23 Organic Polymers, Natural and Synthetic

The glasslike sculpture is made of a polymer, which allows it to stand up to the outdoor weather. The repeating design, though random, recognizes the randomness and repetitiveness of the structure of polymers.

Dale Chihuly, Chihuly Bridge of Glass, Crystal Towers detail, 2002, Tacoma, Washington. Photo by Scott M. Leen

No single thing abides; but all things flow
Fragment to fragment clings—the
things thus grow
Until we know and name them. By
degrees
They melt, and are no more the things
we know.

—TITUS LUCRETIUS CARUS (92–52 B.C.)
No Single Thing Abides
(Translated by W. H. Mallock)

Chapter Outline

Industrial chemists work more with polymers than with any other class of materials.

In previous chapters we have discussed the chemical and physical properties of many kinds of substances. For the most part, these materials were made up of either small molecules or simple ions. In this chapter, we will be concerned with an important class of compounds containing large molecules. We call these compounds **polymers**.

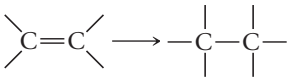
A large number of small molecular units, called **monomers**, combined together chemically make up a polymer. A typical polymer molecule contains a chain of monomers several thousand units long. The monomer units that comprise a given polymer may be the same or different.

We start with synthetic organic polymers. Since about 1930, a variety of synthetic polymers have been made available by the chemical industry. The monomer units are joined together either by addition (Section 23-1) or by condensation (Section 23-2). They are used to make cups, plates, fabrics, automobile tires, and even artificial hearts.

The remainder of this chapter deals with natural polymers. These are large molecules, produced by plants and animals, that carry out the many life-sustaining processes in a living cell. The cell membranes of plants and the woody structure of trees are composed in large part of cellulose, a polymeric carbohydrate. We will look at the structures of a variety of different carbohydrates in Section 23-3. Another class of natural polymers are the proteins. Section 23-4 deals with these polymeric materials, which make up our tissues, bone, blood, and even hair.

23-1 Synthetic Addition Polymers

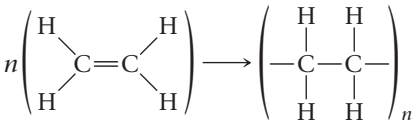
When monomer units add directly to one another, the result is an **addition polymer.** Table 23.1 lists some of the more familiar synthetic addition polymers. You will notice that each of these is derived from a monomer containing a carbon-carbon double bond. Upon polymerization, the double bond is converted to a single bond:



and successive monomer units add to one another.

Polyethylene

Perhaps the most familiar addition polymer is *polyethylene*, a solid derived from the monomer ethylene.[i] We might represent the polymerization process as

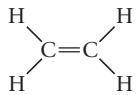
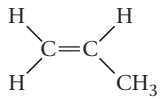
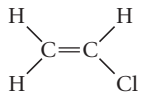
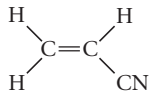
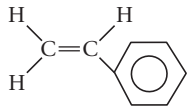
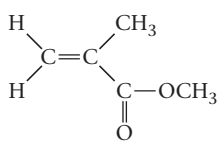
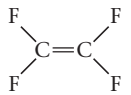


ethylene polyethylene

where n is a very large number, of the order of 2000.

[i] These polymers are usually called plastics.

Table 23.1 Some Common Addition Polymers

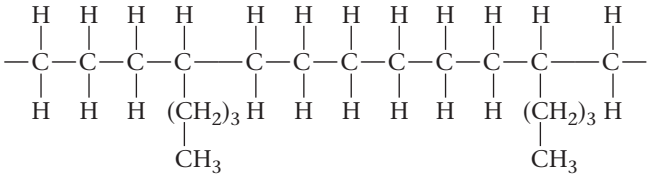
Monomer	Name	Polymer	Uses
	Ethylene	Polyethylene	Bags, coatings, toys
	Propylene	Polypropylene	Beakers, milk cartons
	Vinyl chloride	Polyvinyl chloride (PVC)	Floor tile, raincoats, pipe, phonograph records
	Acrylonitrile	Polyacrylonitrile (PAN)	Rugs; Orlon and Acrilan are copolymers with other monomers
	Styrene	Polystyrene	Cast articles using a transparent plastic
	Methyl methacrylate	Plexiglas, Lucite, acrylic resins	High-quality transparent objects, latex paints
	Tetrafluoroethylene	Teflon	Gaskets, insulation, bearings, pan coatings

Mama G. Clarke

Figure 23.1 Branched and linear polyethylene. The polyethylene bottle at the left is made of pliable, branched polyethylene. The one at the right is made of semirigid, linear polyethylene.

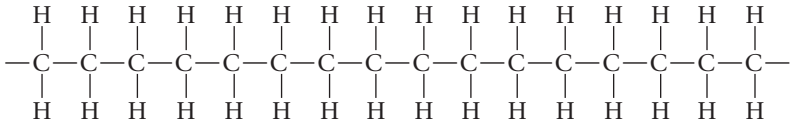
Depending upon the conditions of polymerization, the product may be—

- *branched* polyethylene, which has a structure of the type



Here, neighboring chains are arranged in a somewhat random fashion, producing a soft, flexible solid (Figure 23.1). The plastic bags at the vegetable counters of supermarkets are made of this material.

- *linear* polyethylene, which consists almost entirely of unbranched chains:

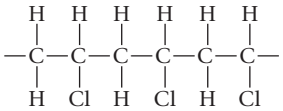


Neighboring chains in linear polyethylene line up nearly parallel to each other. This gives a polymer that approaches a crystalline material. It is used for bottles, toys, and other semirigid objects.

The two forms of polyethylene differ slightly in density. Linear polyethylene is referred to in the recycling business as *h*igh-*d*ensity *p*oly*e*thylene, represented by the symbol "HDPE #2" on the bottom of a plastic bottle. The corresponding symbol for branched polyethylene is "LDPE #4," indicating low-density polyethylene. (The smaller the number, the easier it is to recycle.)

EXAMPLE 23.1

The addition polymer polyvinyl chloride (PVC) has the structure

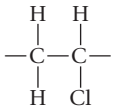


a Draw the structure of the monomer from which PVC is made.

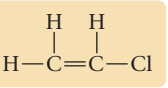
STRATEGY AND SOLUTION

Find the repeating unit from which the polymer chain is constructed.

repeating unit:



monomer:



b How many monomer units are in a PVC polymer that has a molar mass of 1.33×10^5 g/mol?

ANALYSIS

Information given:	From part (a): monomer ($H_2C = CHCl$) molar mass of polymer (1.33×10^5 g/mol)
Information implied:	molar mass of monomer
Asked for:	number of monomer units

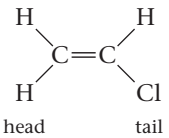
continued

STRATEGY	
1. Determine the molar mass of the monomer.	
2. Divide the molar mass of polymer by the molar mass of the monomer.	
SOLUTION	
1. Molar mass of the monomer	62.49 g/mol
2. Number of units	$\frac{1.33 \times 10^5 \text{ g/mol}}{62.49 \text{ g/mol}} = 2.13 \times 10^3$

Polyvinyl Chloride

PVC is a stiff, rugged, cheap polymer.

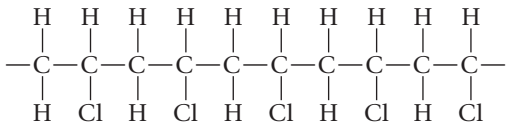
Vinyl chloride, in contrast to ethylene, is an unsymmetrical molecule. We might refer to the CH_2 group in vinyl chloride as the "head" of the molecule and the CHCl group as the "tail":



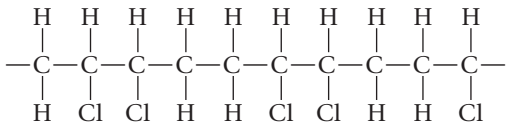
vinyl chloride

In principle at least, vinyl chloride molecules can add to one another in any of three ways to form:

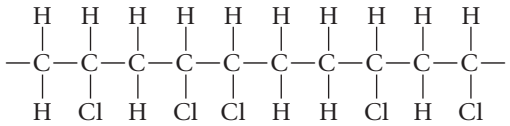
1. A *head-to-tail polymer*, in which there is a Cl atom on every other C atom in the chain:



2. A *head-to-head, tail-to-tail polymer*, in which Cl atoms occur in pairs on adjacent carbon atoms in the chain:



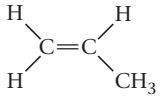
3. A *random polymer*:



Similar arrangements are possible with polymers made from other unsymmetrical monomers (Example 23.2).

EXAMPLE 23.2

Consider propene:

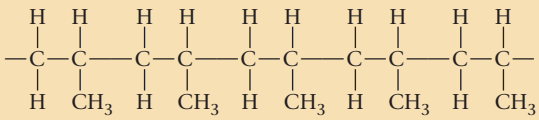


Sketch the structure of a head-to-tail polymer derived from it and sketch another structure assuming a head-to-head, tail-to-tail polymer.

continued

SOLUTION

head-to-tail polymer



head-to-head, tail-to-tail polymer

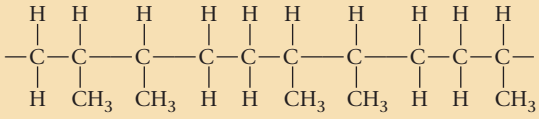
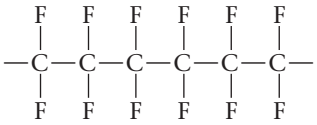


Figure 23.2 Teflon. The Teflon coating helps prevent food from sticking to this cookware.

Teflon

Teflon $(C_2F_2)_n$, where n is of the order of 10^4 to 10^5, is a versatile but expensive polymer ($10–20/kg). It is virtually impervious to chemical attack, even at high temperatures. Apparently the fluorine atoms form a protective shield around the central carbon chain:

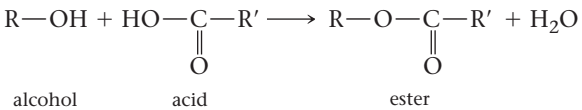


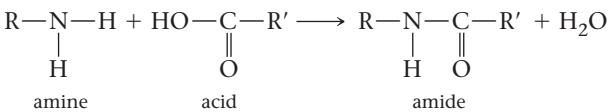
For much the same reason, Teflon is essentially invulnerable to attack by aqueous or organic solvents. Beyond that, Teflon is an excellent electrical insulator. Indeed, its largest industrial use is in that area.

