25

The strength of one kind of polymer, called Lexan, is so great that it is used to make bullet-proof windows. The models show the starting monomers bisphenol-A ($C_{15}H_{16}O_2$) and phosgene ($COCl_2$) and a repeating unit of Lexan.

Synthetic and Natural Organic Polymers

25.1 Properties of Polymers

25.2 Synthetic Organic Polymers

25.3 Proteins

25.4 Nucleic Acids

A LOOK AHEAD

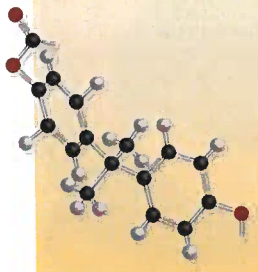
- We begin with a discussion of the general properties of organic polymers. (25.1)
- We then study the synthesis of organic polymers by addition reactions and condensation reactions. We examine both natural and synthetic rubber and other synthetic polymers. (25.2)
- Next, we learn that proteins are polymers of amino acids. We examine the structure of a protein molecule in terms of its primary, secondary, tertiary, and quaternary structures. We also study the stability of a protein molecule, the cooperativity effect, and protein denaturation. (25.3)
- The chapter ends with a brief discussion of the structure and composition of the genetic materials deoxyribonucleic acids (DNA) and ribonucleic acids (RNA). (25.4)

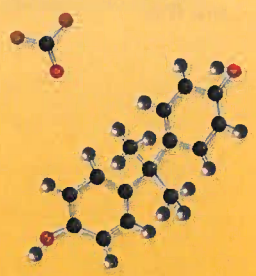
Interactive Activity Summary

1. Interactivity: Synthetic Organic Polymers (25.2)
2. Interactivity: The World of Polymers (25.2)

Polymers are very large molecules containing hundreds or thousands of atoms. People have been using polymers since prehistoric time, and chemists have been synthesizing them for the past century. Natural polymers are the basis of all life processes, and our technological society is largely dependent on synthetic polymers.

This chapter discusses some of the preparation and properties of important synthetic organic polymers in addition to two naturally occurring polymers that are vital to living systems—proteins and nucleic acids.





25.1 Properties of Polymers

A ***polymer*** is *a molecular compound distinguished by a high molar mass, ranging into thousands and millions of grams, and made up of many repeating units.* The physical properties of these so-called macromolecules differ greatly from those of small, ordinary molecules, and special techniques are required to study them.

Naturally occurring polymers include proteins, nucleic acids, cellulose (polysaccharides), and rubber (polyisoprene). Most synthetic polymers are organic compounds. Familiar examples are nylon, poly(hexamethylene adipamide); Dacron, poly(ethylene terephthalate); and Lucite or Plexiglas, poly(methyl methacrylate).

The development of polymer chemistry began in the 1920s with the investigation into a puzzling behavior of certain materials, including wood, gelatin, cotton, and rubber. For example, when rubber, with the known empirical formula of C_5H_8, was dissolved in an organic solvent, the solution displayed several unusual properties—high viscosity, low osmotic pressure, and negligible freezing-point depression. These observations strongly suggested the presence of solutes of very high molar mass, but chemists were not ready at that time to accept the idea that such giant molecules could exist. Instead, they postulated that materials such as rubber consist of aggregates of small molecular units, like C_5H_8 or $C_{10}H_{16}$, held together by intermolecular forces. This misconception persisted for a number of years, until Hermann Staudinger[†] clearly showed that these so-called aggregates are, in fact, enormously large molecules, each of which contains many thousands of atoms held together by covalent bonds.

Once the structures of these macromolecules were understood, the way was open for manufacturing polymers, which now pervade almost every aspect of our daily lives. About 90 percent of today's chemists, including biochemists, work with polymers.

25.2 Synthetic Organic Polymers

Interactivity:
Synthetic Organic Polymers
ARIS, Interactives

Because of their size, we might expect molecules containing thousands of carbon and hydrogen atoms to form an enormous number of structural and geometric isomers (if C=C bonds are present). However, these molecules are made up of ***monomers,*** *simple repeating units,* and this type of composition severely restricts the number of possible isomers. Synthetic polymers are created by joining monomers together, one at a time, by means of addition reactions and condensation reactions.

Addition Reactions

Addition reactions were described on p. 1013.

Addition reactions involve unsaturated compounds containing double or triple bonds, particularly C=C and C≡C. Hydrogenation and reactions of hydrogen halides and halogens with alkenes and alkynes are examples of addition reactions.

Polyethylene, a very stable polymer used in packaging wraps, is made by joining ethylene monomers via an addition-reaction mechanism. First an *initiator* molecule (R_2) is heated to produce two radicals:

$$R_2 \longrightarrow 2R\cdot$$

[†]Hermann Staudinger (1881–1963). German chemist. One of the pioneers in polymer chemistry. Staudinger was awarded the Nobel Prize in Chemistry in 1953.

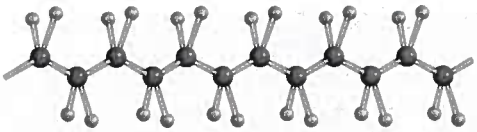


Figure 25.1 *Structure of polyethylene. Each carbon atom is sp^3-hybridized.*

The reactive radical attacks an ethylene molecule to generate a new radical:

$$R\cdot + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2\cdot$$

which further reacts with another ethylene molecule, and so on:

$$R{-}CH_2{-}CH_2\cdot + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_2{-}CH_2\cdot$$

Very quickly a long chain of CH_2 groups is built. Eventually, this process is terminated by the combination of two long-chain radicals to give the polymer called polyethylene:

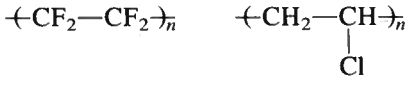
$$R{+}CH_2{-}CH_2{+}_n CH_2CH_2\cdot + R{+}CH_2{-}CH_2{+}_n CH_2CH_2\cdot \longrightarrow R{+}CH_2{-}CH_2{+}_n CH_2CH_2{-}CH_2CH_2{+}CH_2{-}CH_2{+}_n R$$

where $+CH_2{-}CH_2+_n$ is a convenient shorthand convention for representing the repeating unit in the polymer. The value of n is understood to be very large, on the order of hundreds.

The individual chains of polyethylene pack together well and so account for the substance's crystalline properties (Figure 25.1). Polyethylene is mainly used in films in frozen food packaging and other product wrappings. A specially treated type of polyethylene called Tyvek is used for home insulation.

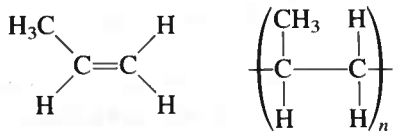
Common mailing envelopes made of Tyvek.

Polyethylene is an example of a ***homopolymer,*** which is *a polymer made up of only one type of monomer.* Other homopolymers that are synthesized by the radical mechanism are Teflon, polytetrafluoroethylene (Figure 25.2) and poly(vinyl chloride) (PVC):



Teflon PVC

The chemistry of polymers is more complex if the starting units are asymmetric:



propene polypropene

Several geometric isomers can result from an addition reaction of propenes (Figure 25.3). If the additions occur randomly, we obtain *atactic* polypropenes, which do not pack together well. These polymers are rubbery, amorphous, and relatively weak. Two other possibilities are an *isotactic* structure, in which the R groups are all on the same side of the asymmetric carbon atoms, and a *syndiotactic* form, in which the R groups alternate to the left and right of the asymmetric carbons. Of these, the isotactic isomer has the highest melting point and greatest crystallinity and is endowed with superior mechanical properties.

Figure 25.2 *A cooking utensil coated with Silverstone, which contains polytetrafluoroethylene.*

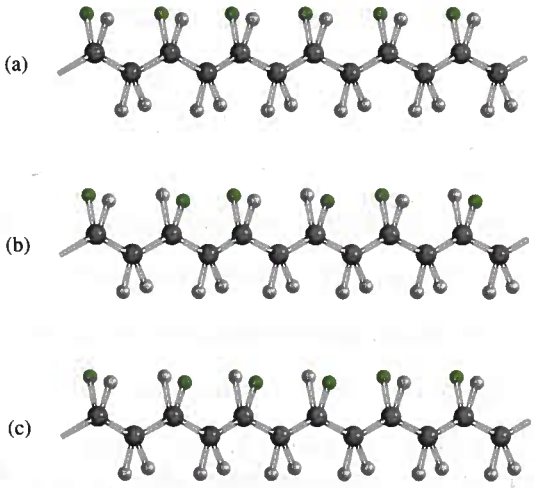
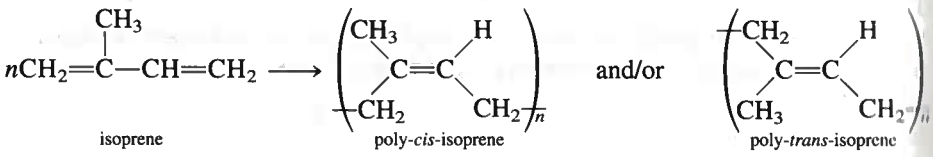


Figure 25.3 *Stereoisomers of polymers. When the R group (green sphere) is CH_3, the polymer is polypropene. (a) When the R groups are all on one side of the chain, the polymer is said to be isotactic. (b) When the R groups alternate from side to side, the polymer is said to be syndiotactic. (c) When the R groups are disposed at random, the polymer is atactic.*

Interactivity:
The World of Polymers
ARIS, Interactives

A major problem that the polymer industry faced in the beginning was how to synthesize either the isotactic or syndiotactic polymer selectively without having it contaminated by other products. The solution came from Giulio Natta[†] and Karl Ziegler,[‡] who demonstrated that certain catalysts, including triethylaluminum $[Al(C_2H_5)_3]$ and titanium trichloride ($TiCl_3$), promote the formation only of specific isomers. Using Natta-Ziegler catalysts, chemists can design polymers to suit any purpose.

Rubber is probably the best known organic polymer and the only true hydrocarbon polymer found in nature. It is formed by the radical addition of the monomer isoprene. Actually, polymerization can result in either poly-*cis*-isoprene or poly-*trans*-isoprene—or a mixture of both, depending on reaction conditions:



Note that in the *cis* isomer the two CH_2 groups are on the same side of the C=C bond, whereas the same groups are across from each other in the *trans* isomer. Natural rubber is poly-*cis*-isoprene, which is extracted from the tree *Hevea brasiliensis* (Figure 25.4).

An unusual and very useful property of rubber is its elasticity. Rubber will stretch up to 10 times its length and, if released, will return to its original size. In contrast, a piece of copper wire can be stretched only a small percentage of its length and still return to its original size. Unstretched rubber has no regular X-ray diffraction pattern and is therefore amorphous. Stretched rubber, however, possesses a fair amount of crystallinity and order.

