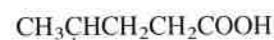




Butanoic acid



Benzoic acid



4-Bromopentanoic acid

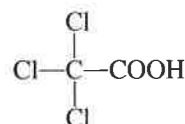
Trichloroethanoic acid  
(trichloroacetic acid)

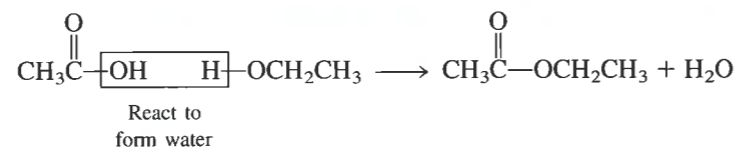
Figure 22.15

Some carboxylic acids.

potassium permanganate:



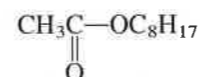
A carboxylic acid reacts with an alcohol to form an **ester** and a water molecule. For example, the reaction of acetic acid and ethanol produces ethyl acetate and water:



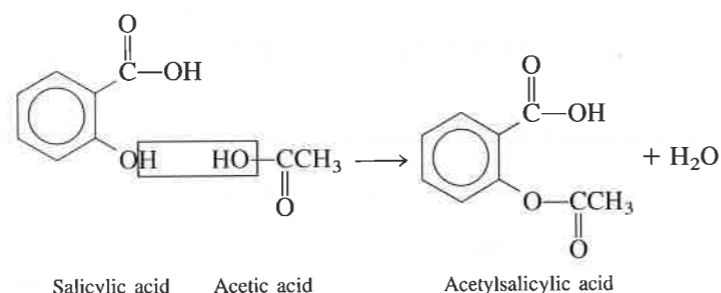
Esters often have a sweet, fruity odor that is in contrast to the often pungent odors of the parent carboxylic acids. For example, the odor of bananas is from *n*-amyl acetate,



and that of oranges is from *n*-octyl acetate,



A very important ester can be formed from the reaction of salicylic acid and acetic acid:



Salicylic acid

Acetic acid

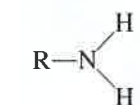
Acetylsalicylic acid

The product is acetylsalicylic acid, commonly known as *aspirin*, which is used in huge quantities as an analgesic (pain-killer).

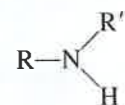
### Amines

**Amines** are probably best viewed as derivatives of ammonia in which one or more N—H bonds are replaced by N—C bonds. The resulting amines are classified as *primary* if one N—C bond is present, *secondary* if they contain two N—C bonds, and *tertiary* if all three N—H bonds in  $\text{NH}_3$  have been replaced by N—C bonds (Fig. 22.16). Examples of some common amines are given in Table 22.7.

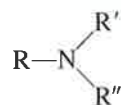
Common names are often used for simple amines; the systematic nomenclature for more complex molecules uses the name *amino-* for the  $-\text{NH}_2$  functional group. For example, the molecule



Primary amine



Secondary amine



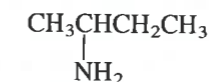
Tertiary amine

Figure 22.16

The general formulas for primary, secondary, and tertiary amines. R, R', and R'' represent carbon-containing substituents.

Table 22.7

Some Common Amines		
Formula	Common Name	Type
$\text{CH}_3\text{NH}_2$	Methylamine	Primary
$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethylamine	Primary
$(\text{CH}_3)_2\text{NH}$	Dimethylamine	Secondary
$(\text{CH}_3)_3\text{N}$	Trimethylamine	Tertiary
	Aniline	Primary
	Diphenylamine	Secondary



is named 2-aminobutane.

Many amines have unpleasant "fishlike" odors. For example, the odors associated with decaying animal and human tissues are due to amines such as putrescine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) and cadaverine ( $\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ).

Aromatic amines are primarily used to make dyes. Since many of them are carcinogenic, they must be handled with great care.

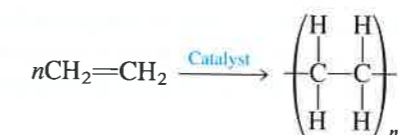
## 22.6 Polymers

### Purpose

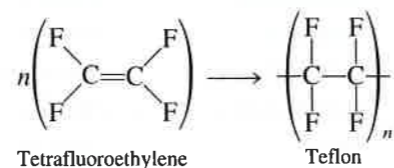
- To show how polymers are formed from monomers via two types of polymerization reactions.

**Polymers** are large, usually chainlike molecules that are built from small molecules called **monomers**. Polymers form the basis for synthetic fibers, rubbers, and plastics and have played a leading role in the revolution brought about in daily life by chemistry during the past 50 years.