You are probably most familiar with Teflon as a nonstick coating for kitchen utensils (Figure 23.2). The slippery surface of Teflon-coated fry pans and muffin tins results from Teflon's extremely low coefficient of friction.

23-2 Synthetic Condensation Polymers

As we pointed out in Chapter 22, a condensation reaction is one in which two molecules combine by splitting out a small molecule such as water. The reaction of an alcohol, ROH, or an amine, RNH_2, with a carboxylic acid R′COOH is a condensation:





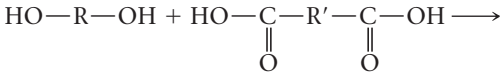
A **condensation polymer** is formed in a similar way; the molecule split out is most often water. In order to produce a condensation polymer, *the monomers involved must have functional groups at both ends of the molecule.* Most often these groups are

$$—NH_2 \qquad —OH \qquad —COOH$$

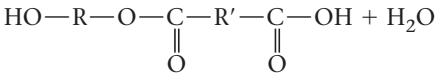
The products formed are referred to as polyesters and polyamides.

Polyesters

Consider what happens when an alcohol with two —OH groups, HO—R—OH, reacts with a dicarboxylic acid, HOOC—R′—COOH. In this case the ester formed still has a reactive group at both ends of the molecule.

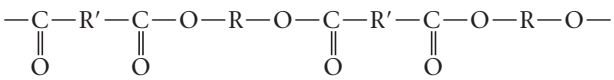


dihydroxy alcohol — dicarboxylic acid



ester with active end groups

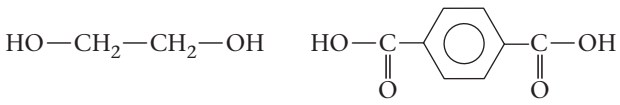
The COOH group at one end of the ester molecule can react with another alcohol molecule. The OH group at the other end can react with an acid molecule. This process can continue, leading eventually to a long-chain polymer containing 500 or more ester groups. The general structure of the **polyester** can be represented as



section of a polyester molecule

Perhaps the most important polyester is poly(ethylene terephthalate), commonly known as PET (or "PETE 1" on plastic beverage bottles). The annual production of PET in the United States is of the order of 10^8 kg (10^5 metric tons). Much of this is converted into fabric (trade name, Dacron) or magnetically coated film (Mylar).

The two monomers used to make PET are



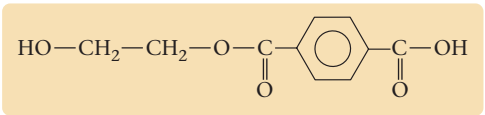
ethylene glycol — terephthalic acid

EXAMPLE 23.3

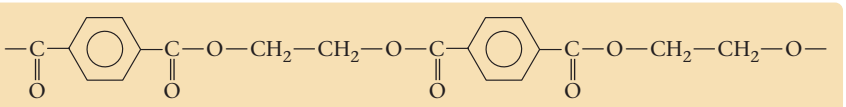
Write the structural formula of the ester formed when one molecule of ethylene glycol reacts with one molecule of terephthalic acid, and draw a section of the "PET" polymer.

SOLUTION

ester

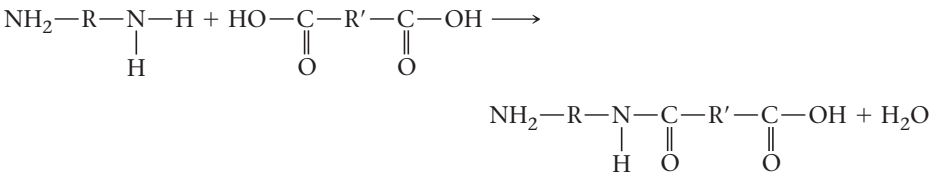


"PET" polymer



Polyamides

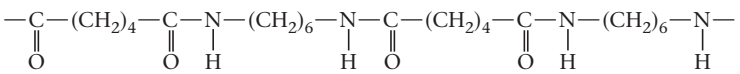
When a diamine (molecule containing two NH_2 groups) reacts with a dicarboxylic acid (two COOH groups), a **polyamide** is formed. This condensation polymerization is entirely analogous to that used to make polyesters. In this case, the NH_2 group of the diamine reacts with the COOH group of the dicarboxylic acid:



Condensation can continue to form a long-chain polymer.

EXAMPLE 23.4

Consider the following polyamide:



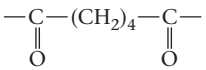
Give the structures of the two monomers, dicarboxylic acid and diamine, used to make this polymer.

STRATEGY

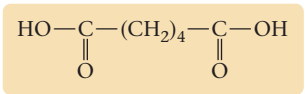
1. Break the polymer into two fragments. Each fragment should be one of the monomers.
2. Add an OH group to the —C═O terminal carbon atoms of the first monomer.
3. Add a H atom to the N terminal atoms of the second monomer.

SOLUTION

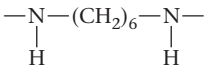
Monomer 1



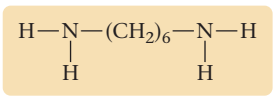
Add an OH group.

Dicarboxylic acid: 

Monomer 2



Add an H atom.

Diamine: 

The polymer in Example 23.4 is "Nylon-66" (the numbers indicate the number of carbon atoms in the diamine and dicarboxylic acid molecules). This polymer was first made in 1935 by Wallace Carothers (1896–1937) working at DuPont (Figure 23.3). Since then, other nylons, all polyamides, have been synthesized.

The elasticity of nylon fibers is due in part to hydrogen bonds between adjacent polymer chains. These hydrogen bonds join carbonyl oxygen atoms on one chain to NH groups on adjacent chains (Figure 23.4).

Figure 23.3 Nylon. Nylon can be made by the reaction between hexamethylenediamine, $H_2N—(CH_2)_6—NH_2$, and adipic acid, $HOOC—(CH_2)_4—COOH$. It forms at the interface between the two reagents.

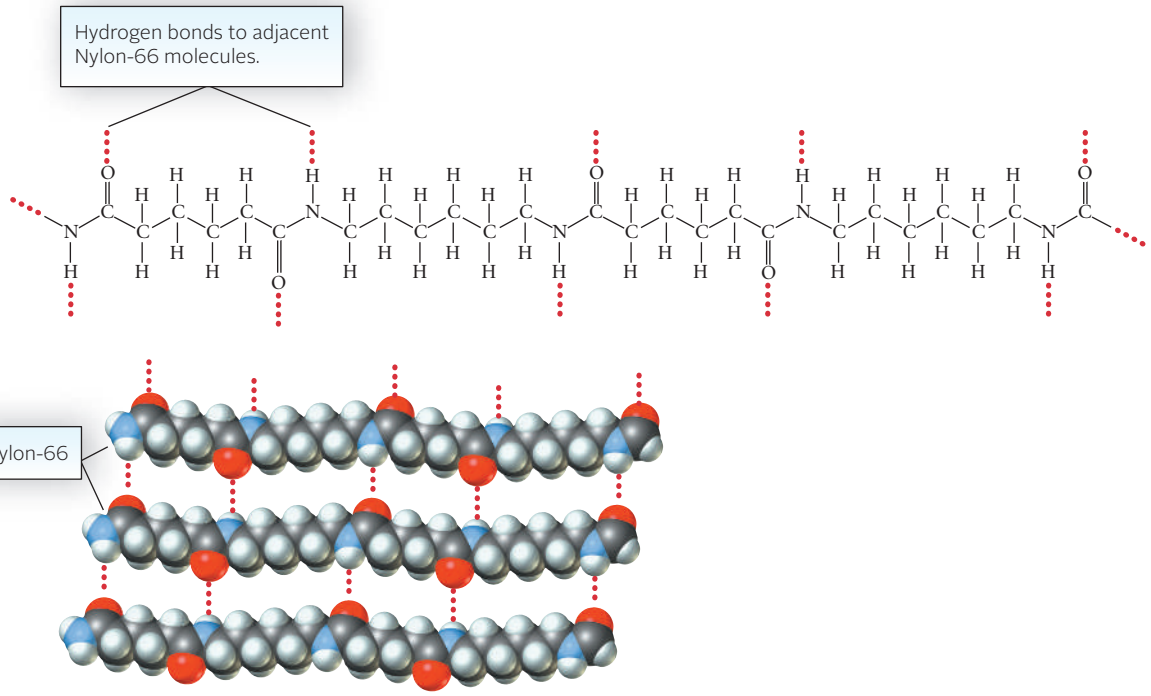


Figure 23.4 Hydrogen bonding in Nylon-66.

23-3 Carbohydrates

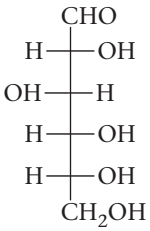
Carbohydrates, which comprise one of the three basic classes of foodstuffs, contain carbon, hydrogen, and oxygen atoms. Their general formula, $C_n(H_2O)_m$, is the basis for their name. They can be classified as

1. **Monosaccharides,** which cannot be broken down chemically to simpler carbohydrates. The most familiar monosaccharides contain either six carbon atoms per molecule (glucose, fructose, galactose, . . .) or five (ribose, arabinose, . . .).

2. **Disaccharides,** which are dimers formed when two monosaccharide units combine with the elimination of H_2O. The monosaccharides may be the same (two glucose units in maltose) or different (a glucose and fructose unit in sucrose).
3. **Polysaccharides,** which are condensation polymers containing from several hundred to several thousand monosaccharide units. Cellulose and starch are the most common polysaccharides.

