chitin, and chitosan.

Chitin. As mentioned earlier, a chitin molecule consists of 2-acetamido-2-deoxy-D-glucose units connected through a β (1-4) linkage, as shown in Figure 8-5.[*] Chitin occurs in two structural forms. The less abundant form is β-chitin, characterized by weak intermolecular forces due to the parallel arrangement of chitin molecules; α-chitin has stronger interactions due to its antiparallel arrangement. The high nitrogen content of chitin makes it useful as a chelating agent. Chitin is obtained as a waste product from the processing of seafood.

The chemical modification of chitin, as in the case of cellulose (see Section 2.4.2), is difficult due to its limited solubility. Chitin can be transformed into chitosan[†] that has free amino groups by deacetylating chitin. The degree of deacetylation is typically in the range from 70% to 95%. Deacetylation of chitin was reported as early as 1859 by Rouget, who boiled chitin in a concentrated hydroxide solution. The first U.S. patents reporting the production of chitosan and the preparation of film and fiber from chitosan were issued in 1934.

A comparison of the chemical structures of cellulose, chitin, and chitosan is shown in Figure 8-5. One of the most useful properties of chitosan is its ability to chelate harmful metal ions such as copper, lead, mercury, and uranium from waste

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[*] Poly-β(1→4)-2-acetamide-2-deoxy-D-glucopyranose.
[†] Poly-β(1→4)-2-amino-2-deoxy-D-glucopyranose.

water. Membranes prepared from chitosan can be used for water clarification, filtration, and controlled release. Chitosan is insoluble in water and in alkali and organic solvents but is soluble in most solutions of organic acids, such as acetic and formic acid, at a pH below 6.

Reactions of Polysaccharides. Polysaccharides can be hydrolyzed to oligosaccharides and glucose. Hydrolysis can occur by enzymatic action such as the action of amylase on the amylose fraction of starch. Polysaccharides can also be hydrolyzed by non-enzymatic processes including their hydrolysis in aqueous acid.

The available hydroxyl groups of cellulose provide sites for chemical modification including esterification and etherification. Such reactions have a significant effect on the properties and usefulness of cellulose. For example, cellulose nitrate is produced by the nitration of cellulose in a mixture of nitric acid and sulfuric acid. Cellulose acetate is obtained by reacting cellulose with acetic acid or acetic anhydride (see Section 2.4.2). Cellulose ethers can be prepared by reacting alkali-cellulose[*] with an alkyl halide such as methyl chloride. Methylcellulose is soluble in water and used as an adhesive, a foam stabilizer, and a binder in ink. Carboxy-methylcellulose is obtained from the reaction of alkaline cellulose with chloroacetic acid or chloroacetate as shown by Figure 8-6. The sodium form of carboxymethyl-cellulose is called cellulose gum. It is also water soluble and is used as a thickening, binding, and stabilization agent in foods and other applications.
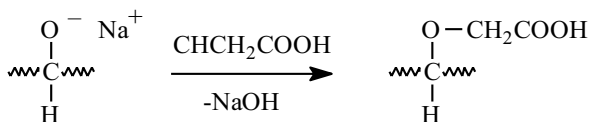

Figure 8-6   Preparation of carboxymethylcellulose by a reaction of sodium cellulose with chloroacetic acid.

Rayon, regenerated cellulose, can be made by two processes. These are the xanthate process, an esterification reaction with aqueous sodium hydroxide and carbon disulfide, and the cuprammonium process, which uses ammonium hydroxide and copper oxide to dissolve cellulose as described in Section 8.2.2.

8.1.4 Naturally Occurring Elastomers

Elastin. Elastin is a protein rich in glycine, alanine, and valine. Molecular weight is typically greater than 70,000. Its structure is mostly that of a random coil with some

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[*] Sodium cellulose formed by reacting cellulose with aqueous sodium hydroxide.

α-helix structure. It has properties similar to those of rubber and imparts elasticity to arterial walls and ligaments. Crosslinking of elastin is achieved through the formation of a desmosine structure by four lysine side chains, as illustrated in Figure 8-7.
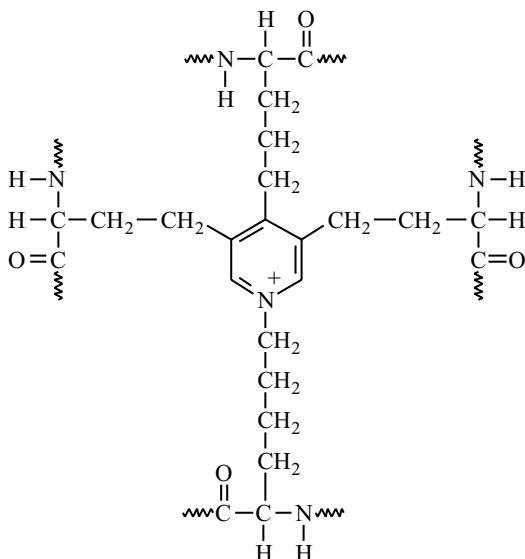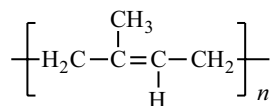

Figure 8-7   Central desmosine structure of an elastin network.