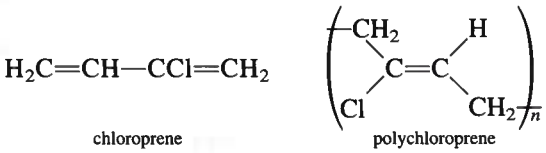
[†]Giulio Natta (1903–1979). Italian chemist. Natta received the Nobel Prize in Chemistry in 1963 for discovering stereospecific catalysts for polymer synthesis.

[‡]Karl Ziegler (1898–1976). German chemist. Ziegler shared the Nobel Prize in Chemistry in 1963 with Natta for his work in polymer synthesis.

Figure 25.4 *Latex (aqueous suspension of rubber particles) being collected from a rubber tree.*

The elastic property of rubber is due to the flexibility of its long-chain molecules. In the bulk state, however, rubber is a tangle of polymeric chains, and if the external force is strong enough, individual chains slip past one another, thereby causing the rubber to lose most of its elasticity. In 1839, Charles Goodyear† discovered that natural rubber could be cross-linked with sulfur (using zinc oxide as the catalyst) to prevent chain slippage (Figure 25.5). His process, known as *vulcanization,* paved the way for many practical and commercial uses of rubber, such as in automobile tires and dentures.

During World War II a shortage of natural rubber in the United States prompted an intensive program to produce synthetic rubber. Most synthetic rubbers (called *elastomers*) are made from petroleum products such as ethylene, propylene, and butadiene. For example, chloroprene molecules polymerize readily to form polychloroprene, commonly known as *neoprene*, which has properties that are comparable or even superior to those of natural rubber:



Another important synthetic rubber is formed by the addition of butadiene to styrene in a 3:1 ratio to give styrene-butadiene rubber (SBR). Because styrene and butadiene are different monomers, SBR is called a ***copolymer,*** which is *a polymer containing two or more different monomers.* Table 25.1 shows a number of common and familiar homopolymers and one copolymer produced by addition reactions.

†Charles Goodyear (1800–1860). American chemist. Goodyear was the first person to realize the potential of natural rubber. His vulcanization process made rubber usable in countless ways and opened the way for the development of the automobile industry.

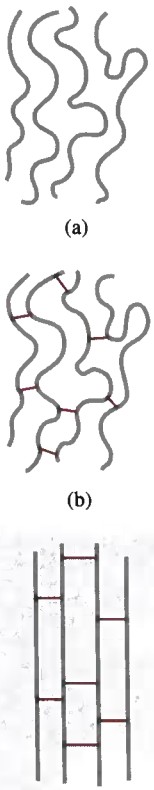


Figure 25.5 *Rubber molecules ordinarily are bent and convoluted. Parts (a) and (b) represent the long chains before and after vulcanization, respectively; (c) shows the alignment of molecules when stretched. Without vulcanization these molecules would slip past one another, and rubber's elastic properties would be gone.*

TABLE 25.1 Some Monomers and Their Common Synthetic Polymers

Monomer		Polymer	
Formula	**Name**	**Name and Formula**	**Uses**
$H_2C{=}CH_2$	Ethylene	Polyethylene $+CH_2{-}CH_2+_n$	Plastic piping, bottles, electrical insulation, toys
$H_2C{=}C(H)(CH_3)$	Propene	Polypropene $+CH(CH_3){-}CH_2{-}CH(CH_3){-}CH_2+_n$	Packaging film, carpets, crates for soft-drink bottles, lab wares, toys
$H_2C{=}C(H)(Cl)$	Vinyl chloride	Poly(vinyl chloride) (PVC) $+CH_2{-}CH(Cl)+_n$	Piping, siding, gutters, floor tile, clothing, toys
$H_2C{=}C(H)(CN)$	Acrylonitrile	Polyacrylonitrile (PAN) $(CH_2{-}CH(CN))_n$	Carpets, knitwear
$F_2C{=}CF_2$	Tetrafluoro-ethylene	Polytetrafluoroethylene (Teflon) $+CF_2{-}CF_2+_n$	Coating on cooking utensils, electrical insulation, bearings
$H_2C{=}C(COOCH_3)(CH_3)$	Methyl methacrylate	Poly(methyl methacrylate) (Plexiglas) $+CH_2{-}C(COOCH_3)(CH_3)+_n$	Optical equipment, home furnishings
$H_2C{=}C(H)(C_6H_5)$	Styrene	Polystyrene $+CH_2{-}CH(C_6H_5)+_n$	Containers, thermal insulation (ice buckets, water coolers), toys
$H_2C{=}C(H){-}C(H){=}CH_2$	Butadiene	Polybutadiene $+CH_2CH{=}CHCH_2+_n$	Tire tread, coating resin
See above structures	Butadiene and styrene	Styrene-butadiene rubber (SBR) $+CH(C_6H_5){-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2+_n$	Synthetic rubber

Bubble gums contain synthetic styrene-butadiene rubber.

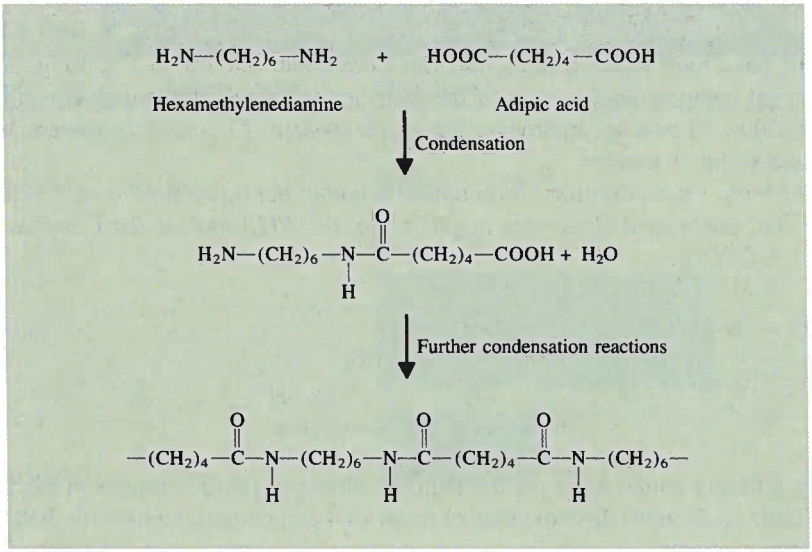


Figure 25.6 *The formation of nylon by the condensation reaction between hexamethylenediamine and adipic acid.*

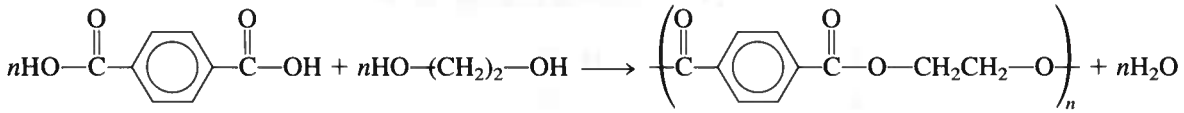
Figure 25.7 *The nylon rope trick. Adding a solution of adipoyl chloride (an adipic acid derivative in which the OH groups have been replaced by Cl groups) in cyclohexane to an aqueous solution of hexamethylenediamine causes nylon to form at the interface of the two solutions, which do not mix. It can then be drawn off.*

Condensation Reactions

One of the best-known polymer condensation processes is the reaction between hexamethylenediamine and adipic acid, shown in Figure 25.6. The final product, called nylon 66 (because there are six carbon atoms each in hexamethylenediamine and adipic acid), was first made by Wallace Carothers[‡] at Du Pont in 1931. The versatility of nylons is so great that the annual production of nylons and related substances now amounts to several billion pounds. Figure 25.7 shows how nylon 66 is prepared in the laboratory.

Condensation reaction was defined on p. 1021.

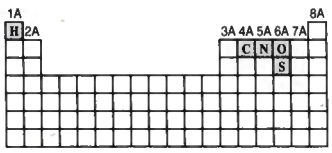
Condensation reactions are also used in the manufacture of Dacron (polyester)



Polyesters are used in fibers, films, and plastic bottles.

25.3 Proteins

Proteins are *polymers of amino acids;* they play a key role in nearly all biological processes. Enzymes, the catalysts of biochemical reactions, are mostly proteins. Proteins also facilitate a wide range of other functions, such as transport and storage of vital substances, coordinated motion, mechanical support, and protection against diseases. The human body contains an estimated 100,000 different kinds of proteins, each of which has a specific physiological function. As we will see in this section, the chemical composition and structure of these complex natural polymers are the basis of their specificity.



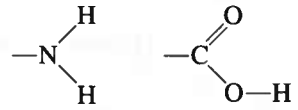
Elements in proteins.

[‡]Wallace H. Carothers (1896–1937). American chemist. Besides its enormous commercial success, Carothers' work on nylon is ranked with that of Staudinger in clearly elucidating macromolecular structure and properties. Depressed by the death of his sister and convinced that his life's work was a failure, Carothers committed suicide at the age of 41.

Amino Acids

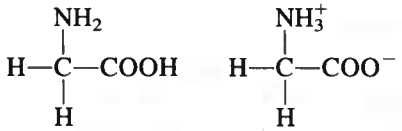
Proteins have high molar masses, ranging from about 5000 g to 1×10^7 g, and yet the percent composition by mass of the elements in proteins is remarkably constant: carbon, 50 to 55 percent; hydrogen, 7 percent; oxygen, 23 percent; nitrogen, 16 percent; and sulfur, 1 percent.

The basic structural units of proteins are *amino acids.* An ***amino acid*** is *a compound that contains at least one amino group ($-NH_2$) and at least one carboxyl group ($-COOH$):*



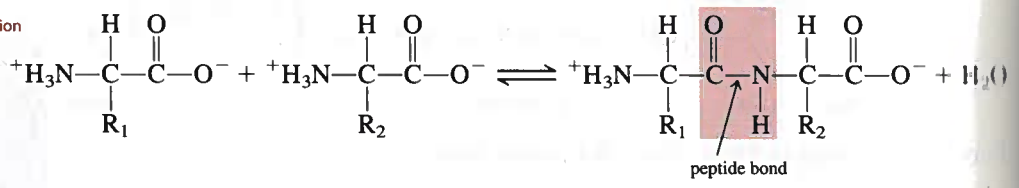
Twenty different amino acids are the building blocks of all the proteins in the human body. Table 25.2 shows the structures of these vital compounds, along with their three-letter abbreviations.

Amino acids in solution at neutral pH exist as *dipolar ions,* meaning that the proton on the carboxyl group has migrated to the amino group. Consider glycine, the simplest amino acid. The un-ionized form and the dipolar ion of glycine are shown below:



The first step in the synthesis of a protein molecule is a condensation reaction between an amino group on one amino acid and a carboxyl group on another amino acid. The molecule formed from the two amino acids is called a *dipeptide,* and the bond joining them together is a *peptide bond:*

It is interesting to compare this reaction with the one shown in Figure 25.6.