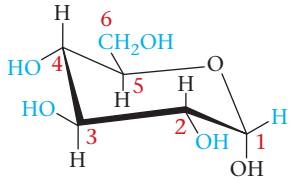
Glucose

By far the most important monosaccharide is glucose. As a pure solid, it has the "straight-chain" structure shown in the margin. In water solution, glucose exists primarily as six-membered ring molecules, shown below. The rings are not planar but have a three-dimensional "chair" form. The carbon atoms at each corner of the ring are not shown in the structure; they are represented by the numbers 1 to 5. The sixth atom in the ring is oxygen. There is a CH_2OH group bonded to carbon atom 5. There is an H atom bonded to each of the ring carbons; an OH group is bonded to carbon atoms 1 through 4. The heavy lines indicate the front of the ring, projected toward you.

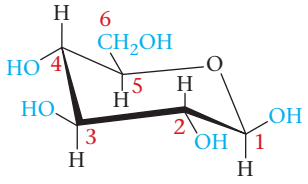


D-glucose

The bonds to the H and OH groups from the ring carbons are oriented either in the plane of the ring (*equatorial,* shown in blue) or perpendicular to it *(axial)*. In β-glucose, all four OH groups are equatorial. This keeps these rather bulky groups out of each other's way. In α-glucose, the OH group on carbon atom 1 is axial; all the others are equatorial. In water solution, glucose exists as an equilibrium mixture, about 37% in the alpha form and 63% in the beta form; the straight-chain structure accounts for less than 0.1% of the dissolved glucose.



α-glucose



β-glucose

As you can see from their structures, α- and β-glucose have several chiral carbon atoms. Both isomers are optically active; they are *not* enantiomers (mirror images of one another) because they differ in configuration only at carbon atom 1. As it happens, both α- and β-glucose rotate the plane of polarized light to the right (clockwise).

EXAMPLE 23.5

Consider the monosaccharide glucose.

a What is the molecular formula of glucose?

STRATEGY AND SOLUTION

Count the number of carbon, hydrogen, and oxygen atoms.

$C_6H_{12}O_6$

b How many chiral carbon atoms are there in a molecule of α-glucose? β-glucose? The straight-chain isomer?

SOLUTION

For both α- and β-glucose, only C_6 is not chiral. It has two hydrogen atoms bonded to it.

The straight chain structure has four chiral carbon atoms (C_2—C_5).

END POINT

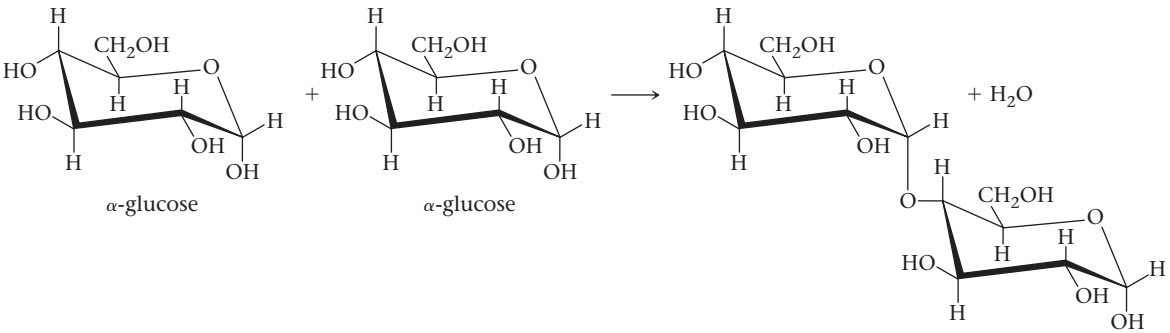
The general formula for carbohydrates is $C_n(H_2O)_m$. For glucose, $n = m = 6$.

Glucose is also called "blood sugar." It is absorbed readily into the bloodstream and is normally found there at concentrations ranging from 0.004 to 0.008 mol/L. If the concentration of glucose drops below 0.003 *M*, a condition called hypoglycemia is created, with symptoms ranging from nervousness to loss of consciousness. If the glucose level rises above 0.01 *M*, as can easily happen with diabetics, it is excreted in the urine.

Although glucose can exist as a simple sugar, it is most often found in nature in combined form, as a disaccharide or polysaccharide. Several glucose-containing disaccharides are known. We will consider two of these, maltose and sucrose.

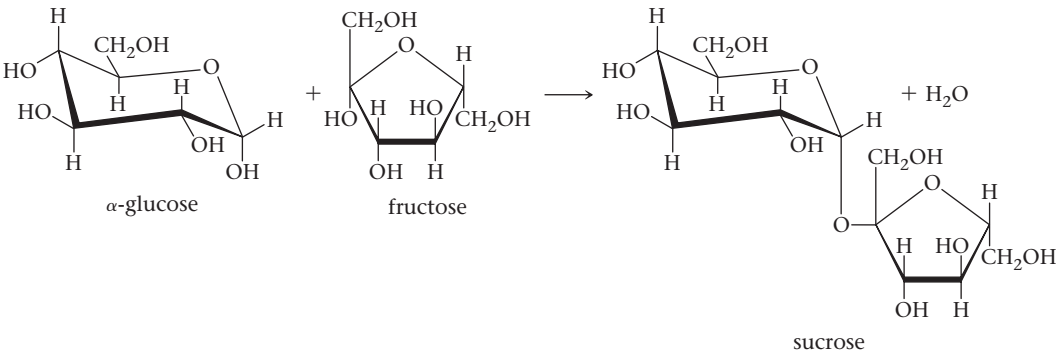
Maltose and Sucrose

Maltose, a decomposition product of starch, is a dimer of two glucose molecules. These are combined head-to-tail; carbon atom 1 of one molecule is joined through an oxygen atom to carbon atom 4 of the second molecule. To form maltose, the two OH groups on these carbon atoms react, condensing out H_2O and leaving the O atom bridge.



This reaction can be reversed either by using the enzyme maltase as a catalyst or by heating with acid. Two molecules of glucose are formed when this happens.

Sucrose, the compound we call "sugar," is the most common disaccharide. One of the monomer units in sucrose is α-glucose. The other is fructose, a monosaccharide found in honey and natural fruit juices.



In the body, this reaction is reversed by the enzyme sucrase. This occurs in digestion, which makes glucose and fructose available for absorption into the blood. Honey bees also carry an enzyme that can hydrolyze sucrose. Honey consists mostly of a 1 : 1 mol mixture of glucose and fructose with a small amount of unreacted sucrose.

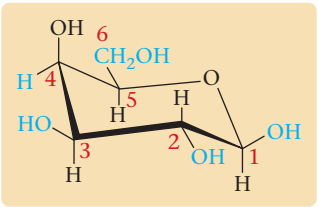
EXAMPLE 23.6

Another common disaccharide is lactose, the sugar found in milk. Lactose is a dimer of glucose and galactose, a monosaccharide that is identical to glucose except that the positions of the H and OH groups at carbon atom 4 are switched.

a Draw the structure of β-galactose.

STRATEGY AND SOLUTION

The structure of β-galactose is identical to that of β-glucose except at C_4. In this carbon atom, the placement of the H atom and OH group is reversed. Equatorial groups are shown in color.



b Draw the structure of lactose, which is broken down by the enzyme lactase to give equimolar amounts of β-galactose and β-glucose. Linkage occurs between carbon atom 1 of galactose and 4 of glucose.

SOLUTION

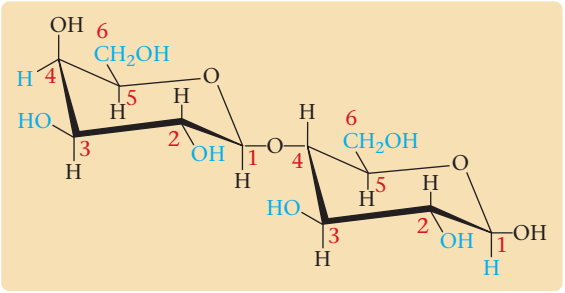


Table 23.2 Sweetness Relative to Sucrose

Lactose	0.16	Glucose	0.74	Aspartame (Equal)	180
Galactose	0.32	Sucrose	1.00	Saccharin (Sweet'N Low)	300
Maltose	0.33	Fructose	1.74	Sucralose (Splenda)	600

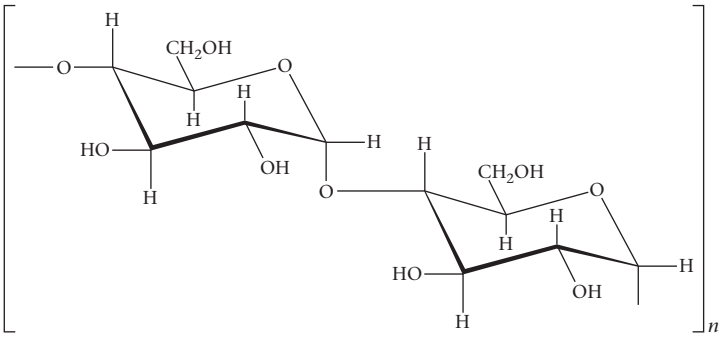
Table 23.2 gives the relative sweetness of the mono- and disaccharides considered here, along with sucrose substitutes.

Starch

Starch and cellulose are both condensation polymers of glucose.

Starch is a polysaccharide found in many plants, where it is stored in roots and seeds. It is particularly abundant in corn and potatoes, the major sources of commercial starch. Perhaps as much as 50% of our food energy comes from starch, mostly in the form of wheat products.

Starch is actually a mixture of two types of α-glucose polymers. One of these, called amylose, is insoluble in water and comprises about 20% of natural starch. It consists of long single chains of 1000 or more α-glucose units joined head-to-tail (Figure 23.5). The other glucose polymer found in starch is amylopectin, which is soluble in water. The linkage between α-glucose units is the same as in amylose. However, amylopectin has a highly branched structure. Short chains of 20 to 25 glucose units are linked through oxygen atom bridges. The oxygen atom joins a number 1 carbon atom at the end of one chain to a number 6 carbon atom on an adjacent chain.