Polyisoprenes. Several geometric isomers (see Section 1.2.3) of polyisoprene

$$\left[H_2C-\underset{\underset{H}{\overset{\overset{CH_3}{|}}{|}}{C}=C-CH_2 \right]_n$$

are produced by trees and plants. As described in Section 9.2.1, these can also be commercially obtained by standard polymerization techniques. Depending upon their stereochemistry, some naturally occurring polyisoprenes are suitable to use either as hard plastic material (e.g., gutta percha and balata) or as elastomers (*Hevea brasiliensis* or natural rubber). Both gutta percha (*Palaquium oblongifolium*) and balata (*Mimusops globosa*) are obtained from trees, although from different regions of the globe. The hardness of these polyisoprenes is attributed to their *trans*-configuration

$$\left[\begin{array}{c} H_3C \\ H_2C \end{array} \!\! C=C \!\! \begin{array}{c} CH_2 \\ H \end{array} \right]_n$$
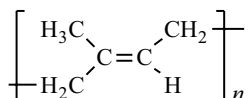
which facilitates chain packing and results in reduced chain flexibility. Gutta percha was used as early as 1850 for cable insulation. Both gutta percha and balata find limited applications as covers for golf balls but, more recently, as material for orthopedic splints. Both *cis-* and *trans*-1,4-polyisoprene are found in chicle (*Achras sapota*) used as a base for chewing gum.

Cis-1,4-polyisoprene is a flexible or rubbery polymer obtained from the tree *Hevea brasiliensis* (Hevea rubber). In nature, Hevea or natural rubber (NR) is obtained by the enzymatic polymerization of isopentylpyrophosphate

$$H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2-CH_2O-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-O-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}-OH\ .$$
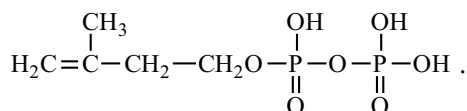
It is harvested as a latex containing about 35% rubber and 5% solids (e.g., proteins, sugars, resins, and salts). The rubber is obtained by coagulation of the latex. Natural rubber can also be obtained, although at a reduced yield, from a variety of plants including guayule, which grows in the southwestern United States and northern Mexico. By sulfur vulcanization, a process patented by Charles Goodyear in 1844 (see Section 9.2.1), individual chains of *cis*-1,4-polyisoprene can be crosslinked through the formation of disulfide bonds to provide elastomeric properties suitable for tires and other applications.

8.2   Fibers

Fibers are typically semicrystalline polymers that can be spun into long strands that have high strength-to-weight ratios for textile as well as composite applications (see Section 7.4). They are prepared by the melt or solution spinning of both synthetic polymers (e.g., polyesters, nylons, polyolefins, and acrylic polymers such as polyacrylonitrile) and naturally occurring polymers, principally cellulose in the form of rayon (regenerated cellulose) and cellulose acetate.

8.2.1 Natural and Synthetic Fibers

Naturally Occurring Fibers. Fibers obtained from natural resources were used for textile applications long before the first polymer was synthesized in the laboratory. These fibers include those derived from vegetables or plants, such as cotton and jute, and those obtained as animal products, especially wool and silk. The principal component of vegetable or plant fibers is cellulose whose structure was shown in Figure 8-5. With the exception of silk, the principal component of animal fibers is

keratin—a natural cellular system of fibrous proteins that serves as the protective outer barrier (e.g., skin, hair, and scales) for high vertebrates. The protein of a silk filament, which is produced by the silkworm (the caterpillar of a small moth belonging to the species *Bombyx mori*), is *fibroin*, which has a simpler structure than keratin.

Representative properties of some important natural fibers are given in Table 8-4. The tensile strength of a fiber is usually expressed in terms of *tenacity*, which is stress per unit of linear density. SI units of tenacity are Newtons per tex where tex is the weight of the fiber in grams per 1000 m.[*]

Table 8-4   Representative Properties of Some Natural and Synthetic Fibers (at 65% Relative Humidity

Fiber	Tenacity at Break, (N/tex)[a]	Extension at Break, (%)	Elastic Modulus (N/tex[a])	Specific Gravity
Natural Fibers				
Wool	0.09–0.15	25–35	2.2–3.1	1.30
Cotton	0.26–0.44	4–10	9–30	1.54
Cellulosics				
Cellulose[b]	0.12–0.33	10–30	3.7–5.8	1.50–1.54
Cellulose acetate[c]	0.09–0.13	25–40	2.2–3.5	1.30–1.35
Non-cellulosics				
Polyester[d]	0.35–0.53	15–30	7.9	1.38
Nylon[d]	0.40–0.71	15–30	3.5	1.14
Acrylic[d]	0.40–0.44	15–20	5.3–6.2	1.17
Olefin (PP)	0.44–0.79	15–30	2.6–4.0	0.90

[a] To convert N/tex to g/den, multiply by 11.3.
[b] From viscose process.
[c] Secondary acetate (DS less than 2.4).
[d] Continuous filament.

Synthetic Fibers. Synthetic fibers are generally semicrystalline polymers that are capable of being spun into filaments of length-to-diameter ratios in excess of 100. Usually, fibers are uniaxially oriented during the spinning process (melt, dry, or wet) to give materials of high tenacity. Fibers may be spun from the melt or from a concentrated solution (i.e., wet or dry spinning) as described in Section 8.2.4. Textile *yarns* of synthetic polymers are produced by twisting several continuous fibers together to form a uniform structure with all filaments aligned parallel to the yarn axis.