The simplest and one of the best known polymers is *polyethylene*, which is constructed from ethylene monomers:



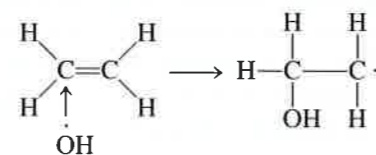
where  $n$  represents a large number (usually several thousand). Polyethylene is a tough, flexible plastic used for pipes, bottles, electrical insulation, packaging films, garbage bags, and many other products. Its properties can be varied by using substituted ethylene monomers. For example, when tetrafluoroethylene is the monomer, the polymer Teflon is obtained:



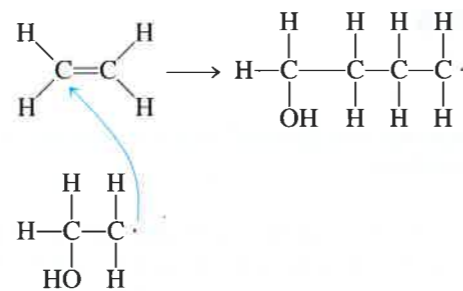
Because of the resistance of the strong C—F bonds to chemical attack, Teflon is an inert, tough, and nonflammable material widely used for electrical insulation, non-stick coatings for cooking utensils, and bearings for low-temperature applications.

Other polyethylene-type polymers are made from monomers containing chloro, methyl, cyano, and phenyl substituents, as summarized in Table 22.8. In each case the double carbon-carbon bond in the substituted ethylene monomer becomes a single bond in the polymer. The different substituents lead to a wide variety of properties.

The polyethylene polymers illustrate one of the major types of polymerization reactions, called **addition polymerization**, in which the monomers simply “add together” to form the polymer, with no other products. The polymerization process is initiated with a **free radical** (a species with an unpaired electron) such as the hydroxyl radical (HO·). The free radical attacks and breaks the  $\pi$  bond of an ethylene molecule to form a new free radical,



which can then attack another ethylene molecule:



Repetition of this process thousands of times creates a long-chain polymer. Termination of the growth of the chain occurs when *two radicals* react to form a bond, a process that consumes two radicals without producing any others.

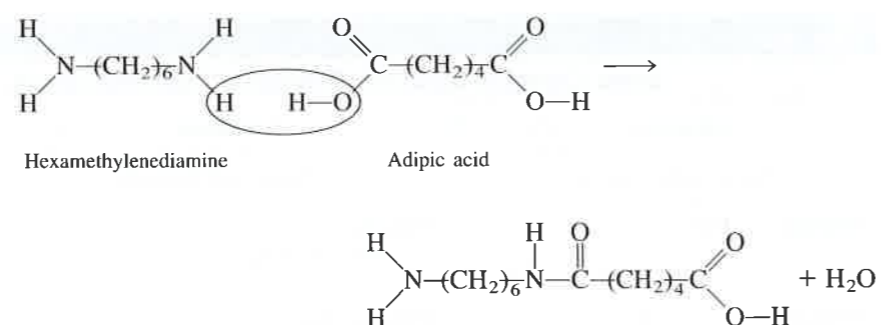
Another common type of polymerization is **condensation polymerization**, in which a small molecule, such as water, is formed for each extension of the polymer chain. The most familiar polymer produced by condensation is *nylon*. Nylon is a

Table 22.8

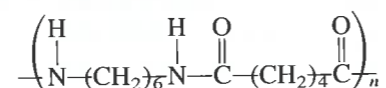
Some Common Synthetic Polymers, Their Monomers, and Applications

Monomer		Polymer	
Name and Formula	Name and Formula	Name and Formula	Uses
Ethylene $\text{H}_2\text{C}=\text{CH}_2$		Polyethylene $-(\text{CH}_2-\text{CH}_2)_n-$	Pipes, bottles, electrical insulation, toys
Propylene $\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{CH}_3 \end{array}$		Polypropylene $-(\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2)_n-$	Films for packaging, carpets, lab wares, toys
Vinyl chloride $\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{Cl} \end{array}$		Polyvinyl chloride (PVC) $-(\text{CH}_2-\text{CH}(\text{Cl}))_n-$	Pipes, siding, floor tile, clothing, toys
Acrylonitrile $\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{CN} \end{array}$		Polyacrylonitrile (PAN) $-(\text{CH}_2-\text{CH}(\text{CN}))_n-$	Carpets, fabrics
Tetrafluoroethylene $\text{F}_2\text{C}=\text{CF}_2$		Teflon $-(\text{CF}_2-\text{CF}_2)_n-$	Cooking utensils, electrical insulation, bearings
Styrene $\begin{array}{c} \text{H} \\   \\ \text{H}_2\text{C}=\text{C} \\   \\ \text{C}_6\text{H}_5 \end{array}$		Polystyrene $-(\text{CH}_2\text{CH}(\text{C}_6\text{H}_5))_n-$	Containers, thermal insulation, toys
Butadiene $\begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{H}_2\text{C}=\text{C} & - & \text{C}=\text{CH}_2 \end{array}$		Polybutadiene $-(\text{CH}_2\text{CH}=\text{CHCH}_2)_n-$	Tire tread, coating resin
Butadiene and styrene (See above.)		Styrene-butadiene rubber $-(\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-$	Synthetic rubber