Amylose

Figure 23.5 In starch, glucose molecules are joined head-to-tail through oxygen atoms. A thousand or more glucose molecules may be linked in this way, either in long single chains (amylose) or branched chains (amylopectin).

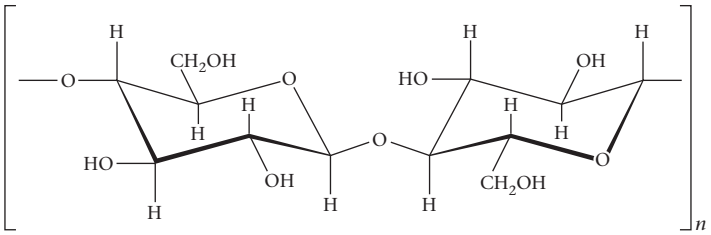


Figure 23.6 The bonding between glucose rings in cellulose is through oxygen bridges in the *β* position for each ring to the left of the bridge. This structure allows for ordered hydrogen bonding between chains and formation of long, strong fibers. Cotton and wood fiber have structures like this.

When you eat "starchy" foods, they are broken down into glucose by enzymes. The process starts in your mouth with the enzyme amylase found in saliva. This explains why, if you chew a piece of bread long enough, it starts to taste sweet. The breakdown of starch molecules continues in other parts of the digestive system. Within 1 to 4 hours after eating, all the starch in food is converted into glucose.

Cellulose

Cellulose contains long, unbranched chains of glucose units, about 10,000 per chain. It differs from starch in the way the glucose units are joined to each other. In starch, the oxygen bridge between the units is in the alpha position, as shown in Figure 23.5. In cellulose, it is in the beta position (Figure 23.6). Because humans lack the enzymes required to catalyze the hydrolysis of beta linkages, we cannot digest cellulose. The cellulose that we take in from fruits and vegetables remains undigested as "fiber." Ruminants, like cows and deer, and termites have bacteria in their intestines capable of breaking cellulose down into glucose.

The molecular structure of cellulose, unlike that of starch, allows for strong hydrogen bonding between polymer chains. This results in the formation of strong water-resistant fibers such as those found in cotton, which is 98% cellulose. Cotton actually has a tensile strength greater than that of steel. The major industrial source of cellulose is wood (~50% cellulose).

23-4 Proteins

The natural polymers known as **proteins** make up about 15% by mass of our bodies. They serve many functions. Fibrous proteins are the main components of hair, muscle, and skin. Other proteins found in body fluids transport oxygen, fats, and other substances needed for metabolism. Still others, such as insulin and

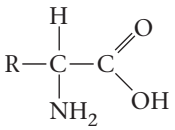
vasopressin, are hormones. Enzymes, which catalyze reactions in the body, are chiefly protein.

Protein is an important component of most foods. Nearly everything we eat contains at least a small amount of protein. Lean meats and vegetables such as peas and beans are particularly rich in protein. In our digestive system, proteins are broken down into small molecules called *α-amino acids*. These molecules can then be reassembled in cells to form other proteins required by the body.

Proteins are condensation polymers of α-amino acids.

α-Amino Acids

The monomers from which proteins are derived have the general structure shown below. These compounds are called **α-amino acids.** They have an NH_2 group attached to the carbon atom (the α carbon) adjacent to a COOH group.



α-amino acid

The 20 α-amino acids shown in Table 23.3 are those most commonly found in natural proteins. They differ from one another in the nature of the R group attached to the alpha carbon. As you can see, R can be

- a H atom (glycine).
- a simple hydrocarbon group (alanine, valine, . . .).
- a more complex group containing one or more atoms of oxygen (serine, aspartic acid, etc.), nitrogen (lysine, etc.), or sulfur (methionine, etc.).

EXAMPLE 23.7

Consider the structures shown in Table 23.3.

(a) How many α-amino acids contain only one chiral carbon atom?

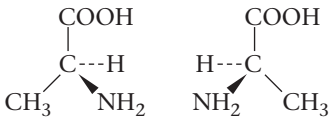
(b) How many contain only one —NH_2 group?

SOLUTION

(a) 17; the exceptions are glycine (0), isoleucine (2), and threonine (2).

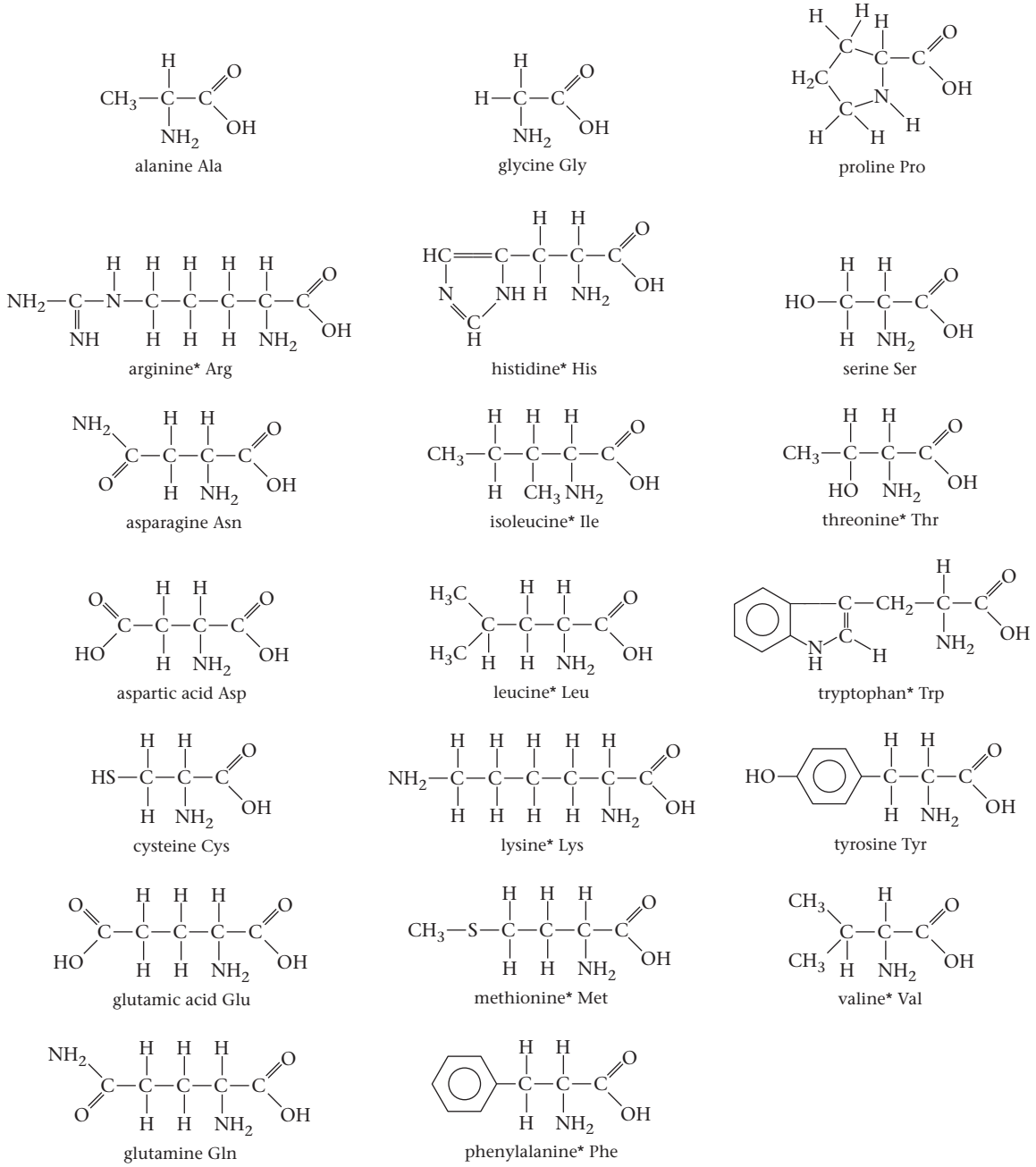
(b) 17; the exceptions are proline (0), lysine (2), and glutamine (2).

In all the amino acids shown in Table 23.3 except glycine, the α-carbon is chiral. This means that these compounds are optically active. With alanine, for example, there should be two optical isomers:



Of the 20 common amino acids, ten are "essential" in the sense that they are required by humans for protein construction and cannot be synthesized in the body. These are designated by an asterisk in Table 23.3. Clearly the proteins we eat should contain these essential amino acids. Beyond that, a "high-quality" protein contains the various amino acids in the approximate ratio required by the body for protein synthesis. Generally speaking, animal proteins are of higher

Table 23.3 The Common α-Amino Acids (names and abbreviations below structures)



*These are essential amino acids that cannot be synthesized by the body and therefore must be obtained from the diet.

quality than plant proteins, with eggs at the head of the class. This is something to keep in mind if you're a vegetarian.

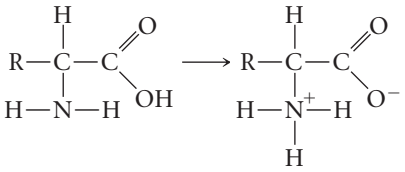
Acid-Base Properties of Amino Acids

You may recall from Example 22.8 that the reaction

$$CH_3COOH(aq) + CH_3NH_2(aq) \longrightarrow CH_3COO^-(aq) + CH_3NH_3^+(aq)$$

in which there is a proton transfer from a —COOH group to an —NH_2 group has a large equilibrium constant, 7×10^5. In other words, this reaction goes virtually to completion when solutions of acetic acid and methylamine are mixed.

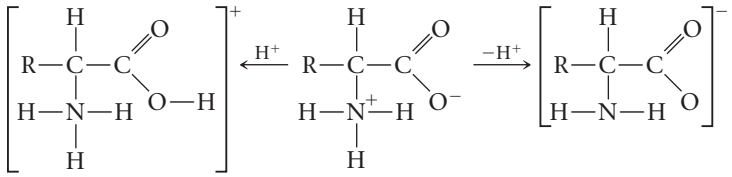
A very similar reaction occurs with an amino acid; there is a proton transfer from the —COOH group to the $—NH_2$ group:



amino acid zwitterion

Here, too, the equilibrium constant is large and the reaction goes essentially to completion. Putting it another way, an amino acid does not exist in the form shown in Table 23.3, either in water solution or in the solid state. Instead it occurs as a **zwitterion,** which behaves like a polar molecule. Within it, there is a +1 charge on the nitrogen atom and a −1 charge at one of the oxygen atoms of the COOH group. Overall, the zwitterion has no net charge.