Commercially processed fibers may be classified as cellulosic or non-cellulosic. *Cellulosics*, regenerated cellulose (rayon) and cellulose acetate (acetate),

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[*] An older term was the denier (d), which is the number of grams per 9000 m.

are derived from naturally occurring cellulose through chemical reaction and modi-fication. The *non-cellulosics* (polyester, nylon, polyolefin, and acrylic) are all syn-thetic polymers. They clearly constitute the largest part of the commercial market, as shown by the production data given in Table 8-5. Over recent years, cellulosic fibers represent only a small and decreasing share of the U.S. fiber market over the past decade; overall, the size of the synthetic fiber market in the United States has been decreasing. The methods of synthesis and the spinning techniques used to pre-pare synthetic fibers are presented in the following sections.

Table 8-5   U.S. Production of Synthetic Fibers in 2012[a]

Fiber	Thousands of Metric Tons[b]	Annual Change %, 2002–2012
Cellulosics (acetate and rayon)	27	-10.3
Non-cellulosics		
Nylon	562	-6.6
Olefin	1021	-3.1
Polyester	1203	-2.2

[a]Adapted from Chemical and Engineering News, July 1, 2013, p. 44.
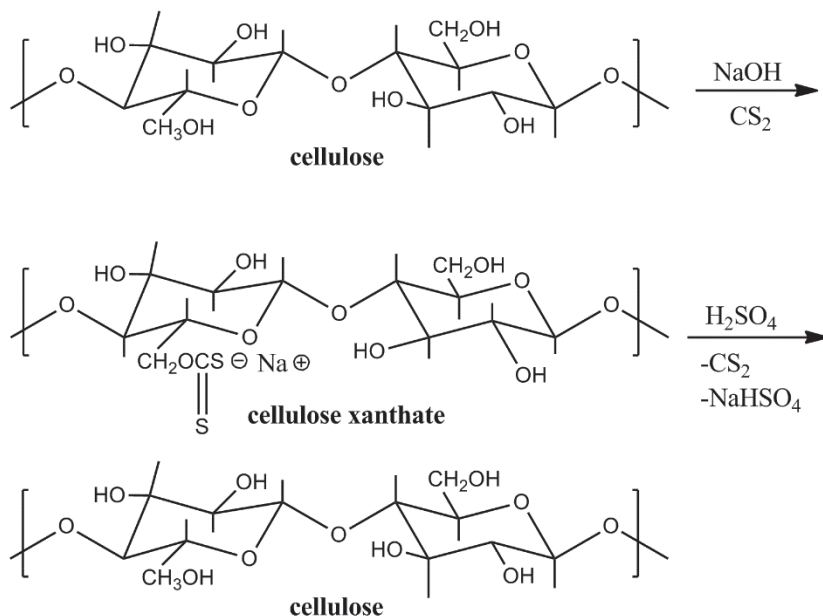[b]Conversion: 2206.6 lbs per metric ton.

Figure 8-8   Viscose process for the production of regenerated cellulose.

8.2.2 Cellulosics

Cellulose. Cellulose for fiber applications is obtained from wood pulp and short fibers left from cotton recovery. The rigid chain of cellulose is strongly hydrogen bonded and highly crystalline. For these reasons, cellulose is essentially insoluble and infusible (i.e., degrades before melting) and, therefore, fibers and films can be obtained only by chemically modifying cellulose, as discussed next. Cellulose in fiber (rayon) or film (cellophane) form is usually obtained by the viscose process, which dates from the 1920s.[*] The approach is to regenerate cellulose from an intermediate soluble form, which is called *cellulose xanthate*. In this highly capital- and energy-intensive process, cellulose pulp (wood pulp or cotton linters) is treated with a concentrated (18%) aqueous sodium hydroxide solution at room temperature. During treatment, cellulose is oxidatively degraded to lower molecular weight and is partially solubilized. After an aging period, the slurry is reacted with carbon disulfide (CS_2) to produce cellulose xanthate, whose structure is shown in Figure 8-8. Typically, about one in every six hydroxyl groups is reacted during this process. The yellow colloidal dispersion (viscose) of cellulose xanthate is spun into an aqueous bath of an acid (sulfuric) and a salt ($NaHSO_4$), which convert the xanthate back to cellulose, now in fiber form. During spinning, the fiber can be stretched to impart greater strength for textiles and tire cord applications. Fibers obtained from regenerated cellulose are hydrophilic and have less developed crystalline structure than natural cellulose. Typical properties of cellulose fibers are included in Table 8-4. A problem with rayon and its derivatives is their flammability, which necessitates the addition of flame retardants.

Cellulose Derivatives. As shown in Figure 8-9, a cellulose derivative of important fiber and film properties, cellulose triacetate, is obtained by reacting cellulose with glacial acetic acid in the presence of acetic anhydride and traces of sulfuric acid in refluxing methylene chloride. Although CTA is still moderately crystalline, it has higher solubility than native cellulose and can be wet spun from a methylene chloride–alcohol mixture into toluene. This derivative can be partially hydrolyzed to give cellulose diacetate (CA), which can be dry spun from acetone. The secondary acetate groups of CTA are the least stable and, therefore, will hydrolyze first. About 65% to 75% of the acetate groups are left unhydrolyzed in commercial cellulose acetate. Cellulose acetate was first produced in 1865 and rapidly replaced its more volatile relative, cellulose nitrate. Large-scale production of cellulose acetate began during World War I.