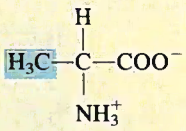
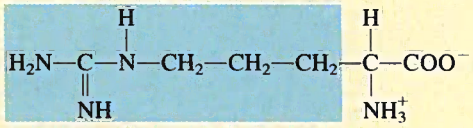
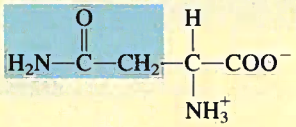
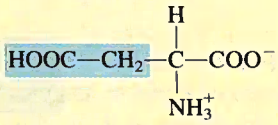
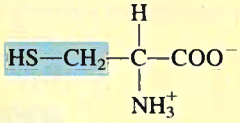
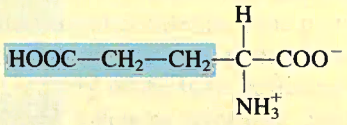
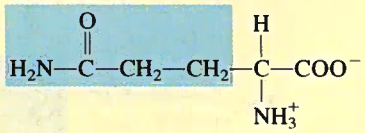
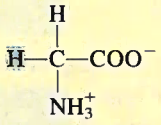
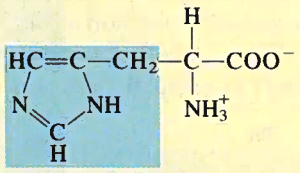
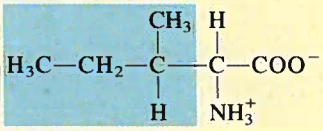


where R_1 and R_2 represent a H atom or some other group; —CO—NH— is called the *amide group.* Because the equilibrium of the reaction joining two amino acids lies to the left, the process is coupled to the hydrolysis of ATP (see p. 808).

Either end of a dipeptide can engage in a condensation reaction with another amino acid to form a *tripeptide,* a *tetrapeptide,* and so on. The final product, the protein molecule, is a *polypeptide;* it can also be thought of as a polymer of amino acids.

An amino acid unit in a polypeptide chain is called a *residue.* Typically, a polypeptide chain contains 100 or more amino acid residues. The sequence of amino acids in a polypeptide chain is written conventionally from left to right, starting with the amino-terminal residue and ending with the carboxyl-terminal residue. Let us consider a dipeptide formed from glycine and alanine. Figure 25.8 shows that alanylglycine and glycylalanine are different molecules. With 20 different amino acids to choose from, 20^2, or 400, different dipeptides can be generated. Even for a very small protein such as insulin, which contains only 50 amino acid residues, the number of chemically different

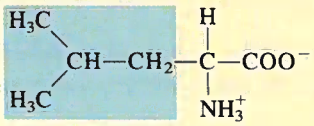
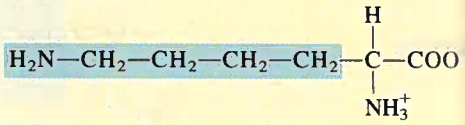
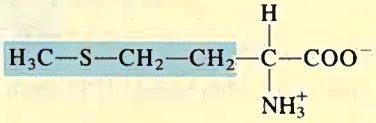
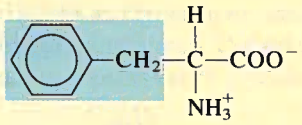
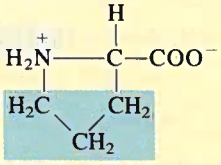
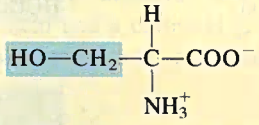
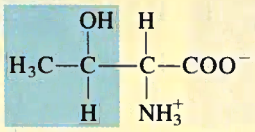
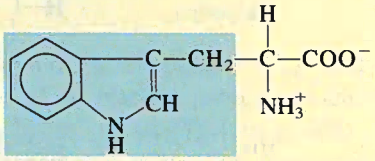
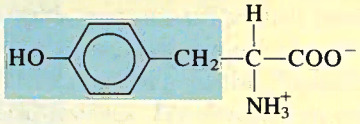
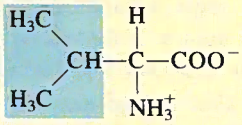
TABLE 25.2 The 20 Amino Acids Essential to Living Organisms*

Name	Abbreviation	Structure
Alanine	Ala	
Arginine	Arg	
Asparagine	Asn	
Aspartic acid	Asp	
Cysteine	Cys	
Glutamic acid	Glu	
Glutamine	Gln	
Glycine	Gly	
Histidine	His	
Isoleucine	Ile	

(Continued)

*The shaded portion is the R group of the amino acid.

TABLE 25.2 The 20 Amino Acids Essential to Living Organisms—Cont.

Name	Abbreviation	Structure
Leucine	Leu	
Lysine	Lys	
Methionine	Met	
Phenylalanine	Phe	
Proline	Pro	
Serine	Ser	
Threonine	Thr	
Tryptophan	Trp	
Tyrosine	Tyr	
Valine	Val	

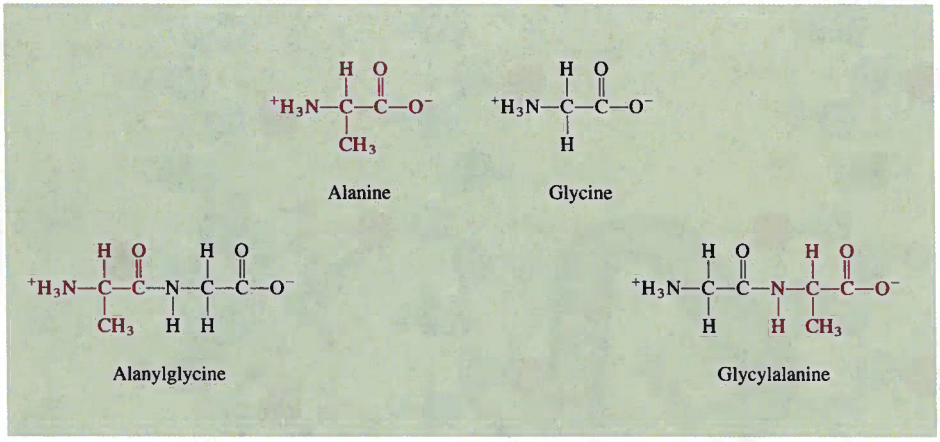


Figure 25.8 *The formation of two dipeptides from two different amino acids. Alanylglycine is different from glycylalanine in that in alanylglycine the amino and methyl groups are bonded to the same carbon atom.*

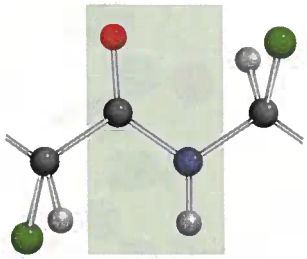
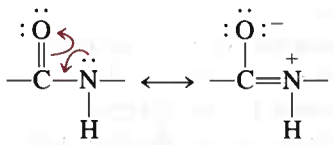


Figure 25.9 *The planar amide group in protein. Rotation about the peptide bond in the amide group is hindered by its double-bond character. The black atoms represent carbon; blue, nitrogen; red, oxygen; green, R group; and gray, hydrogen.*

structures that is possible is of the order of 20^{50} or 10^{65}! This is an incredibly large number when you consider that the total number of atoms in our galaxy is about 10^{68}. With so many possibilities for protein synthesis, it is remarkable that generation after generation of cells can produce identical proteins for specific physiological functions.

Protein Structure

The type and number of amino acids in a given protein along with the sequence or order in which these amino acids are joined together determine the protein's structure. In the 1930s Linus Pauling and his coworkers conducted a systematic investigation of protein structure. First they studied the geometry of the basic repeating group, that is, the amide group, which is represented by the following resonance structures:



Because it is more difficult (that is, it would take more energy) to twist a double bond than a single bond, the four atoms in the amide group become locked in the same plane (Figure 25.9). Figure 25.10 depicts the repeating amide group in a polypeptide chain.

On the basis of models and X-ray diffraction data, Pauling deduced that there are two common structures for protein molecules, called the *α helix* and the *β-pleated* sheet. The α-helical structure of a polypeptide chain is shown in Figure 25.11. The helix

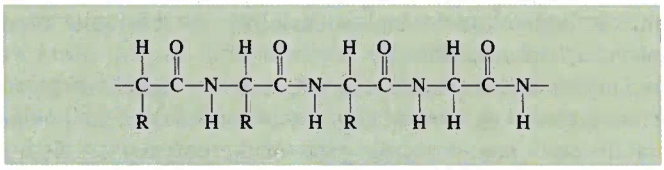


Figure 25.10 *A polypeptide chain. Note the repeating units of the amide group. The symbol R represents part of the structure characteristic of the individual amino acids. For glycine, R is simply a H atom.*

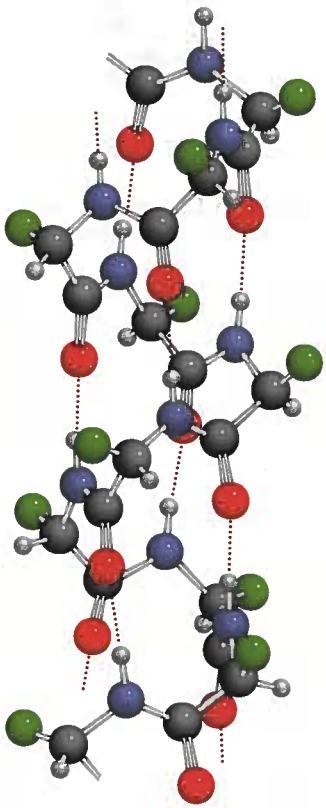


Figure 25.11 *The α-helical structure of a polypeptide chain. The structure is held in position by intramolecular hydrogen bonds, shown as dotted lines. For color key, see Fig. 25.9.*