In water, zwitterions are stable only over a certain pH range. At low pH (high H^+ concentration), the COO^- group picks up a proton. The product, shown at the left below, has a +1 charge. At high pH (low H^+ concentration), the NH_3^+ group loses a proton. The species formed, shown at the right below, has a −1 charge.



cation zwitterion anion

In a very real sense, a zwitterion is analogous to a species such as the HCO_3^- ion, which accepts a proton at low pH and donates a proton at high pH:

$$\underset{\text{low pH}}{H_2CO_3(aq)} \xleftarrow{H^+} HCO_3^-(aq) \xrightarrow{-H^+} \underset{\text{high pH}}{CO_3^{2-}(aq)}$$

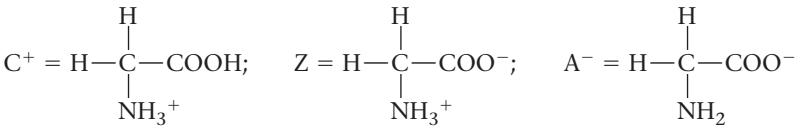
Both the zwitterion and the HCO_3^- ion are amphiprotic, capable of acting as either a Brønsted acid or a Brønsted base.

To treat acid-base equilibria involving zwitterions, it is convenient to consider the cation stable at low pH to be a diprotic acid (analogous to H_2CO_3), which ionizes in two steps. Using the symbols C^+, Z, and A^- to stand for the cation, zwitterion, and anion, respectively, we have

$$C^+(aq) \rightleftharpoons H^+(aq) + Z(aq); \qquad K_{a1} = \frac{[H^+][Z]}{[C^+]}$$

$$Z(aq) \rightleftharpoons H^+(aq) + A^-(aq); \qquad K_{a2} = \frac{[H^+][A^-]}{[Z]}$$

For glycine,



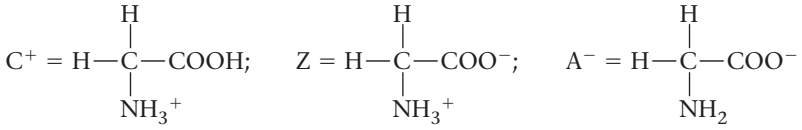
$$K_{a1} = 4.6 \times 10^{-3}; \qquad K_{a2} = 2.5 \times 10^{-10}$$

EXAMPLE 23.8

Using these acid dissociation constants for glycine, calculate the ratios [Z]/[C$^+$] and [Z]/[A$^-$] at pH 2.00, 6.00, and 10.00.

STRATEGY

Substitute into the general K_a expression where



For the first dissociation:

$$C^+(aq) \rightleftharpoons H^+(aq) + Z(aq) \qquad K_{a1} = 4.6 \times 10^{-3}$$

For the second dissociation:

$$Z(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad K_{a2} = 2.5 \times 10^{-10}$$

SOLUTION

pH = 2.00

$$[H^+] = 1.0 \times 10^{-2}$$

$$\frac{[Z]}{[C^+]} \qquad 4.6 \times 10^{-3} = \frac{[H^+][Z]}{[C^+]} \longrightarrow \frac{[Z]}{[C^+]} = \frac{4.6 \times 10^{-3}}{1.0 \times 10^{-2}} = 0.46$$

$$\frac{[Z]}{[A^-]} \qquad 2.5 \times 10^{-10} = \frac{[H^+][A^-]}{[Z]} \longrightarrow \frac{[Z]}{[A^-]} = \frac{1.0 \times 10^{-2}}{2.5 \times 10^{-10}} = 4.0 \times 10^7$$

pH = 6.00

$$[H^+] = 1.0 \times 10^{-6}$$

$$\frac{[Z]}{[C^+]} \qquad \frac{[Z]}{[C^+]} = \frac{4.6 \times 10^{-3}}{1.0 \times 10^{-6}} = 4.6 \times 10^3$$

$$\frac{[Z]}{[A^-]} \qquad 2.5 \times 10^{-10} = \frac{[H^+][A^-]}{[Z]} \longrightarrow \frac{[Z]}{[A^-]} = \frac{1.0 \times 10^{-6}}{2.5 \times 10^{-10}} = 4.0 \times 10^3$$

pH = 10.00

$$[H^+] = 1.0 \times 10^{-10}$$

$$\frac{[Z]}{[C^+]} \qquad \frac{[Z]}{[C^+]} = \frac{4.6 \times 10^{-3}}{1.0 \times 10^{-10}} = 4.6 \times 10^7$$

$$\frac{[Z]}{[A^-]} \qquad 2.5 \times 10^{-10} = \frac{[H^+][A^-]}{[Z]} \longrightarrow \frac{[Z]}{[A^-]} = \frac{1.0 \times 10^{-10}}{2.5 \times 10^{-10}} = 0.40$$

END POINTS

1. At low pH, [Z] < [C$^+$], so there is more cation than zwitterion and essentially no anion.
2. At intermediate pH, the zwitterion is the principal species present.
3. At high pH, the anion [A$^-$] is the principal species.

From Example 23.8 or Figure 23.7, it is clear that the zwitterion of glycine is the principal species over a wide pH range, certainly from pH 3 to pH 9. The maximum concentration of zwitterion occurs at about pH 6; this is referred to as the **isoelectric point** of glycine. At this pH, glycine does not migrate in an electric field, since the zwitterion is a neutral species. At low pH, the cation moves to the cathode; at high pH the anion migrates to the anode. In general, for an amino acid like glycine, where there is only one —COOH group and one —NH_2 group:

$$\text{pH at isoelectric point} = \frac{pK_{a1} + pK_{a2}}{2}$$

where K_{a1} and K_{a2} are the successive dissociation constants of the cation of the amino acid.

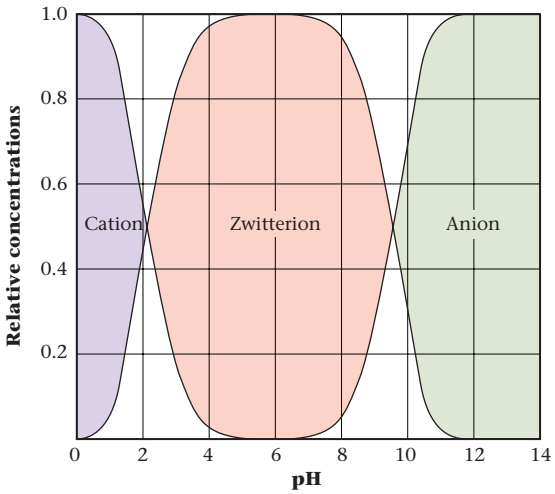
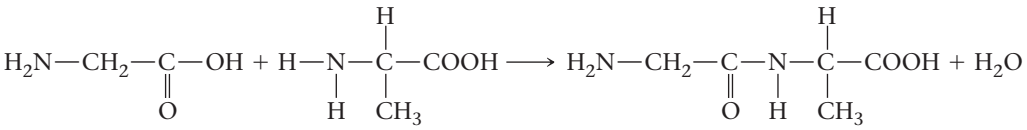
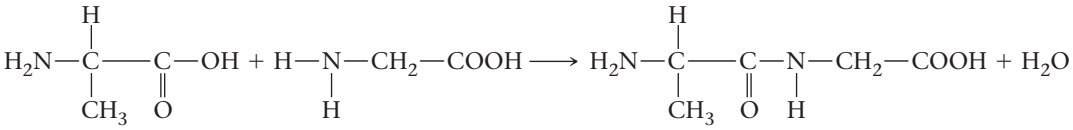


Figure 23.7 Relative concentrations of different glycine species as a function of pH. Between about pH 3 and 9, the zwitterion is the principal species; it has its maximum concentration at pH 6, the isoelectric point. Below pH 2, the cation dominates; above pH 10, the anion is the principal species.

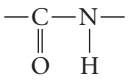
Polypeptides

As noted in Section 23-2, molecules containing NH_2 and COOH groups can undergo condensation polymerization. Amino acids contain both groups in the same molecule. Hence, two amino acid molecules can combine by the reaction of the COOH group in one molecule with the NH_2 group of the other molecule. If the acids involved are different, two different structural isomers are possible:





Each of these isomers is a dipeptide, formed from two amino acids by condensing out a water molecule and containing the group



commonly called a **peptide linkage.**  Dipeptides are named by writing first (far left) the amino acid that retains a free NH_2 group; the amino acid with a free COOH group is written last (far right).

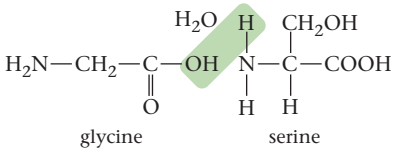
This linkage is similar to that in nylon.

EXAMPLE 23.9

Draw the structural formula of glycylserine (Gly-Ser).

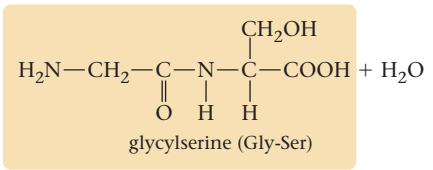
STRATEGY AND SOLUTION

1. Write the structural formula of the two amino acids side by side. Put glycine on the left with the NH_2 group on the left and the COOH group on the right. Put the serine group on the right in a similar fashion.



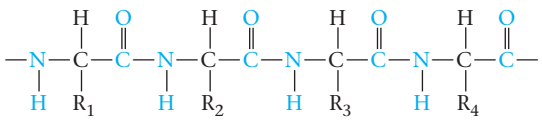
continued

2. The two amines react by condensing out a water molecule made up of the OH group from glycine and the H atom from serine.



glycylserine (Gly-Ser)

The dipeptide formed in Example 23.9 has a reactive group at both ends of the molecule (NH_2 at one end, COOH at the other). Hence it can combine further to give tripeptides (three amino acid units), tetrapeptides, . . . , and eventually long-chain polymers called polypeptides. A protein containing a large number of amino acid units is a **polypeptide**:



(peptide linkages in color).