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[*] In the cuprammonium process, cellulose is dissolved in a solution of ammonium hydroxide and copper oxide. The regenerated fiber is then obtained by extrusion into water. Although the cuprammonium process is simpler than the xanthate process, it is less preferred due to the cost of lost copper during processing.
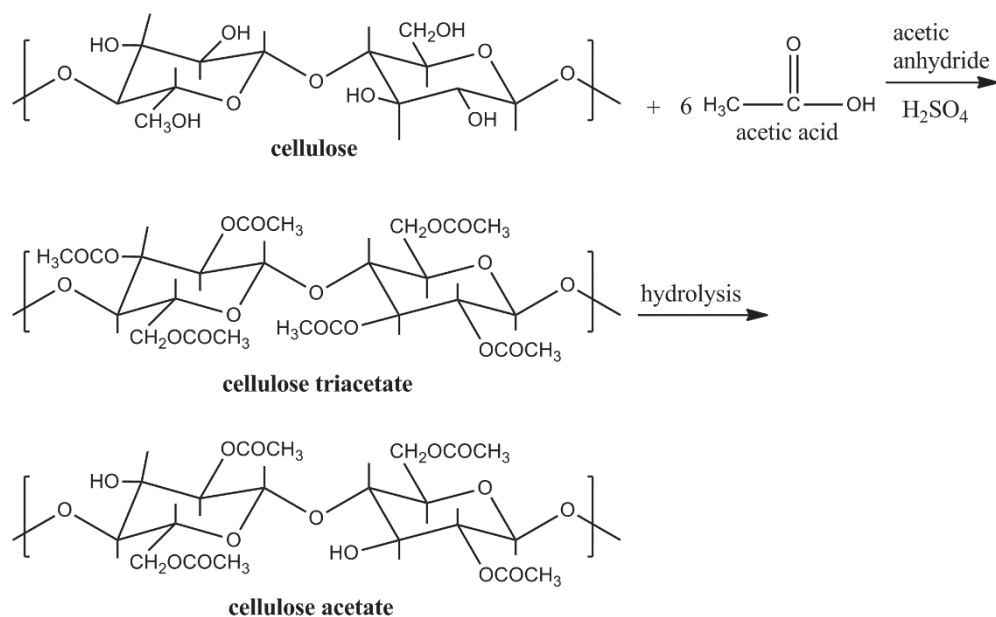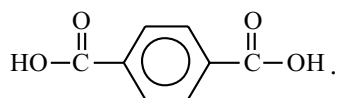
cellulose

cellulose triacetate

cellulose acetate

Figure 8-9   Acetylation of cellulose and partial hydrolysis of cellulose triacetate to yield cellulose diacetate.

8.2.3 Non-cellulosics

Polyesters. A polyester fiber is defined as one composed of at least 85 wt % of an ester of a dihydric alcohol (HOROH) and terephthalic acid whose structure is

$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{}{\bigcirc}-\overset{\overset{\displaystyle O}{\|}}{C}-OH.$$

Of all possible polyester combinations, poly(ethylene terephthalate) (PET) is by far the most important and is the largest-volume synthetic fiber (see Table 8-5) although film (Mylar) and bottle applications are also important (as discussed in Section 9.1.3). The first polyester fibers became commercially available in the United States in 1953 (DuPont Dacron). About 61% of PET produced for fiber applications is used for apparel. Staple blends of polyester and cotton are used for permanent-press garments. The remaining production finds applications in tire cord and home furnishing.

Poly(ethylene terephthalate) has a relatively low T_g (ca. 69°C) but a high T_m (ca. 265°C) with moderate crystallinity. Mechanical properties of polyester fiber were compared with other commercial fibers in Table 8-4. For fiber applications,

typical molecular weights range from 10,000 to 15,000. Higher molecular weights provide high-strength fibers for industrial applications. Polyester is resistant to many solvents and to weak mineral acid. In addition, polyester fibers are abrasion and oxidation resistant and display good lightfastness.

Properties of polyester fibers can be modified by copolymerization or by blending with a variety of additives. For example, dyeability can be improved by copolymerization with small amounts of comonomers such as adipic acid and isophthalic acid, which increase the amorphous content available for dye penetration. Additives are widely used to enhance properties such as fire retardancy (e.g., bromine or phosphorous compounds) and antistatic properties (e.g., carbon and PEG).

A next-generation polyester is poly(trimethylene terephthalate) or PTT,

$$\left[O-\overset{\overset{\textstyle O}{\|}}{C}-\bigcirc-\overset{\overset{\textstyle O}{\|}}{C}-O-CH_2CH_2CH_2 \right]_n$$
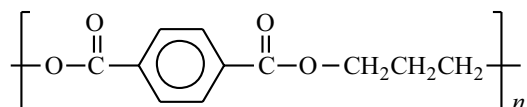
obtained by the polycondensation of terephthalic acid and 1,3-propanediol (in place of ethylene glycol used in the manufacture of PET). This polyester may provide superior dyeability, better stretch, and better softness than PET for apparel applications and better wear and stain resistance for carpet use. Poly(trimethylene terephthalate) may also find a small market in engineering resin and film applications.