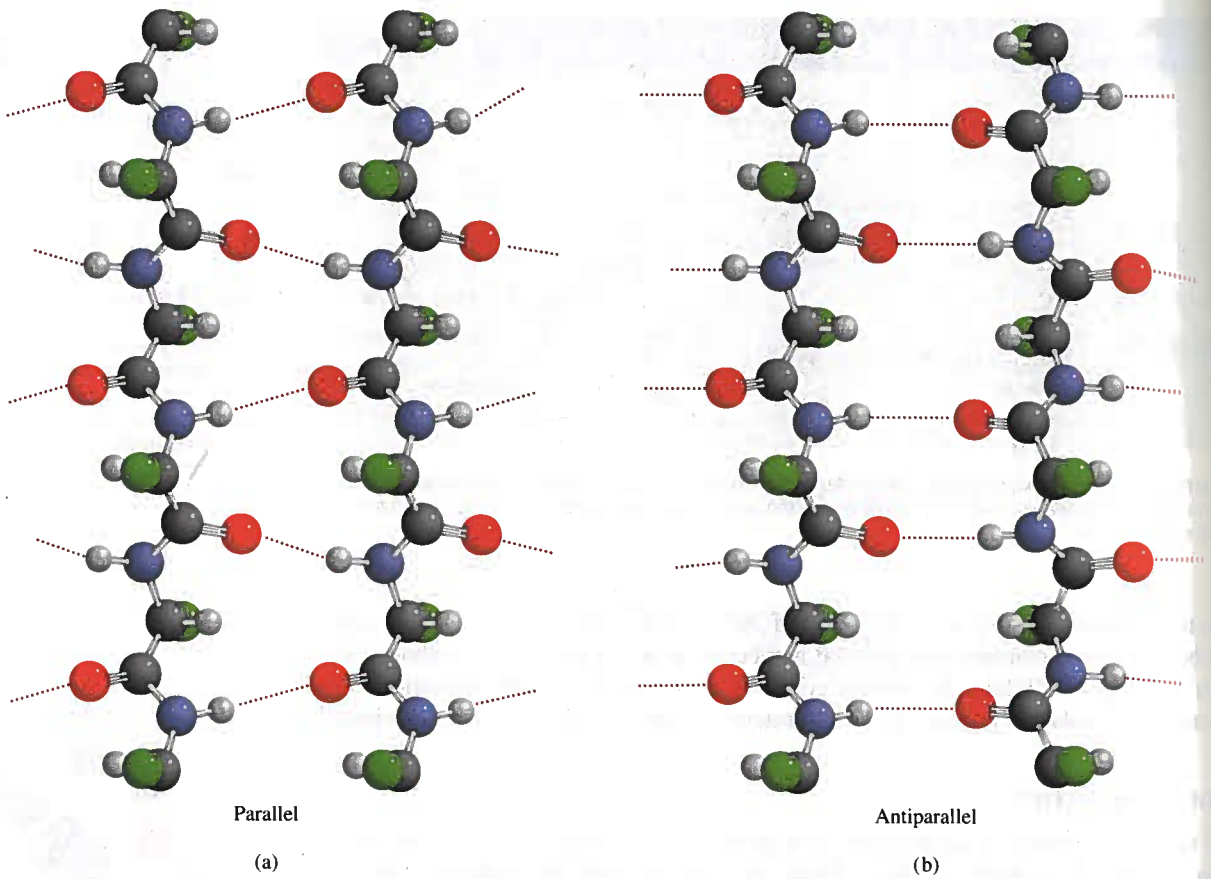


Figure 25.12 *Hydrogen bonds (a) in a parallel β-pleated sheet structure, in which all the polypeptide chains are oriented in the same direction, and (b) in an antiparallel β-pleated sheet, in which adjacent polypeptide chains run in opposite directions. For color key, see Fig. 25.9.*

is stabilized by *intramolecular* hydrogen bonds between the NH and CO groups of the main chain, giving rise to an overall rodlike shape. The CO group of each amino acid is hydrogen-bonded to the NH group of the amino acid that is four residues away in the sequence. In this manner all the main-chain CO and NH groups take part in hydrogen bonding. X-ray studies have shown that the structure of a number of proteins, including myoglobin and hemoglobin, is to a great extent α-helical in nature.

The β-pleated structure is markedly different from the α helix in that it is like a sheet rather than a rod. The polypeptide chain is almost fully extended, and each chain forms many *intermolecular* hydrogen bonds with adjacent chains. Figure 25.12 shows the two different types of β-pleated structures, called *parallel* and *antiparallel*. Silk molecules possess the β structure. Because its polypeptide chains are already in extended form, silk lacks elasticity and extensibility, but it is quite strong due to the many intermolecular hydrogen bonds.

It is customary to divide protein structure into four levels of organization. The *primary structure* refers to the unique amino acid sequence of the polypeptide chain. The *secondary structure* includes those parts of the polypeptide chain that are stabilized by a regular pattern of hydrogen bonds between the CO and NH groups of the backbone, for example, the α helix. The term *tertiary structure* applies to the

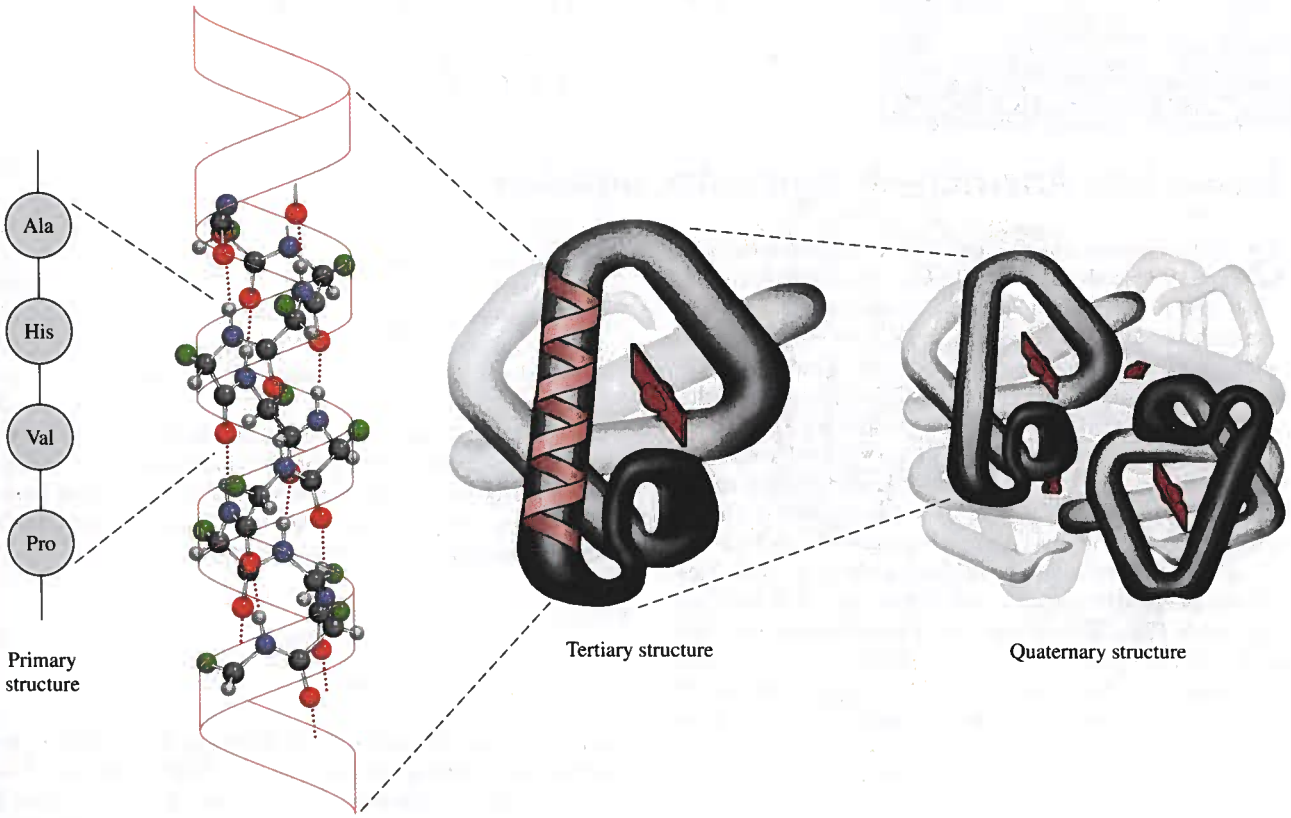
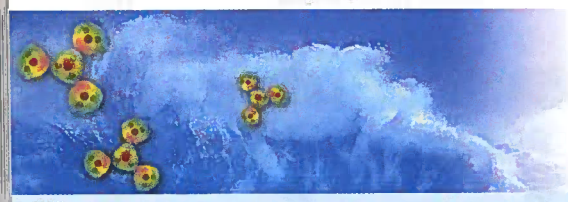


Figure 25.13 *The primary, secondary, tertiary, and quaternary structure of the hemoglobin molecule.*

three-dimensional structure stabilized by dispersion forces, hydrogen bonding, and other intermolecular forces. It differs from secondary structure in that the amino acids taking part in these interactions may be far apart in the polypeptide chain. A protein molecule may be made up of more than one polypeptide chain. Thus, in addition to the various interactions *within* a chain that give rise to the secondary and tertiary structures, we must also consider the interaction *between* chains. The overall arrangement of the polypeptide chains is called the *quaternary structure*. For example, the hemoglobin molecule consists of four separate polypeptide chains, or *subunits*. These subunits are held together by van der Waals forces and ionic forces (Figure 25.13).

Pauling's work was a great triumph in protein chemistry. It showed for the first time how to predict a protein structure purely from a knowledge of the geometry of its fundamental building blocks—amino acids. However, there are many proteins whose structures do not correspond to the α-helical or β structure. Chemists now know that the three-dimensional structures of these biopolymers are maintained by several types of intermolecular forces in addition to hydrogen bonding (Figure 25.14). The delicate balance of the various interactions can be appreciated by considering an example: When glutamic acid, one of the amino acid residues in two of the four polypeptide chains in hemoglobin, is replaced by valine, another amino acid, the protein molecules aggregate to form insoluble



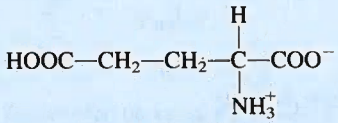
CHEMISTRY *in Action*

Sickle Cell Anemia—A Molecular Disease

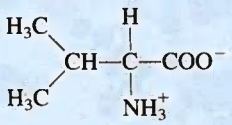
Sickle cell anemia is a hereditary disease in which abnormally shaped red blood cells restrict the flow of blood to vital organs in the human body, causing swelling, severe pain, and in many cases a shortened life span. There is currently no cure for this condition, but its painful symptoms are known to be caused by a defect in hemoglobin, the oxygen-carrying protein in red blood cells.

The hemoglobin molecule is a large protein with a molar mass of about 65,000 g. Normal human hemoglobin (HbA) consists of two α chains, each containing 141 amino acids, and two β chains made up of 146 amino acids each. These four polypeptide chains, or subunits, are held together by ionic and van der Waals forces.