Proteins differ from the other polymers we have discussed in that they may contain up to 20 different monomer units. This means that there are a huge number of possible proteins. Using the amino acids listed in Table 23.3, we could make

$20 \times 20 = 400$ different dipeptides.
$20 \times 20 \times 20 = 8000$ different tripeptides.
20^n polypeptides containing n monomer units.

For a relatively simple protein containing only 50 monomer units, we have

$20^{50} = 1 \times 10^{65}$ possibilities.

Proteins; Primary Structure

To determine the **primary structure** of a protein that may contain a hundred or more amino acid units, it is necessary to

1. identify the amino acids present.
2. *determine the relative amounts of each amino acid.*
3. establish the *sequence* of amino acid units in the protein.

The amino acid sequence in hemoglobin, with 574 units, is known.

Tasks (1) and (2) are relatively easy to accomplish. The sample is first heated with hydrochloric acid to break all of the "peptide linkages" (amide bonds) in the protein. The resulting solution is then passed through a chromatographic column (recall the discussion in Chapter 1). This separates the different amino acids and allows you to determine their identities and concentrations.

Task (3) is more difficult. It uses a series of reagents each of which is capable of breaking only certain amide bonds. One of these reagents is the enzyme trypsin, which breaks only those bonds formed by the carboxyl groups in arginine and lysine. It would break the polypeptide

Ala-Gly-Ser-Lys-Gly-Leu-Arg-Met

into three fragments:

Ala-Gly-Ser-Lys; Gly-Leu-Arg; Met

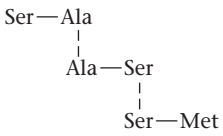
Remember that, by convention, the NH_2 group of each amino acid is written at the left; the COOH group is at the right. Other reagents split the chain at different points. By correlating the results of different hydrolysis experiments, it is possible to deduce the primary structure of the protein (or polypeptide). Example 23.10 shows how this is done in a particularly simple case.

EXAMPLE 23.10

A certain polypeptide is shown by acid hydrolysis to contain only three amino acids: serine (Ser), alanine (Ala), and methionine (Met) with mole fractions of $\frac{1}{2}$, $\frac{1}{4}$, and $\frac{1}{4}$, respectively. Enzymatic hydrolysis yields the following fragments: Ser-Ala; Ser-Met; Ala-Ser. Deduce the primary structure of the polypeptide.

STRATEGY AND SOLUTION

Align the fragments vertically so that they overlap one another



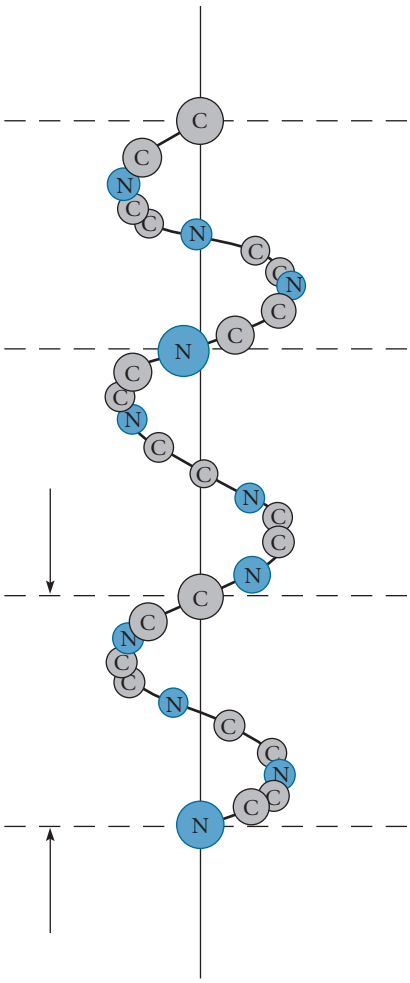
There are four amino acid units: Ser – Ala – Ser – Met

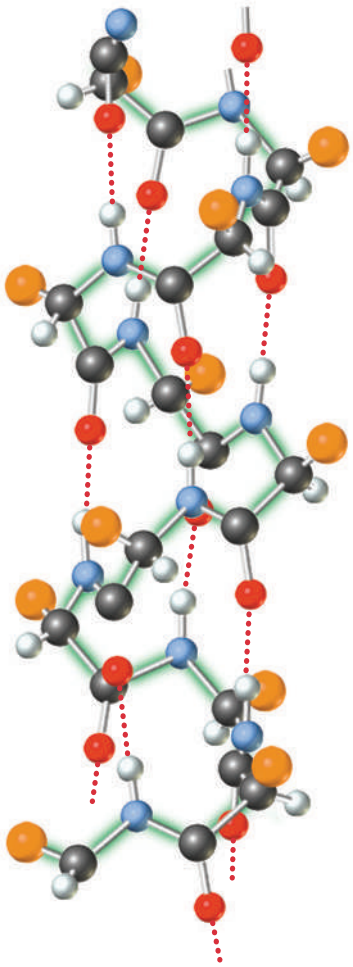
Since there are two serine units, one alanine unit, and one methionine unit, their mole fractions are

$$\frac{2}{4} = \frac{1}{2} \text{ for serine} \qquad \frac{1}{4} \text{ for alanine} \qquad \frac{1}{4} \text{ for methionine}$$

In the body, proteins are built up by a series of reactions that in general produce a specific sequence of amino acids. Even tiny errors in this sequence may have serious effects. Among the genetic diseases known to be caused by improper sequencing are hemophilia, sickle cell anemia, and albinism. Sickle cell anemia is caused by the substitution of *one* valine unit for a glutamic acid unit in a chain containing 146 monomers.

Fortunately nature doesn't make too many mistakes.





Proteins; Secondary and Tertiary Structures

Protein chains (Figure 23.8) can align themselves so that certain patterns are repeated. These repeating patterns establish what we call the **secondary structure** of the protein. The nature of the pattern is determined in large part by hydrogen bonding. Oxygen atoms on C═O groups can interact with H atoms in nearby N—H groups to form these bonds. This can occur within a single protein chain or between neighboring chains.

A common secondary structure is an α-helix, which maximizes hydrogen bonding between peptide linkages. At the left of Figure 23.8 is the outline of the protein chain forming the helix. The more complete structure is given at the right. This shows where the hydrogen bonds form between amino acid units in the protein chain. Notice that the bulky R groups are all on the outside of the helix, where they have the most room. The actual structure of the helix is nearly independent of the nature of the R groups. The dimensions of the helix correspond

Figure 23.8 α-Helix structures of proteins. The main atom chain in the helix is shown schematically on the left. The sketch on the right more nearly represents the actual positions of atoms and shows where intrachain hydrogen bonding occurs. Wool and many other fibrous proteins have the α-helix structure.

closely to those observed in such fibrous proteins as wool, hair, skin, feathers, and fingernails.

The three-dimensional conformation of a protein is called its **tertiary structure.** An α-helix can be either twisted, folded, or folded and twisted into a definite geometric pattern. These structures are stabilized by dispersion forces, hydrogen bonding,◂ and other intermolecular forces.

ℹ This is a rather special kind of H bond.

Collagen, the principal fibrous protein in mammalian tissue, has a tertiary structure made up of twisted α-helices. Three polypeptide chains, each of which is a left-handed helix, are twisted into a right-handed super helix to form an extremely strong tertiary structure. It has remarkable tensile strength, which makes it important in the structure of bones, tendons, teeth, and cartilage.

CHEMISTRY **BEYOND** THE CLASSROOM

DNA Fingerprinting

Within every living cell, there is an organic natural polymer called **d**eoxyribo**n**ucleic **a**cid or, more commonly, DNA. The DNA molecule is enormous; its molar mass is estimated to be of the order of 2×10^{10} g. The molecule takes the form of a narrow, tightly coiled band, which, if straightened out, would have a length of about 1 m.

Figure A shows the primary structure of the DNA molecule. Notice that

- the backbone of the molecule consists of alternating units derived from phosphoric acid, H_3PO_4, and a 5-carbon sugar called deoxyribose.
- bonded to each sugar is a nitrogen base (amine). The base may be thymine (shown at the top in orange), adenine (red), guanine (blue), or cytosine (green). These are often abbreviated as the letters T, A, G, and C, respectively
- the structural unit of DNA, repeated over and over along the chain, is built from an H_3PO_4 molecule, a sugar molecule, and a nitrogen base, which may be any one of the four shown. Figure A shows four such structural units called *nucleotides;* an actual molecule of DNA would contain literally billions of such nucleotides.

The secondary structure of DNA is shown in Figure B. This "double helix" model was first proposed in 1953 by James Watson (1928–) and Francis Crick (1916–2004), who used the x-ray crystallographic data of Rosalind Franklin (1920–1958) and Maurice Wilkins (1916–2004). Beyond that, they were intrigued by the results of analyses that showed that in DNA the ratio of adenine to thymine molecules is almost exactly 1 : 1, as is the ratio of cytosine to guanine:

$$A/T = C/G = 1.00$$

This behavior is readily explained by the double helix; an A molecule in one strand is always hydrogen-bonded to a T molecule in the second strand. Similarly, a C molecule in one strand is situated properly to form a hydrogen bond with a G molecule in the other strand. In 1962, Watson, Crick, and Wilkins received the Nobel Prize in medicine.