Polyamides. The fibers with the next largest sales volume are the polyamides, which find major uses in carpets, apparel, tire reinforcement, and various industrial applications. These are either A–A/B–B condensation polymers prepared from diamines and dicarboxylic acids or A–B condensation polymers prepared from lactams (see Section 2.1). Aliphatic polyamides are called *nylons*. When at least 85% of the amide groups are attached to aromatic groups, the polyamides are called *aramids*. Aramids (e.g., Nomex and Kevlar) are expensive, high-performance fibers that are not used for consumer textile applications. Instead, they find important use as reinforcing fibers for composites, substitutes for asbestos, and material for tire cords (see Chapters 7 and 10). In addition to fiber applications, nylons are available as engineering thermoplastics that can be injection molded into a wide variety of products such as gear wheels, electrical switches and connectors, ski shoes, and automotive coolant tanks.

Principal among the A–A/B–B aliphatic polyamides is nylon-6,6 (or PA 66),[*] more descriptively called poly(hexamethylene adipamide). Nylon-6,6 is synthesized

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[*] Nylons are designated by the number of carbons in the chain. The first and second numbers in the name of A–A/B–B polyamides such as nylon-6,6 refer to the number of carbons in the diamine and dicarboxylic acid, respectively. For example, a nylon prepared from hexamethylene diamine (6 carbons) and adipic acid (10 carbons) would be designated as nylon-6,10.

by the step-growth polymerization of hexamethylene diamine and adipic acid. An exact stoichiometric equivalence of functional groups is achieved by the formation of an intermediate hexamethylene diammonium adipate salt, as shown in Figure 8-10. A slurry of 60% to 80% of recrystallized salt is heated rapidly, thereby releasing steam, which is air-purged from the reaction vessel. The temperature is then raised to 220°C and finally to 280°C near the end of monomer conversion (80% to 90%). The pressure of steam generated during the polymerization is maintained at 1.38 to 1.72 MPa (200 to 250 psi). At this point, pressure is reduced to atmospheric and heating is continued until the polymerization is complete. Small concentrations of monofunctional acids, such as 0.5 mol % of aluric or acetic acid, can be added to the polymerization mixture to control molecular weight. Other nylons of less commercial importance may be made by using difunctional acids of longer or shorter chains.
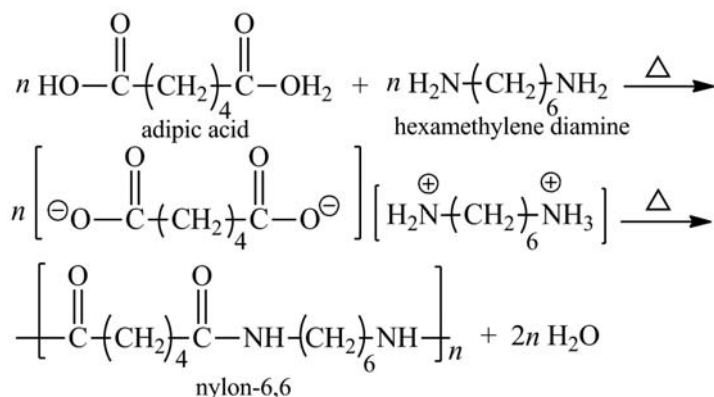
$$n \; HO-\overset{\overset{\displaystyle O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{\displaystyle O}{\|}}{C}-OH_2 \; + \; n \; H_2N\text{-}(CH_2)_6\text{-}NH_2 \; \xrightarrow{\;\Delta\;}$$

adipic acid   hexamethylene diamine

$$n \left[{}^{\ominus}O-\overset{\overset{\displaystyle O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} \right] \left[H_2\overset{\oplus}{N}\text{-}(CH_2)_6\text{-}\overset{\oplus}{N}H_3 \right] \xrightarrow{\;\Delta\;}$$

$$\left[\overset{\overset{\displaystyle O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{\displaystyle O}{\|}}{C}-NH\text{-}(CH_2)_6\text{-}NH \right]_n \; + \; 2n \; H_2O$$

nylon-6,6

Figure 8-10   Synthesis of nylon-6,6 by means of the A–A/B–B step-growth polycondensation of adipic acid and hexamethylene diamine following intermediate salt formation.

Other important polyamides are obtained by the ring-opening polymerization of lactams. Poly(ε-caprolactam), or nylon-6 (PA 6), represents about 25% of the total nylon production. High-molecular-weight nylon-6 may be obtained from the anionic polymerization of ε-caprolactam using strong bases such as sodium hydride or commercially by the hydrolytic polymerization of ε-caprolactam, as shown in Figure 8-11. Although the actual mechanism of the latter scheme is not fully understood, it is believed to involve a mixed chain- and step-growth mechanism involving the intermediate formation of the amino acid obtained from the ring opening of caprolactam.
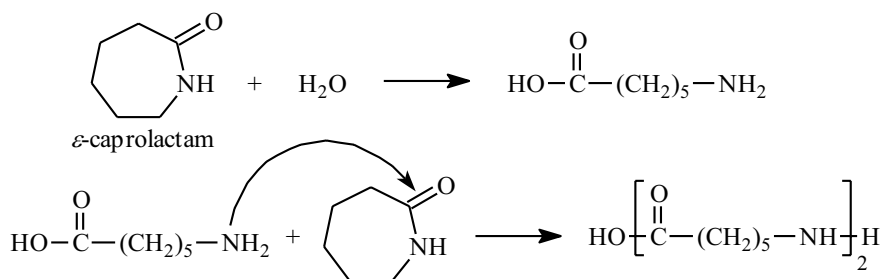
Figure 8-11   Hydrolytic polymerization of ε-caprolactam to the dimer. High-molecular-weight nylon-6 is obtained by the subsequent addition of caprolactam.