There are many mutant hemoglobin molecules—molecules with an amino acid sequence that differs somewhat from the sequence in HbA. Most mutant hemoglobins are harmless, but sickle cell hemoglobin (HbS) and others are known to cause serious diseases. HbS differs from HbA in only one very small detail. A valine molecule replaces a glutamic acid molecule on each of the two β chains:

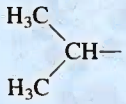


glutamic acid



valine

Yet this small change (two amino acids out of 292) has a profound effect on the stability of HbS in solution. The valine groups are located at the bottom outside of the molecule to form a protruding "key" on each of the β chains. The nonpolar portion of valine



can attract another nonpolar group in the α chain of an adjacent HbS molecule through dispersion forces. Biochemists often refer to this kind of attraction between nonpolar groups as *hydrophobic* (see Chapter 12) interaction. Gradually, enough HbS molecules will aggregate to form a "superpolymer."

A general rule about the solubility of a substance is that the larger its molecules, the lower its solubility because the solvation

polymers, causing the disease known as sickle cell anemia (see the above Chemistry in Action essay).

In spite of all the forces that give proteins their structural stability, most proteins have a certain amount of flexibility. Enzymes, for example, are flexible enough to change their geometry to fit substrates of various sizes and shapes. Another interesting

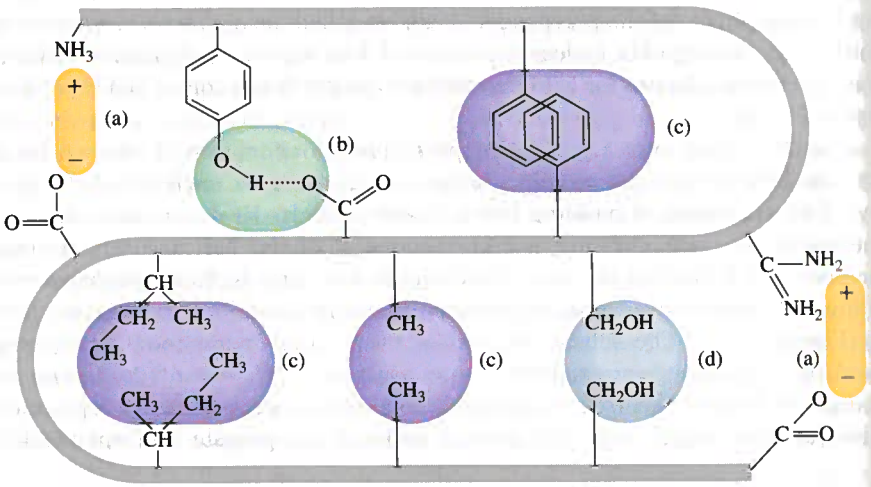
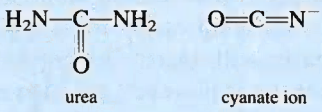


Figure 25.14 *Intermolecular forces in a protein molecule: (a) ionic forces, (b) hydrogen bonding, (c) dispersion forces, and (d) dipole-dipole forces.*

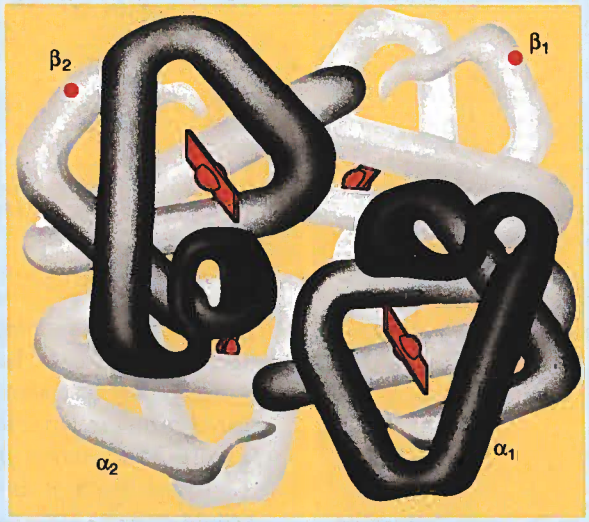
process becomes unfavorable with increasing molecular surface area. For this reason, proteins generally are not very soluble in water. Therefore, the aggregated HbS molecules eventually precipitate out of solution. The precipitate causes normal disk-shaped red blood cells to assume a warped crescent or sickle shape (see figure on p. 284). These deformed cells clog the narrow capillaries, thereby restricting blood flow to organs of the body. It is the reduced blood flow that gives rise to the symptoms of sickle cell anemia. Sickle cell anemia has been termed a molecular disease by Linus Pauling, who did some of the early important chemical research on the nature of the affliction, because the destructive action occurs at the molecular level and the disease is, in effect, due to a molecular defect.

Some substances, such as urea and the cyanate ion,



urea cyanate ion

can break up the hydrophobic interaction between HbS molecules and have been applied with some success to reverse the "sickling" of red blood cells. This approach may alleviate the pain and suffering of sickle cell patients, but it does not prevent the body from making more HbS. To cure sickle cell anemia, researchers must find a way to alter the genetic machinery that directs the production of HbS.



The overall structure of hemoglobin. Each hemoglobin molecule contains two α chains and two β chains. Each of the four chains is similar to a myoglobin molecule in structure, and each also contains a heme group for binding oxygen. In sickle cell hemoglobin, the defective regions (the valine groups) are located near the ends of the β chains, as indicated by the dots.

example of protein flexibility is found in the binding of hemoglobin to oxygen. Each of the four polypeptide chains in hemoglobin contains a heme group that can bind to an oxygen molecule (see Section 22.7). In deoxyhemoglobin, the affinity of each of the heme groups for oxygen is about the same. However, as soon as one of the heme groups becomes oxygenated, the affinity of the other three hemes for oxygen is greatly enhanced. This phenomenon, called *cooperativity,* makes hemoglobin a particularly suitable substance for the uptake of oxygen in the lungs. By the same token, once a fully oxygenated hemoglobin molecule releases an oxygen molecule (to myoglobin in the tissues), the other three oxygen molecules will depart with increasing ease. The cooperative nature of the binding is such that information about the presence (or absence) of oxygen molecules is transmitted from one subunit to another along the polypeptide chains, a process made possible by the flexibility of the three-dimensional structure (Figure 25.15). It is believed that the Fe^{2+} ion has too large a radius to fit into the porphyrin ring of deoxyhemoglobin. When O_2 binds to Fe^{2+}, however, the ion shrinks somewhat so that it can fit into the plane of the ring. As the ion slips into the ring, it pulls the histidine residue toward the ring and thereby sets off a sequence of structural changes from one subunit to another. Although the details of the changes are not clear, biochemists believe that this is how the binding of an oxygen molecule to one heme group affects another heme group. The structural changes drastically affect the affinity of the remaining heme groups for oxygen molecules.

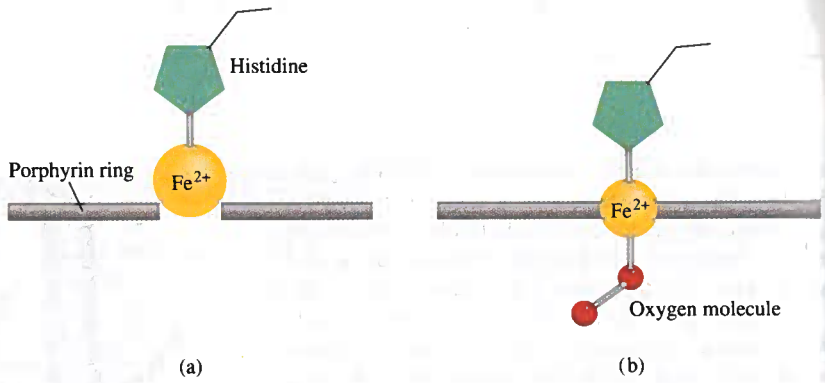


Figure 25.15 *The structural changes that occur when the heme group in hemoglobin binds to an oxygen molecule. (a) The heme group in deoxyhemoglobin. (b) Oxyhemoglobin.*

Hard-boiling an egg denatures the proteins in the egg white.

When proteins are heated above body temperature or when they are subjected to unusual acid or base conditions or treated with special reagents called *denaturants,* they lose some or all of their tertiary and secondary structure. Called ***denatured proteins,*** proteins in this state *no longer exhibit normal biological activities.* Figure 25.16 shows the variation of rate with temperature for a typical enzyme-catalyzed reaction. Initially, the rate increases with increasing temperature, as we would expect. Beyond the optimum temperature, however, the enzyme begins to denature and the rate falls rapidly. If a protein is denatured under mild conditions, its original structure can often be regenerated by removing the denaturant or by restoring the temperature to normal conditions. This process is called *reversible denaturation.*

25.4 Nucleic Acids

If the DNA molecules from all the cells in a human were stretched and joined end to end, the length would be about 100 times the distance to the sun!

Nucleic acids are *high molar mass polymers that play an essential role in protein synthesis.* ***Deoxyribonucleic acid (DNA)*** and ***ribonucleic acid (RNA)*** are *the two types of nucleic acid.* DNA molecules are among the largest molecules known; they have molar masses of up to tens of billions of grams. On the other hand, RNA molecules vary greatly in size, some having a molar mass of about 25,000 g. Compared with proteins, which are made of up to 20 different amino acids, nucleic acids are fairly simple in composition. A DNA or RNA molecule contains only four types of building blocks: purines, pyrimidines, furanose sugars, and phosphate groups (Figure 25.17). Each purine or pyrimidine is called a *base.*

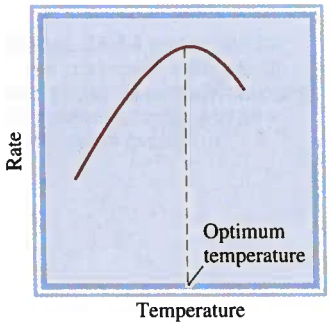


Figure 25.16 *Dependence of the rate of an enzyme-catalyzed reaction on temperature. Above the optimum temperature at which an enzyme is most effective, its activity drops off as a consequence of denaturation.*

In the 1940s, Erwin Chargaff[†] studied DNA molecules obtained from various sources and observed certain regularities. *Chargaff's rules,* as his findings are now known, describe these patterns:

1. The amount of adenine (a purine) is equal to that of thymine (a pyrimidine); that is, A = T, or A/T = 1.
2. The amount of cytosine (a pyrimidine) is equal to that of guanine (a purine); that is, C = G, or C/G = 1.
3. The total number of purine bases is equal to the total number of pyrimidine bases; that is, A + G = C + T.

[†]Erwin Chargaff (1905–2002). American biochemist of Austrian origin. Chargaff was the first to show that different biological species contain different DNA molecules.