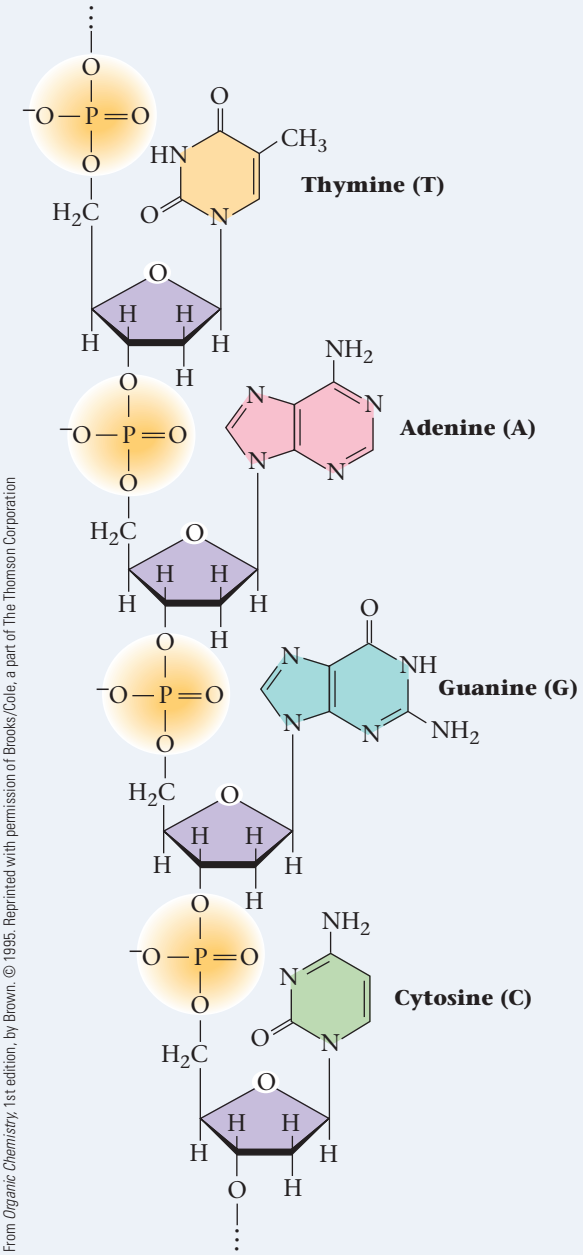


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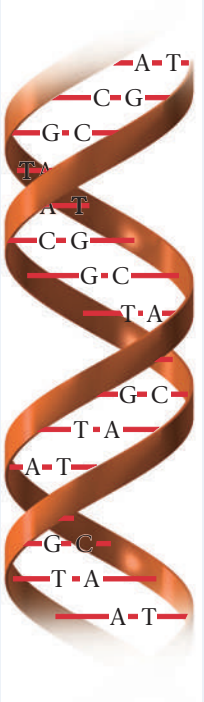
Figure A A tetranucleotide section of a single-stranded DNA.



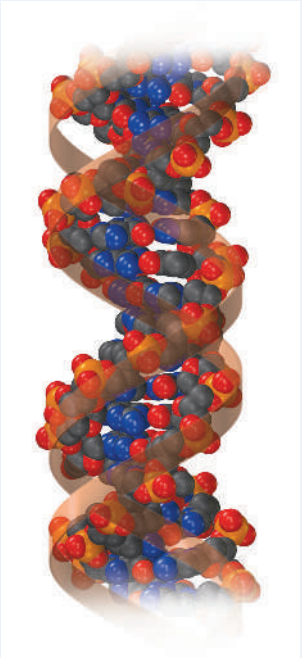


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Figure B The double-helical strand of a DNA molecule. The diagram at the left shows the hydrogen bonding between base pairs adenine-thymine and cystosine-guanine that hold the strands together.

The double helix model provides a simple explanation for cell division and reproduction. In the reproduction process, the two DNA chains unwind from each other. As this happens, a new matching chain of DNA is synthesized on each of the original ones, creating two double helices. Since the base pairs in each new double helix must match in the same way as in the original, the two new double helices must be identical to the original. Exact replication of genetic data is thereby accomplished, however complex that data may be.

The many millions of DNA molecules in the cells of your body are identical to each other. That is, the base sequence in all of these molecules is the same. In contrast, the base sequence of the DNA molecules in every other person in the world differs at least slightly from yours. In that sense, your "DNA fingerprint" is unique.

Alec Jeffreys (1950–), an English geneticist, discovered in the 1980s how to apply this principle to forensics. To do this, it is necessary to locate that portion of the DNA molecule in which the base sequence differs significantly from one individual to another. That part of the molecule is cut out by a "restrictive enzyme" in much the same way that trypsin splits a protein molecule into fragments. The DNA sample obtained in this way from a suspect can be compared with that derived from blood, hair, semen, saliva, and so on, found at the scene of a violent crime.

At least in principle, comparison of DNA fingerprints can determine the guilt or innocence of a suspect beyond a reasonable doubt. If the two fingerprints differ, the suspect is innocent. Conversely, if the fingerprints match perfectly, the odds that the suspect is guilty are about 80 billion to one.

In practice, the situation isn't quite that simple. DNA samples taken from a victim are almost certain to be contaminated with DNA from fungi or bacteria. Certain dyes can combine with restriction enzymes, causing them to cut in the wrong places. Finally, DNA may decay in a warm or moist environment.

A DNA fingerprint can be used for many purposes other than solving violent crimes. In particular, it can serve to identify deceased individuals. In June of 1998 the "Vietnam Unknown" buried in the Tomb of the Unknown Soldier at Arlington National Cemetery was identified by DNA technology. He was shown to be First Lieutenant Michael Blassie, shot down over Vietnam in May of 1972. DNA samples taken from his mother matched those obtained from his body. A month later Blassie, a native of St. Louis, Missouri, was reburied in a national cemetery located in that city.

Key Concepts

1. Relate the structure of an addition polymer to that of the corresponding monomer.
   (Examples 23.1, 23.2; Problems 1–6, 37, 38)
2. Relate the structure of a condensation polymer to that of the corresponding monomer.
   (Examples 23.3, 23.4; Problems 9–14, 37, 38)
3. Relate the molar mass of a polymer to the number of monomer units.
   (Example 23.1; Problems 1, 2, 7, 17, 18)
4. Draw the structures of mono- and disaccharides.
   (Example 23.6; Problems 19, 20)
5. Identify the chiral carbon atoms in a carbohydrate or α-amino acid.
   (Examples 23.5, 23.7; Problems 21, 22)
6. Carry out equilibrium calculations relating pH to [Z], $[C^+]$, and $[A^-]$.
   (Example 23.8; Problems 29, 30)
7. Relate the structure of a polypeptide to that of the amino acids from which it is formed.
   (Example 23.9; Problems 23–26)
8. Deduce the structure of a polypeptide from hydrolysis data.
   (Example 23.10; Problems 31, 32)

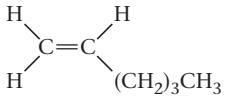
Key Terms

addition polymer
α-amino acids
carbohydrates
condensation polymer
disaccharides
isoelectric point
monomers
monosaccharides
peptide linkage
polyamide
polyester
polymers
polypeptide
polysaccharides
primary structure
proteins
secondary structure
tertiary structure
zwitterion

Summary Problem

All of these questions pertain to six-carbon molecules.

(a) Sketch the head-to-tail and tail-to-tail addition polymers derived from



(b) If the molar mass of the polymer is 1.2×10^4 g/mol, how many monomer units are present? What is the mass percent of carbon in the polymer?

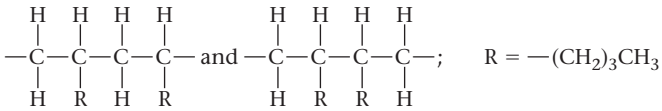
(c) Write the structure of the condensation polymer formed when a straight-chain, saturated, six-carbon dialcohol reacts with a straight-chain, saturated, six-carbon dicarboxylic acid.

(d) Write the structure of the disaccharide formed when α-glucose and β-glucose, both of formula $C_6H_{12}O_6$, combine to form an isomer of maltose.

(e) Draw the structures of the two polypeptides derived from the six-carbon amino acids lysine and leucine.

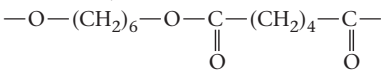
Answers

(a)



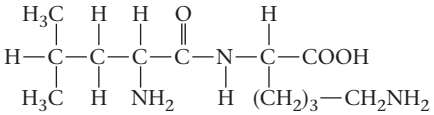
(b) **1.4×10^2; 85.6**

(c)

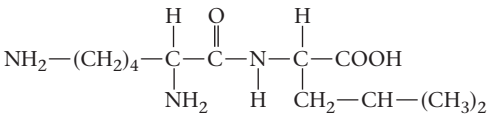


(d) **See maltose structure (page 585); invert OH and H on carbon atom at lower right.**

(e)



Leu-Lys



Lys-Leu

Questions and Problems

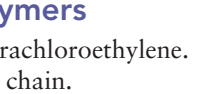
Even-numbered questions and Challenge Problems have answers in Appendix 5 and fully worked solutions in the *Student Solutions Manual*.

23-1 Synthetic Addition Polymers

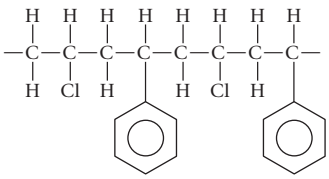
1. Consider a polymer made from tetrachloroethylene.
(a) Draw a portion of the polymer chain.
(b) What is the molar mass of the polymer if it contains 3.2×10^3 tetrachloroethylene molecules?
(c) What are the mass percents of C and Cl in the polymer?

2. Consider Teflon, the polymer made from tetrafluoroethylene.
(a) Draw a portion of the Teflon molecule.
(b) Calculate the molar mass of a Teflon molecule that contains 5.0×10^4 CF_2 units.
(c) What are the mass percents of C and F in Teflon?

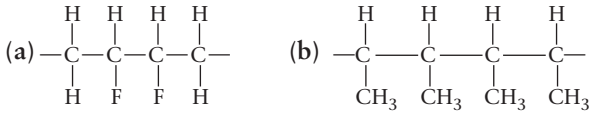
3. Sketch a portion of the acrylonitrile polymer (Table 23.1), assuming it is a
(a) head-to-tail polymer.
(b) head-to-head, tail-to-tail polymer.