Acrylics. Acrylic fibers, primarily used for apparel (70%) and home furnishings (30%), are copolymers of principally acrylonitrile (AN). Polyacrylonitrile (PAN) alone cannot be used for thermoplastic applications because it undergoes cyclization at processing temperatures, as discussed in Section 6.1.1. The resulting "ladder" polymer can be used as a starting material for the preparation of graphite filaments, which are obtained by further heat treatment at elevated temperatures (see Section 7.1.2). Acrylonitrile (AN) finds use in thermoplastic and elastomeric applications only as a copolymer with other monomers such as styrene (e.g., ABS, SAN, and NBR). Like PVC, PAN is insoluble in its own monomer, which means that the polymer will precipitate during bulk polymerization. It can also be solution polymerized by free-radical mechanism in water or dimethyl formamide (DMF) with ammonium persulfate as an initiator. The homopolymer can be dry spun from DMF directly from the polymerization reactor (or wet spun from DMF into water). Fibers are also made from copolymers with styrene, vinyl acetate, vinyl chloride, vinylpyridine, acrylic esters, and acrylamide. Fibers with greater than 85% AN content are termed *acrylic*, while those with lower AN composition (35% to 85%) are called *modacrylic*. The presence of the nitrile group ($-C\equiv N$) in acrylic fibers results in strong intermolecular hydrogen bonding, allowing for high fiber strength.

Olefinics. Olefinic fibers are those that contain at least 85% of any olefin such as ethylene or propylene, the latter being the more common. Olefin fibers are used for home furnishings, such as carpet and upholstery, as well as some industrial applications, such as rope and geotextiles (used in soil engineering for separation, drainage, reinforcement, and filtration). Mechanical properties of polypropylene fibers were compared with other commodity fibers in Table 8-4. Generally, the advantages of olefin fibers include low cost and light weight, while disadvantages include susceptibility to compressive creep and UV degradation. Olefin fibers are hydrophobic and are resistant to most solvents. Unfortunately, these same properties impede dyeing. Acid-dyeable olefin fibers can be prepared by blending the polyolefin with a copolymer, which provides suitable dye sites such as poly(vinyl-

toluene-*co*-α-methylstyrene), which significantly adds to the cost. Usually, olefin fibers are colored by blending the polyolefin with pigments prior to spinning.

8.2.4 Fiber-Spinning Operations

Three processes are commonly used to form polymeric fibers. These include spinning of a polymer melt, called melt spinning, and two processes that are used to spin fibers from a concentrated polymer solution—dry and wet spinning. Polyamide, polyester, and polyolefin fibers are typically obtained by the melt-spinning process. Solution spinning is used for cellulosic and acrylic fibers.

   Melt Spinning. What may be viewed as the most direct process is melt spinning, developed in the late 1930s. During a melt-spinning operation, illustrated in Figure 8-12, a polymer is melted or extruded, clarified by a filter, and pumped by means of a gear pump through a die having one or more small holes. This die is called a *spinneret*. The extruded fiber leaving the spinneret is then cooled and may be uniaxially stretched by take-up rollers called *godets* rotating at different speeds. Fiber stretching orients the fiber chains or crystallites and, therefore, serves to increase modulus and strength in the longitudinal direction. Finally, the cooled oriented fiber is wound onto a spin bobbin for subsequent fiber treatment, such as texturing[*] and dyeing, before being woven into fabric. The most important classes of polymers that are melt spun include the polyolefins (e.g., polyethylene and polypropylene), polyamides (e.g., nylon-6 and nylon-6,6), and polyester (PET). The relatively high melt viscosity of the polyolefins requires the use of an extruder rather than a gear pump, such as may be used for nylons. Typically, PET is melt spun at 286°C through a spinneret containing 24 orifices having 0.5-mm diameters. The average extrusion velocity is 1 to 20 m min^{-1}.