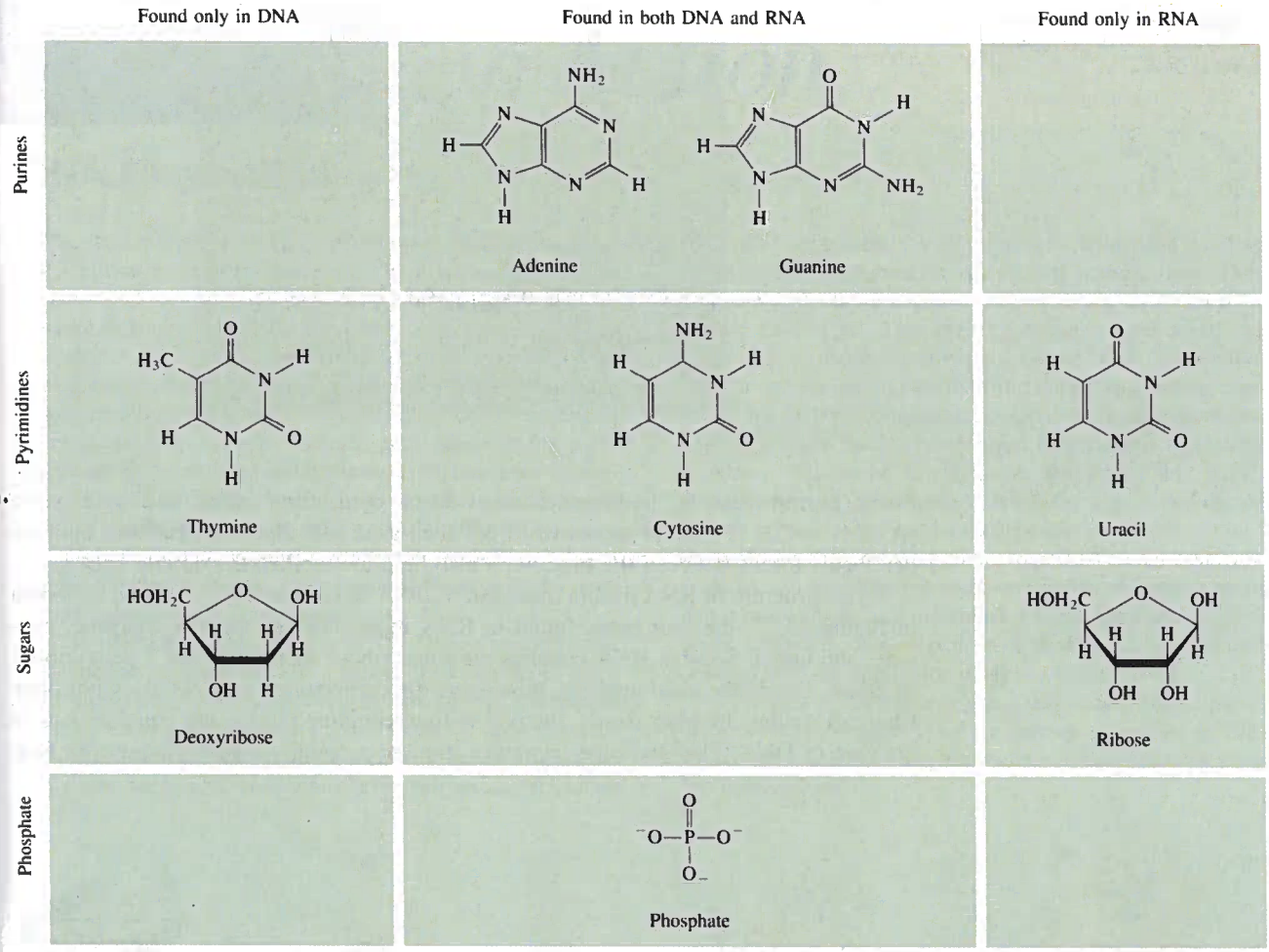
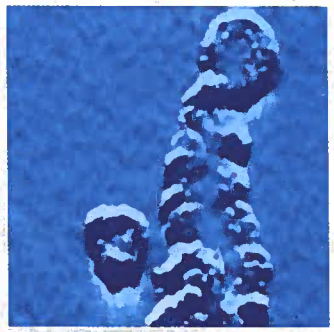


Figure 25.17 *The components of the nucleic acids DNA and RNA.*

Based on chemical analyses and information obtained from X-ray diffraction measurements, James Watson[‡] and Francis Crick[§] formulated the double-helical structure for the DNA molecule in 1953. Watson and Crick determined that the DNA molecule has two helical strands. Each strand is made up of ***nucleotides,*** which *consist of a base, a deoxyribose, and a phosphate group linked together* (Figure 25.18).

The key to the double-helical structure of DNA is the formation of hydrogen bonds between bases in the two strands of a molecule. Although hydrogen bonds can form between any two bases, called *base pairs,* Watson and Crick found that the most favorable couplings are between adenine and thymine and between cytosine and guanine (Figure 25.19). Note that this scheme is consistent with Chargaff's rules, because



An electron micrograph of a DNA molecule. The double-helical structure is evident.

[‡]James Dewey Watson (1928–). American biologist. Watson shared the 1962 Nobel Prize in Physiology or Medicine with Crick and Maurice Wilkins for their work on the DNA structure, which is considered by many to be the most significant development in biology in the twentieth century.

[§]Francis Harry Compton Crick (1916–2004). British biologist. Crick started as a physicist but became interested in biology after reading the book *What Is Life?* by Erwin Schrödinger (see Chapter 7). In addition to elucidating the structure of DNA, for which he was a corecipient of the Nobel Prize in Physiology or Medicine in 1962. Crick has made many significant contributions to molecular biology.

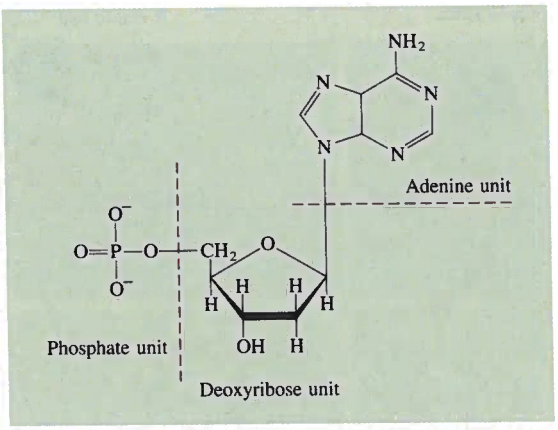


Figure 25.18 *Structure of a nucleotide, one of the repeating units in DNA.*

every purine base is hydrogen-bonded to a pyrimidine base, and vice versa (A + G = C + T). Other attractive forces such as dipole-dipole interactions and van der Waals forces between the base pairs also help to stabilize the double helix.

The structure of RNA differs from that of DNA in several respects. First, as shown in Figure 25.17, the four bases found in RNA molecules are adenine, cytosine, guanine, and uracil. Second, RNA contains the sugar ribose rather than the 2-deoxyribose of DNA. Third, chemical analysis shows that the composition of RNA does not obey Chargaff's rules. In other words, the purine-to-pyrimidine ratio is not equal to 1 as in the case of DNA. This and other evidence rule out a double-helical structure. In fact,

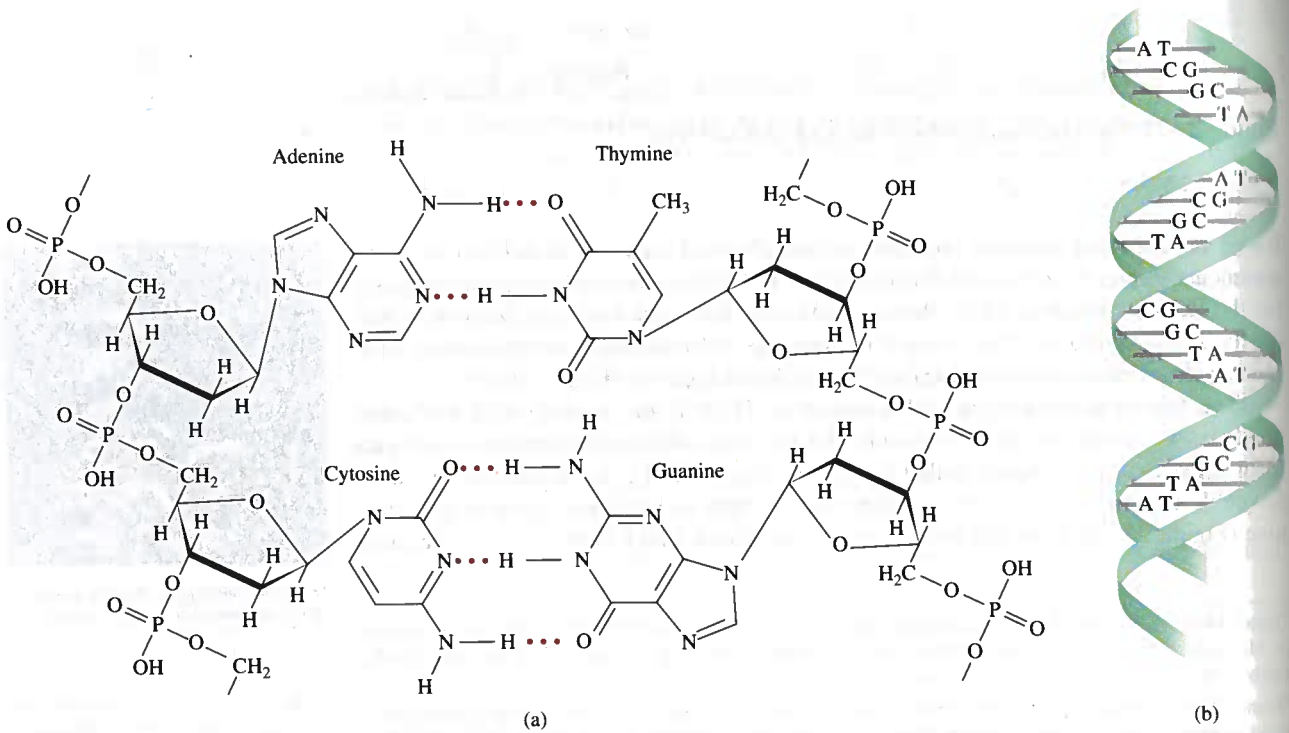


Figure 25.19 *(a) Base-pair formation by adenine and thymine and by cytosine and guanine. (b) The double-helical strand of a DNA molecule held together by hydrogen bonds (and other intermolecular forces) between base pairs A-T and C-G.*