4. Styrene,  , forms a head-to-tail addition polymer.
Sketch a portion of a polystyrene molecule.

5. The polymer whose structure is shown below is made from two different monomers. Identify the monomers.



6. Show the structure of the monomer used to make the following addition polymers.

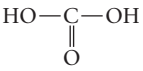


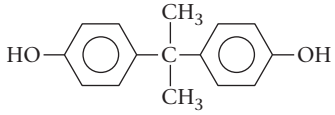
7. Consider the polymers referred to in Table 23.1. If each one contains the same number of monomer units, which one has the largest molar mass?

8. Of the polymers referred to in Table 23.1 which one contains the highest percentage by mass of carbon?

23-2 Synthetic Condensation Polymers

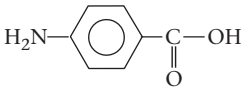
9. A rather simple polymer can be made from ethylene glycol, $HO—CH_2—CH_2—OH$, and oxalic acid, 
Sketch a portion of the polymer chain obtained from these monomers.

10. Lexan is a very rugged polyester in which the monomers can be taken to be carbonic acid, 
and



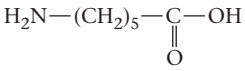
Sketch a section of the Lexan chain.

11. *Para*-aminobenzoic acid is an "essential vitamin" for many bacteria:



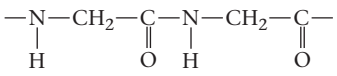
Sketch a portion of a polyamide polymer made from this monomer.

12. Nylon-66 is made from a single monomer:

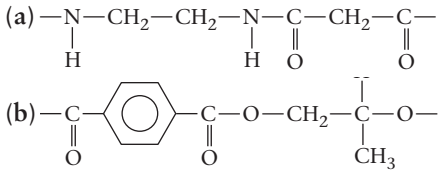


Sketch a section of the polymer chain in Nylon-66.

13. The following condensation polymer is made from a single monomer. Identify the monomer.



14. Identify the monomers from which the following condensation polymers are made.



23-3 Carbohydrates

15. Write a chemical equation, using molecular formulas, for the reaction of sucrose with water to form glucose and fructose.

16. Write a chemical equation, using molecular formulas, for the reaction of maltose with water to form glucose.

17. Cellulose consists of about 10,000 $C_6H_{10}O_5$ units linked together.

(a) What are the mass percents of C, H, and O in cellulose?

(b) What is the molar mass of cellulose?

18. Starch has the same empirical formula as cellulose and a molar mass of about 1.0×10^5 g/mol.

(a) What are the mass percents of C, H, and O in starch?

(b) How many $C_6H_{10}O_5$ units are linked together in a starch molecule?

19. Mannose has the same molecular formula as glucose and the same geometry except at carbon-2, where the H and OH groups are interchanged. Draw the structures of α- and β-mannose.

20. Draw the structure of the disaccharide formed by two moles of α-mannose (see Question 19).

21. How many chiral carbon atoms are there in α-glucose? Fructose?

22. How many chiral carbon atoms are there in sucrose? Maltose?

23-4 Proteins

23. Give the structural formula of two different dipeptides formed between arginine and serine.

24. Give the structural formulas of two different dipeptides formed between leucine and lysine.

25. (a) How many tripeptides can be made from glycine, alanine, and leucine, using each amino acid only once per tripeptide?

(b) Write the structural formulas of these tripeptides and name them in the shorthand abbreviation used for showing amino acid sequences.

26. A tripeptide contains valine, lysine, and phenylalanine residues.

(a) How many tripeptides are possible from these amino acids?

(b) Draw a structural formula for a possible form of the tripeptide and name it, using the shorthand form.

27. Consider the cysteine molecule shown in Table 23.3. Write structural formulas for

(a) the zwitterion of cysteine.

(b) the cation formed in acid.

(c) the anion formed in base.

28. Follow the directions of Question 27 for serine.

29. For alanine, $K_{a1} = 5.1 \times 10^{-3}$, $K_{a2} = 1.8 \times 10^{-10}$. Calculate the ratios $[Z]/[C^+]$ and $[Z]/[A^-]$ at pH

(a) 2.00. (b) 6.00. (c) 10.50.

What is the principal species at each pH?

30. Using the information given in Problem 29, calculate the pH

(a) when $[Z] = [C^+]$.

(b) when $[Z] = [A^-]$.

(c) at the isoelectric point.

31. On complete hydrolysis, a polypeptide gives two alanine, one leucine, one methionine, one phenylalanine, and one valine residue. Partial hydrolysis gives the following fragments: Ala-Phe, Leu-Met, Val-Ala, Phe-Leu. It is known that the first amino acid in the sequence is valine and the last one is methionine. What is the complete sequence of amino acids?

32. Suppose that, in the polypeptide referred to in Question 31, the first amino acid is alanine and the last one is also alanine. What is the complete sequence of amino acids?

Unclassified

33. Which of the following monomers could form an addition polymer? A condensation polymer?

(**a**) C_2H_6 (**b**) C_2H_4

(**c**) $HO—CH_2—CH_2—OH$ (**d**) $HO—CH_2—CH_3$

34. How would you explain to a young science student how to decide whether a given compound might be useful as a monomer for addition polymerization? Condensation polymerization?

35. Explain the difference between

(**a**) a synthetic and natural polymer.

(**b**) a polyester and polyamide.

(**c**) α- and β-glucose.

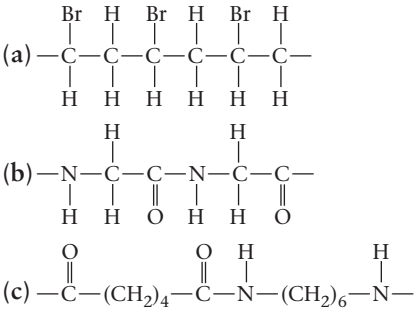
36. Explain the difference between

(**a**) linear and branched polyethylene.

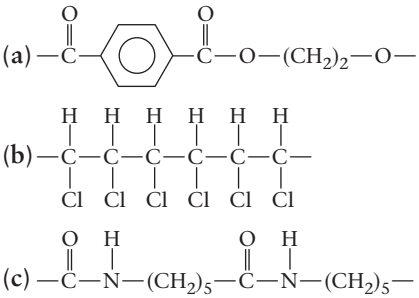
(**b**) glucose and fructose.

(**c**) maltose and sucrose.

37. Draw the structures of the monomers that could be used to make the following polymers:



38. What monomers would be used to make the following polymers?



39. Sketch the tetrapeptide obtained from four molecules of the α-amino acid glycine.

40. Sketch a portion of a head-to-head, tail-to-tail, and a head-to-tail polymer made from acrylonitrile, $H_2C{=}CHCN$.

41. Using bond energies, estimate ΔH for the hydrolysis of maltose to glucose.

42. Sketch the form in which leucine would exist in acid solution; in basic solution.

43. How many tripeptides could one make from glycine, valine, and lysine, using any number of each amino acid?

44. A 1.00-mg sample of a pure protein yielded on hydrolysis 0.0165 mg of leucine and 0.0248 mg of isoleucine. What is the minimum possible molar mass of the protein? (MM leucine = MM isoleucine = 131 g/mol)

45. Describe what is meant by

(**a**) the primary structure of a protein.

(**b**) the secondary structure of a protein.

(**c**) the tertiary structure of a protein.

46. Glycolysis is the process by which glucose is metabolized to lactic acid according to the equation

$$C_6H_{12}O_6(aq) \longrightarrow 2C_3H_6O_3(aq)$$

$$\Delta G^\circ = -198 \text{ kJ at pH 7.0 and } 25^\circ C$$

Glycolysis is the source of energy in human red blood cells. In these cells, the concentration of glucose is 5.0×10^{-3} M, while that of lactic acid is 2.9×10^{-3} M. Calculate ΔG for glycolysis in human blood cells under these conditions. Use the equation $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the concentration quotient, analogous to K.

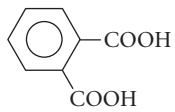
47. Plants synthesize carbohydrates from CO_2 and H_2O by the process of photosynthesis. For example,

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

$\Delta G^\circ = 2.87 \times 10^3$ kJ at pH 7.0 and 25°C. What is K for the reaction at 25°C?

Challenge Problems

48. Glycerol, $C_3H_5(OH)_3$, and orthophthalic acid,



form a cross-linked polymer in which adjacent polymer chains are linked together; this polymer is used in floor coverings and dentures.

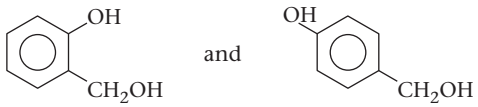
(**a**) Write the structural formula for a portion of the polymer chain.

(**b**) Use your answer in (a) to show how cross-linking can occur between the polymer chains to form a water-insoluble, network covalent solid.

49. Determine the mass percents of the elements in Nylon whose structure is shown in Example 23.4.

50. Using bond energies, estimate ΔH for protein formation, per mole of amino acid added to the chain. Does this value seem reasonable?

51. One of the earliest, and still one of the most important, polymers is the material known as Bakelite, which is a condensation polymer of phenol, C_6H_5OH, and formaldehyde, $H_2C{=}O$. Formaldehyde will react with phenol to produce the following compounds when the ratio is 1 : 1:



These species, which can be taken to be monomers, on being heated condense with each other and themselves, eliminating water (formed from the OH groups on CH_2OH and ring hydrogen atoms) and linking benzene rings by CH_2 groups. If the phenol:formaldehyde ratio is 1 : 1, a linear polymer forms. If the ratio is 1 : 2, two $H_2C{=}O$ molecules react with each ring, and the chains cross-link at every benzene ring, forming the infusible, insoluble, hard, brittle solid we know as Bakelite. Sketch the linear chain polymer and the cross-linked solid.

52. Aspartic acid acts as a triprotic acid with successive dissociation constants of 8.0×10^{-3}, 1.4×10^{-4}, and 1.5×10^{-10}. Depending upon pH, aspartic acid can exist in four different forms in water solution. Draw these forms and calculate the pH range over which each form is the principal species.