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[*] In a texturing operation, straight fiber filaments are twisted or kinked to impart a property called *crimp*, which results in fabrics that have a more pleasing touch similar to those prepared from naturally produced fibers such as wool.
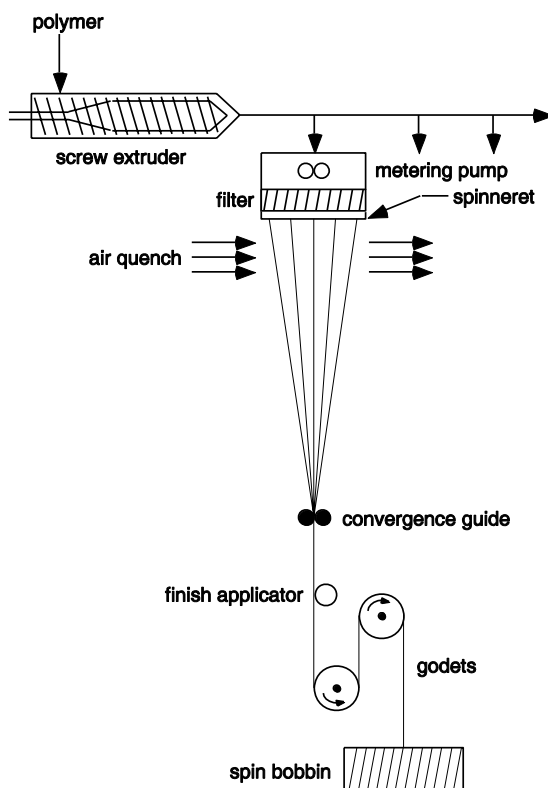
Figure 8-12   Melt spinning of synthetic polymers. Adapted from J. E. McIntyre and M. J. Denton, Fibers, Manufacture, in *The Concise Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz, ed. 1990, New York: John Wiley & Sons. Copyright © 1990 John Wiley & Sons. This material is used by permission of John Wiley & Sons, Inc.

Dry and Wet Spinning. Polymer concentrations in solutions used for dry or wet spinning are typically in the range of 20 to 40 wt%. During a *dry-spinning* process, illustrated in Figure 8-13, the solution is filtered and pumped through a spinneret into a spinning cabinet (up to 25 ft. in length) through which heated air is passed. Solvent from the fiber rapidly evaporates into the airstream and is then carried out of the spinning cabinet for future solvent recovery. For this purpose, volatile solvents such as acetone and carbon disulfide are sometimes used. Water has been used as a solvent for the dry spinning of fibers from poly(vinyl alcohol) (PVA). The dried fiber is then oriented and wound onto a bobbin. The speed of a dry-spinning line can be very high compared to melt- or wet-spinning operations—up to 1000 m min^{-1}. Commodity fibers that are dry spun include cellulose acetate and acrylics.
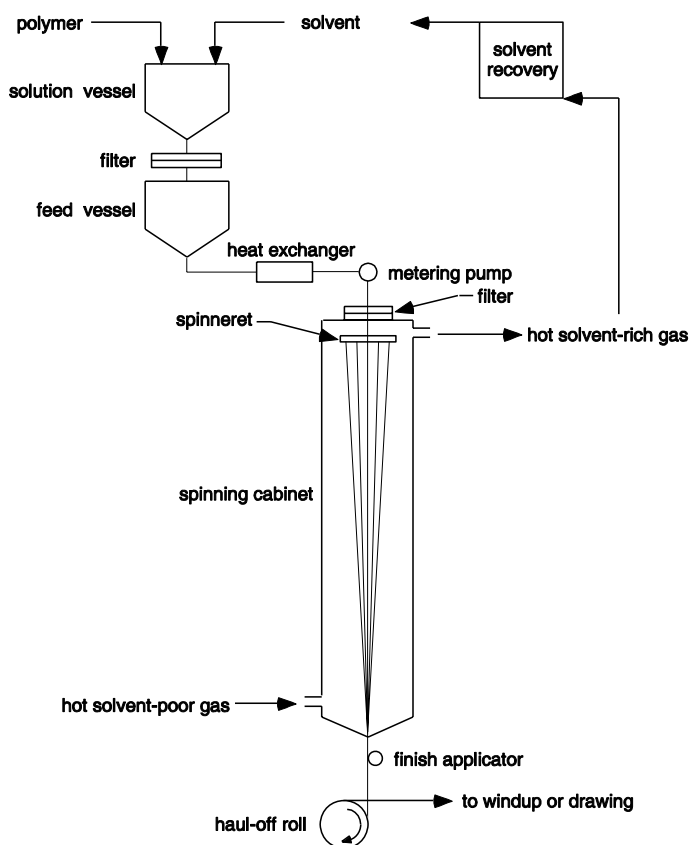
Figure 8-13   A process for the dry spinning of synthetic fibers. Adapted from J. E. McIntyre and M. J. Denton, Fibers, Manufacture, in *The Concise Encyclopedia of Polymer Science and Engineering*, J. I. Kroschwitz, ed. 1990, New York: John Wiley & Sons. Copyright © 1990 John Wiley & Sons. This material is used by permission of John Wiley & Sons, Inc.

Wet spinning, one of the oldest fiber-production methods, differs from dry spinning in that fiber formation results from the coagulation of the polymer solution by immersion in a nonsolvent such as water. As illustrated in Figure 8-14, the spinneret is directly immersed in the nonsolvent bath. Since the coagulation process is slow, the linear velocity of a wet-spinning line is much slower than either melt- or dry-spinning operations; however, high productivity can be obtained by spinning multiple fibers from a single spinneret. The viscose process used to prepare regenerated cellulose (rayon) fiber (see Section 8.2.2) is a wet-spinning process that employs chemical modification of the side groups of cellulose in both the solution and coagulation steps to control solubility properties. Wet spinning has been used to