CHEMISTRY *in Action*

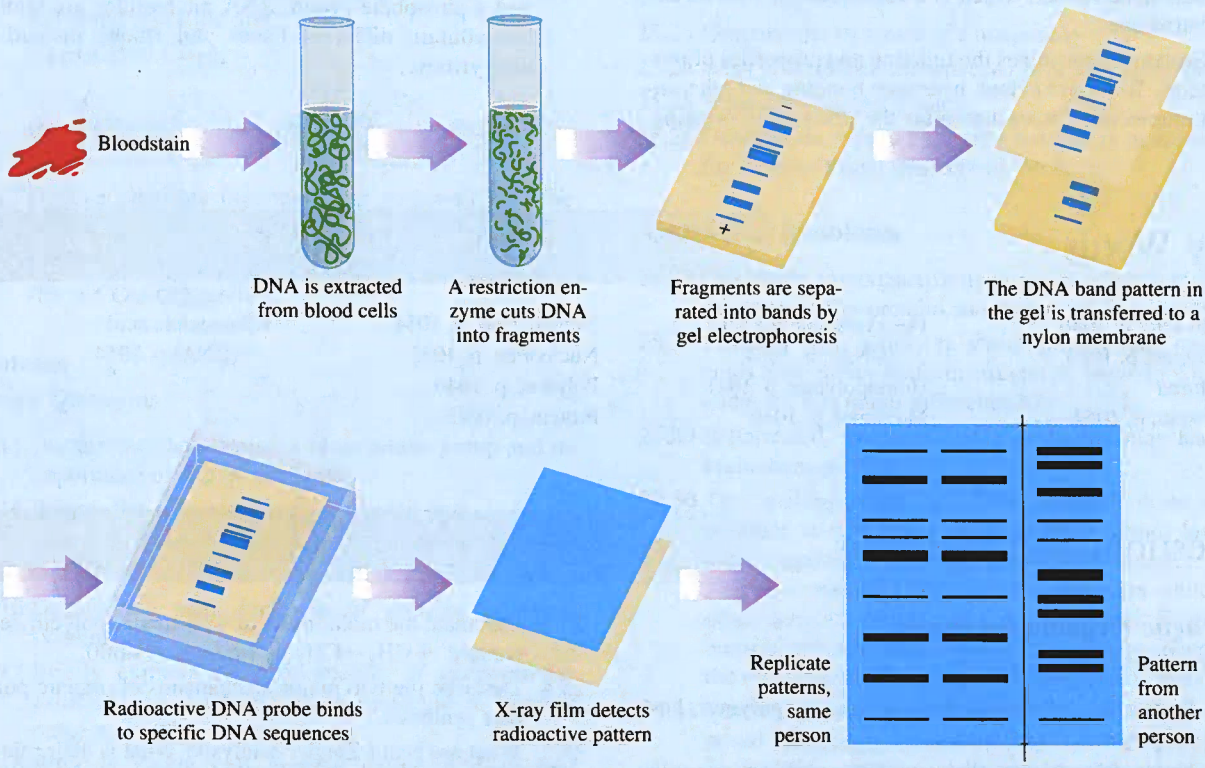
DNA Fingerprinting

The human genetic makeup, or *genome,* consists of about 3 billion nucleotides. These 3 billion units compose the 23 pairs of chromosomes, which are continuous strands of DNA ranging in length from 50 million to 500 million nucleotides. Encoded in this DNA and stored in units called *genes* are the instructions for protein synthesis. Each of about 100,000 genes is responsible for the synthesis of a particular protein. In addition to instructions for protein synthesis, each gene contains a sequence of bases, repeated several times, that has no known function. What is interesting about these sequences, called *minisatellites,* is that they appear many times in different locations, not just in a particular gene. Furthermore, each person has a unique number of repeats. Only identical twins have the same number of minisatellite sequences.

In 1985 a British chemist named Alec Jeffreys suggested that minisatellite sequences provide a means of identification, much like fingerprints. *DNA fingerprinting* has since gained prominence with law enforcement officials as a way to identify crime suspects.

To make a DNA fingerprint, a chemist needs a sample of any tissue, such as blood or semen; even hair and saliva contain DNA. The DNA is extracted from cell nuclei and cut into fragments by the addition of so-called restriction enzymes. These fragments, which are negatively charged, are separated by an electric field in gel. The smaller fragments move faster than larger ones, so they eventually separate into bands. The bands of DNA fragments are transferred from the gel to a plastic membrane, and their position is thereby fixed. Then a DNA probe—a DNA fragment that has been tagged with a radioactive label—is added. The probe binds to the fragments that have a complementary DNA sequence. An X-ray film is laid directly over the plastic sheet, and bands appear on the exposed film in the positions corresponding to the fragments recognized by the probe. About four different probes are needed to obtain a profile that is unique to just one individual. It is estimated that the probability of finding identical patterns in the DNA of two randomly selected individuals is on the order of 1 in 10 billion.

The first U.S. case in which a person was convicted of a crime with the help of DNA fingerprints was tried in 1987. Today, DNA fingerprinting has become an indispensable tool of law enforcement.



Procedure for obtaining a DNA fingerprint. The developed film shows the DNA fingerprint, which is compared with patterns from known subjects.

In the 1980s chemists discovered that certain RNAs can function as enzymes.

the RNA molecule exists as a single-strand polynucleotide. There are actually three types of RNA molecules—messenger RNA (*m*RNA), ribosomal RNA (*r*RNA), and transfer RNA (*t*RNA). These RNAs have similar nucleotides but differ from one another in molar mass, overall structure, and biological functions.

DNA and RNA molecules direct the synthesis of proteins in the cell, a subject that is beyond the scope of this book. Introductory texts in biochemistry and molecular biology explain this process.

The Chemistry in Action essay on p. 1057 describes a technique in crime investigation that is based on our knowledge of DNA sequence.

Summary of Facts and Concepts

1. Polymers are large molecules made up of small, repeating units called monomers.
2. Proteins, nucleic acids, cellulose, and rubber are natural polymers. Nylon, Dacron, and Lucite are examples of synthetic polymers.
3. Organic polymers can be synthesized via addition reactions or condensation reactions.
4. Stereoisomers of a polymer made up of asymmetric monomers have different properties, depending on how the starting units are joined together.
5. Synthetic rubbers include polychloroprene and styrene-butadiene rubber, which is a copolymer of styrene and butadiene.
6. Structure determines the function and properties of proteins. To a great extent, hydrogen bonding and other intermolecular forces determine the structure of proteins.
7. The primary structure of a protein is its amino acid sequence. Secondary structure is the shape defined by hydrogen bonds joining the CO and NH groups of the amino acid backbone. Tertiary and quaternary structures are the three-dimensional folded arrangements of proteins that are stabilized by hydrogen bonds and other intermolecular forces.
8. Nucleic acids—DNA and RNA—are high-molar-mass polymers that carry genetic instructions for protein synthesis in cells. Nucleotides are the building blocks of DNA and RNA. DNA nucleotides each contain a purine or pyrimidine base, a deoxyribose molecule, and a phosphate group. RNA nucleotides are similar but contain different bases and ribose instead of deoxyribose.

Key Words

Amino acid, p. 1046
Copolymer, p. 1043
Denatured protein, p. 1054
Deoxyribonucleic acid (DNA), p. 1054
Homopolymer, p. 1041
Monomer, p. 1040
Nucleic acid, p. 1054
Nucleotide, p. 1055
Polymer, p. 1040
Protein, p. 1045
Ribonucleic acid (RNA) p. 1054

Questions and Problems

Synthetic Organic Polymers

Review Questions

25.1 Define the following terms: monomer, polymer, homopolymer, copolymer.

25.2 Name 10 objects that contain synthetic organic polymers.

25.3 Calculate the molar mass of a particular polyethylene sample, $-(CH_2-CH_2)_n-$, where $n = 4600$.

25.4 Describe the two major mechanisms of organic polymer synthesis.

25.5 What are Natta-Ziegler catalysts? What is their role in polymer synthesis?

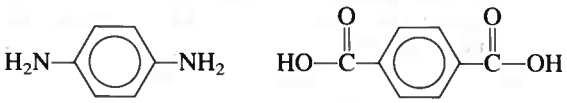
25.6 In Chapter 12 you learned about the colligative properties of solutions. Which of the colligative properties is suitable for determining the molar mass of a polymer? Why?

Problems

25.7 Teflon is formed by a radical addition reaction involving the monomer tetrafluoroethylene. Show the mechanism for this reaction.

25.8 Vinyl chloride, $H_2C{=}CHCl$, undergoes copolymerization with 1,1-dichloroethylene, $H_2C{=}CCl_2$, to form a polymer commercially known as Saran. Draw the structure of the polymer, showing the repeating monomer units.

25.9 Kevlar is a copolymer used in bullet-proof vests. It is formed in a condensation reaction between the following two monomers:

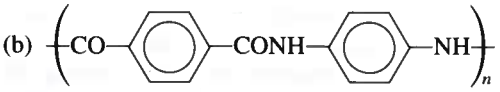


Sketch a portion of the polymer chain showing several monomer units. Write the overall equation for the condensation reaction.

25.10 Describe the formation of polystyrene.

25.11 Deduce plausible monomers for polymers with the following repeating units:

(a) $-(CH_2{-}CF_2)_n-$

(b) 

25.12 Deduce plausible monomers for polymers with the following repeating units:

(a) $-(CH_2{-}CH{=}CH{-}CH_2)_n-$

(b) $-(CO{-}(CH_2)_6NH)_n-$

Proteins

Review Questions

25.13 Discuss the characteristics of an amide group and its importance in protein structure.

25.14 What is the α-helical structure in proteins?

25.15 Describe the β-pleated structure present in some proteins.

25.16 Discuss the main functions of proteins in living systems.

25.17 Briefly explain the phenomenon of cooperativity exhibited by the hemoglobin molecule in binding oxygen.

25.18 Why is sickle cell anemia called a molecular disease?

Problems

25.19 Draw the structures of the dipeptides that can be formed from the reaction between the amino acids glycine and alanine.

25.20 Draw the structures of the dipeptides that can be formed from the reaction between the amino acids glycine and lysine.

25.21 The amino acid glycine can be condensed to form a polymer called polyglycine. Draw the repeating monomer unit.

25.22 The following are data obtained on the rate of product formation of an enzyme-catalyzed reaction:

Temperature (°C)	Rate of Product Formation (M/s)
10	0.0025
20	0.0048
30	0.0090
35	0.0086
45	0.0012

Comment on the dependence of rate on temperature. (No calculations are required.)

Nucleic Acids

Review Questions

25.23 Describe the structure of a nucleotide.

25.24 What is the difference between ribose and deoxyribose?

25.25 What are Chargaff's rules?

25.26 Describe the role of hydrogen bonding in maintaining the double-helical structure of DNA.

Additional Problems

25.27 Discuss the importance of hydrogen bonding in biological systems. Use proteins and nucleic acids as examples.

25.28 Proteins vary widely in structure, whereas nucleic acids have rather uniform structures. How do you account for this major difference?

25.29 If untreated, fevers of 104°F or higher may lead to brain damage. Why?

25.30 The "melting point" of a DNA molecule is the temperature at which the double-helical strand breaks apart. Suppose you are given two DNA samples. One sample contains 45 percent C-G base pairs while the other contains 64 percent C-G base pairs. The total number of bases is the same in each sample. Which of the two samples has a higher melting point? Why?