obtain fibers of PVA, poly(vinyl chloride), and polyacrylonitrile (PAN). In the case of PAN, fibers can be wet spun from a dimethylformamide (DMF) solution into dimethylacetamide (DMAC) or from 50% sodium thiocyanate into aqueous 10% sodium thiocyanate. Polyurethane elastomers such as Spandex (see Section 9.2.2) can be wet spun from DMF solution into water.
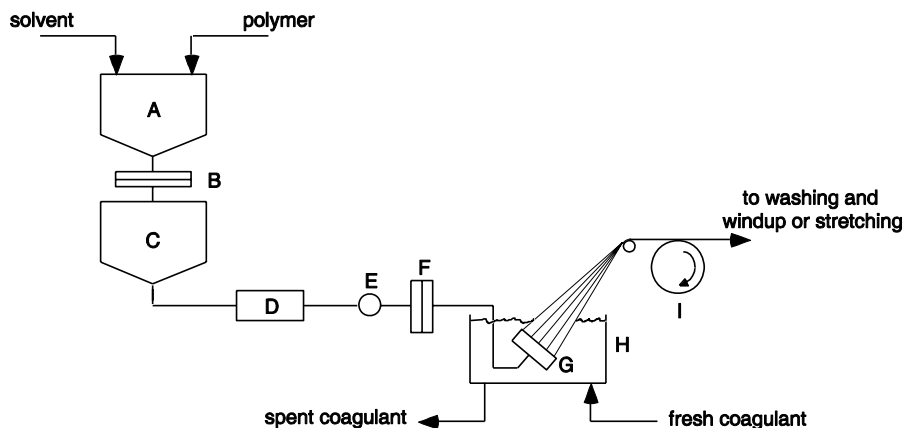

Figure 8-14   Wet-spinning process. A, solution vessel; B and F, filters; C, feed ves-
sel; D, heat exchanger; E, metering pump; G, spinneret; H, spin bath
containing coagulant; I, haul-off roll. Adapted from J. E. McIntyre and
M. J. Denton, in *The Concise Encyclopedia of Polymer Science and
Engineering*, 1990. J. I. Kroschwitz, ed. 1990, New York: John Wiley &
Sons. Copyright © 1990 John Wiley & Sons. This material is used by
permission of John Wiley & Sons, Inc.

For some specialized applications, such as the spinning of hollow-fiber membranes for gas or liquid separation (see Section 12.1.4), the extruded fiber may first pass through air before entering the bath. If the parameters of the spinning process, such as the concentration of the spinning solution, temperature, and extent of air drying, are properly chosen, it is possible to spin asymmetric fibers having a dense thin skin on top of a thick microporous support layer. The thin top layer provides high flux and good selectivity.

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Electrospinning. Polymer fibers with diameters in the nanoscale to microscale range can be produced by electrospinning. This is accomplished by feeding a charged polymer solution or melt through a small aperture toward a grounded collecting plate located about 5 to 30 cm from the electrospinning jet. Diameters as small as 100 nm can be obtained by this process. Solvent evaporates during the electrospinning operation and any residual charges on the fiber dissipate with time.

Crystalline morphology and molecular orientation may be controlled by using a rotating disk collector. Polymers that have been electrospun include polyoxymethylene, poly(ethylene oxide), polystyrene, nylon-6, polyacrylonitrile, SBS, and poly(ethylene terephthalate) (PET). An electron micrograph of a mat of electrospun PET fibers is shown in Figure 8-15. Applications for nanospun fibers include scaffolds for tissue engineering, wound dressings, and controlled drug release.
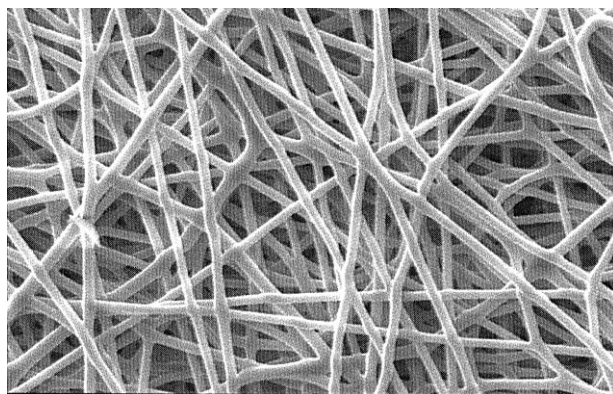

Figure 8-15   Electron micrograph of melt electrospun poly(ethylene terephthalate). Reproduced from J. Lyons and F. Ko, *Melt Spinning of Polymers*: *A Review*. Polymer News, 2005. **30**: p.1-9. Reproduced by permission of Taylor and Francis, Inc., http.www.routledgeny.com.

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PROBLEMS

8.1   The characteristic ratios of cellulose and amylose are reported to be 36 and 5, respectively. Based upon this information, what can you say about the relative flexibility of amylose and cellulose? What structural characteristics contribute to this difference between conformations? Explain why amylose is soluble in water while cellulose is not.

8.2   What specific polymers or blends of polymers are used for olefin, nylon, and polyester fibers in carpet applications? What are the advantages and disadvantages of each?

8.3   How do the thermal and mechanical properties of Nomex and Kevlar compare and how are these differences related to their chemical structure? Which polymer would be expected to have the larger characteristic ratio? How can the molecular weight of these polymers be determined?

8.4   Why can starch but not cellulose be digested by humans? How do cows digest cellulose?

8.5   One of the most interesting computational challenges is the molecular simulation of protein folding. Review what has been done and what are the most difficult obstacles.

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