25.31 When fruits such as apples and pears are cut, the exposed parts begin to turn brown. This is the result of an oxidation reaction catalyzed by enzymes present in the fruit. Often the browning action can be prevented

or slowed by adding a few drops of lemon juice to the exposed areas. What is the chemical basis for this treatment?

25.32 "Dark meat" and "white meat" are one's choices when eating a turkey. Explain what causes the meat to assume different colors. (*Hint:* The more active muscles in a turkey have a higher rate of metabolism and need more oxygen.)

25.33 Nylon can be destroyed easily by strong acids. Explain the chemical basis for the destruction. (*Hint:* The products are the starting materials of the polymerization reaction.)

25.34 Despite what you may have read in science fiction novels or seen in horror movies, it is extremely unlikely that insects can ever grow to human size. Why? (*Hint:* Insects do not have hemoglobin molecules in their blood.)

25.35 How many different tripeptides can be formed by lysine and alanine?

25.36 Chemical analysis shows that hemoglobin contains 0.34 percent Fe by mass. What is the minimum possible molar mass of hemoglobin? The actual molar mass of hemoglobin is four times this minimum value. What conclusion can you draw from these data?

25.37 The folding of a polypeptide chain depends not only on its amino acid sequence but also on the nature of the solvent. Discuss the types of interactions that might occur between water molecules and the amino acid residues of the polypeptide chain. Which groups would be exposed on the exterior of the protein in contact with water and which groups would be buried in the interior of the protein?

25.38 What kind of intermolecular forces are responsible for the aggregation of hemoglobin molecules that leads to sickle cell anemia? (*Hint:* See the Chemistry in Action essay on p. 1052.)

25.39 Draw structures of the nucleotides containing the following components: (a) deoxyribose and cytosine, (b) ribose and uracil.

25.40 When a nonapeptide (containing nine amino acid residues) isolated from rat brains was hydrolyzed, it gave the following smaller peptides as identifiable products: Gly-Ala-Phe, Ala-Leu-Val, Gly-Ala-Leu, Phe-Glu-His, and His-Gly-Ala. Reconstruct the amino acid sequence in the nonapeptide, giving your reasons. (Remember the convention for writing peptides.)

25.41 At neutral pH amino acids exist as dipolar ions. Using glycine as an example, and given that the pK_a of the carboxyl group is 2.3 and that of the ammonium group is 9.6, predict the predominant form of the molecule at pH 1, 7, and 12. Justify your answers using Equation (16.4).

25.42 In Lewis Carroll's tale "Through the Looking Glass," Alice wonders whether "looking-glass milk" on the other side of the mirror would be fit to drink. Based on your knowledge of chirality and enzyme action, comment on the validity of Alice's concern.

25.43 Nylon was designed to be a synthetic silk. (a) The average molar mass of a batch of nylon 66 is 12,000 g/mol. How many monomer units are there in this sample? (b) Which part of nylon's structure is similar to a polypeptide's structure? (c) How many different tripeptides (made up of three amino acids) can be formed from the amino acids alanine (Ala), glycine (Gly), and serine (Ser), which account for most of the amino acids in silk?

25.44 The enthalpy change in the denaturation of a certain protein is 125 kJ/mol. If the entropy change is 397 J/K · mol, calculate the minimum temperature at which the protein would denature spontaneously.

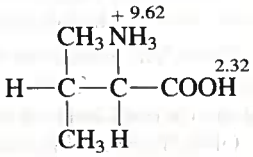
25.45 When deoxyhemoglobin crystals are exposed to oxygen, they shatter. On the other hand, deoxymyoglobin crystals are unaffected by oxygen. Explain. (Myoglobin is made up of only one of the four subunits, or polypeptide chains, in hemoglobin.)

25.46 Draw the structure of the monomer unit shown on p. 1038.

Special Problems

25.47 In protein synthesis, the selection of a particular amino acid is determined by the so-called genetic code, or a sequence of three bases in DNA. Will a sequence of only two bases unambiguously determine the selection of 20 amino acids found in proteins? Explain.

25.48 Consider the fully protonated amino acid valine:



where the numbers denote the pK_a values. (a) Which of the two groups ($-\overset{+}{N}H_3$ or $-COOH$) is more acidic? (b) Calculate the predominant form of valine at pH 1.0, 7.0, and 12.0. (c) Calculate the isoelectric point of valine. (*Hint:* See Problem 16.127.)

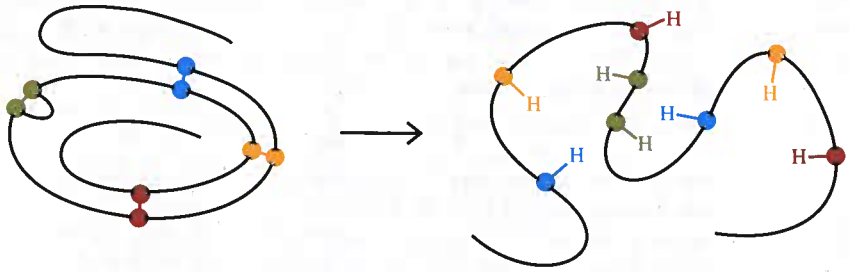
25.49 Consider the formation of a dimeric protein

$$2P \longrightarrow P_2$$

At 25°C, we have $\Delta H^\circ = 17$ kJ/mol and $\Delta S^\circ = 65$ J/K · mol. Is the dimerization favored at this temperature? Comment on the effect of lowering the

temperature. Does your result explain why some enzymes lose their activities under cold conditions?

25.50 The diagram (left) below shows the structure of the enzyme ribonuclease in its native form. The three-dimensional protein structure is maintained in part by the disulfide bonds (—S—S—) between the amino acid residues (each color sphere represents an S atom). Using certain denaturants, the compact structure is destroyed and the disulfide bonds are converted to sulfhydryl groups (—SH) shown on the right of the arrow. (a) Describe the bonding scheme in the disulfide bond in terms of hybridization. (b) Which amino acid in Table 22.2 contains the —SH group? (c) Predict the signs of ΔH and ΔS for the denaturation process. If denaturation is induced by a change in temperature, show why a rise in temperature would favor denaturation. (d) The sulfhydryl groups can be oxidized (that is, removing the H atoms) to form the disulfide bonds. If the formation of the disulfide bonds is totally random between any two —SH groups, what is the fraction of the regenerated protein structures that corresponds to the native form? (e) An effective remedy to deodorize a dog that has been sprayed by a skunk is to rub the affected areas with a solution of an oxidizing agent such as hydrogen peroxide. What is the chemical basis for this action? (*Hint:* An odiferous component of a skunk's secretion is 2-butene-1-thiol, $CH_3CH{=}CHCH_2SH$.)



Native form Denatured form

CHEMICAL *Mystery*

A Story That Will Curl Your Hair

Since ancient times people have experimented with ways to change their hair. Today, getting a permanent wave is a routine procedure that can be done either in a hairdresser shop or at home. Changing straight hair to curly hair is a practical application of protein denaturation and renaturation.

Hair contains a special class of proteins called *keratins,* which are also present in wool, nails, hoofs, and horns. X-ray studies show that keratins are made of α-helices coiled to form a superhelix. The disulfide bonds (—S—S—) linking the α-helices together are largely responsible for the shape of the hair. The figure on p. 1063 shows the basic steps involved in a permanent wave process. Starting with straight hair, the disulfide bonds are first reduced to the sulfhydryl groups (—SH)

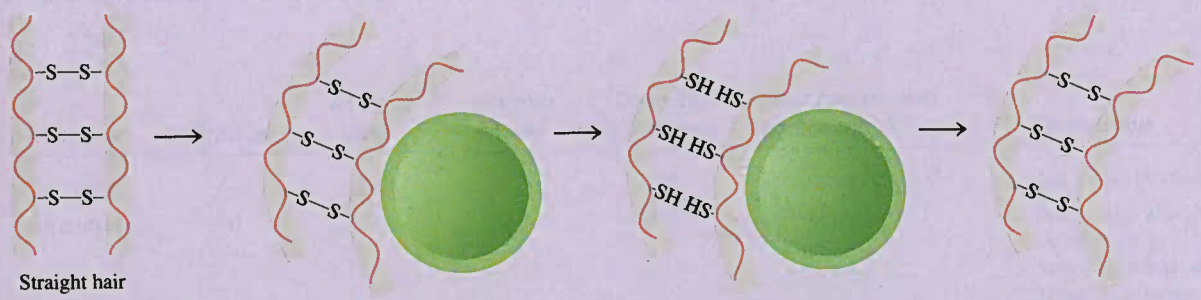
$$2HS{-}CH_2COO^- + \bullet{-}S{-}S{-}\bullet \longrightarrow {}^-OOCCH_2{-}S{-}S{-}CH_2COO^- + 2\,\bullet{-}SH$$

where the red spheres represent different protein molecules joined by the disulfide bonds and thioglycolate ($HS{-}CH_2COO^-$) is the common reducing agent. The reduced hair is then wrapped around curlers and set in the desired pattern. Next, the hair is treated with an oxidizing agent to reform the disulfide bonds. Because the S—S linkages are now formed between different positions on the polypeptide chains, the result is a new hairdo of wavy hairs.

This process involves the denaturation and renaturation of keratins. Although disulfide bonds are formed at different positions in the renatured proteins, there is no biological consequence because keratins in hair do not have any specific functions. The word "permanent" applies only to the portion of hair treated with the reducing and oxidizing agents, and the wave lasts until new and untreated keratins replace it.

Chemical Clues

1. Describe the bonding in the —S—S— linkage.
2. What are the oxidation numbers of S in the disulfide bond and in the sulfhydryl group?



3. In addition to the disulfide bonds, the α helices are joined together by hydrogen bonds. Based on this information, explain why hair swells a bit when it is wet.
4. Hair grows at the approximate rate of 6 in per year. Given that the vertical distance for a complete turn of an α helix is 5.4 Å (1 Å = 10^{-8} cm), how many turns are spun off every second?
5. In the 1980s an English heiress died from a long illness. Autopsy showed that the cause of death was arsenic poisoning. The police suspected that her husband had administered the poison. The year prior to her death the heiress had taken three 1-month trips to America to visit friends on her own. Discuss how forensic analysis eventually helped the law enforcement build their case against her husband. [*Hint:* Arsenic poisoning was discussed in another chemical mystery in Chapter 4 (see p. 167). Studies show that within hours of ingesting as little as 3 mg of arsenic trioxide (As_2O_3), arsenic enters in the blood and becomes trapped and carried up the follicle in the growing hair. At the time of her death, the heiress had shoulder-length hair.]