**copolymer**, since two different types of monomers combine to form the chain; a **homopolymer** results from a single type of monomer. One common form of nylon is produced when hexamethylenediamine and adipic acid react by splitting out a water molecule to form a C—N bond:

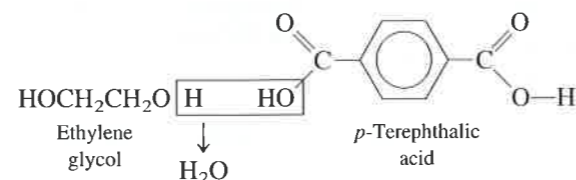


The molecule formed, called a **dimer** (two monomers joined), can undergo further condensation reactions because it has an amino group at one end and a carboxyl group at the other. Thus both ends are free to react with another monomer. Repetition of this process leads to a long chain of the type

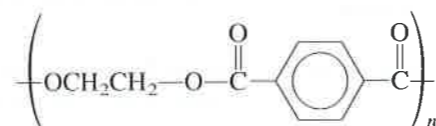


which is the basic structure of nylon. The reaction to form nylon occurs quite readily and is often used as a lecture demonstration (see Fig. 22.17). The properties of nylon can be varied by changing the number of carbon atoms in the chain of the acid or amine monomer.

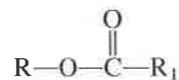
More than 1 million tons of nylon are produced annually in the United States for use in clothing, carpets, rope, and so on. Many other types of condensation polymers are also produced. For example, Dacron is a copolymer formed from the condensation reaction of ethylene glycol (a dialcohol) and *p*-terephthalic acid (a dicarboxylic acid):



The repeating unit of Dacron is



Note that this polymerization involves a carboxylic acid and an alcohol to form an ester group:



Thus Dacron is called a **polyester**. By itself or blended with cotton, Dacron is widely used in fibers for the manufacture of clothing.

More details concerning the manufacturing processes for producing polymers are given in Section 22.7.

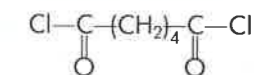


A nylon Velcro fastener.

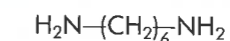


Figure 22.17

The reaction to form nylon can be carried out at the interface of two immiscible liquid layers in a beaker. The bottom layer contains adipoyl chloride



in  $\text{CCl}_4$ , and the top layer contains hexamethylenediamine



dissolved in water. A molecule of  $\text{HCl}$  is formed as each  $\text{C}-\text{N}$  bond forms.

## 22.7 The Polymer Industry

### Purpose

- To discuss the industrial production of polymers.

It has been estimated that approximately 50% of the industrial chemists in the United States work in some area of polymer chemistry, a fact that illustrates just how important polymers are to our economy and standard of living. In Section 22.6 we described the major types of polymers and their uses. In this section we focus on the development of the polymer industry and on the processes used to manufacture several important polymers. These polymers are essential to the production of goods ranging from toys to roofing materials.

### The Development and Properties of Polymers

The development of the polymer industry is a striking example of the importance of serendipity in the progress of science. Many discoveries in polymer chemistry arose from accidental observations.

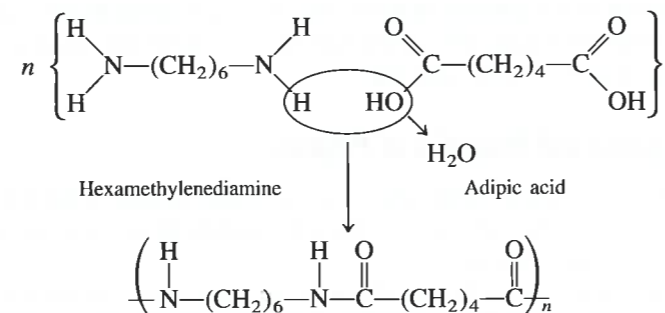
The age of plastics might be traced to a day in 1846 when Christian Schoenbein, a chemistry professor at the University of Basel in Switzerland, spilled a flask containing nitric and sulfuric acids. In his hurry to clean up the spill, he grabbed his wife's cotton apron, which he then rinsed out and hung up in front of a hot stove to dry. Instead of drying, the apron flared and burned. Very interested in this event, Schoenbein repeated the reaction under more controlled conditions and found that the new material, which he correctly concluded to be nitrated cellulose, had some surprising properties. As he had experienced, the nitrated cellulose was extremely flammable and, under certain circumstances, highly explosive. In addition, he found that it could be molded at moderate temperatures to give objects that were,

upon cooling, tough but elastic. Predictably, the explosive nature of the substance was initially of more interest than its other properties, and cellulose nitrate rapidly became the basis for smokeless gun powder. Although Schoenbein's discovery cannot be described as a truly synthetic polymer because he simply found a way to modify the natural polymer cellulose (see Section 23.2), it formed the basis for a large number of industries that grew up to produce photographic films, artificial fibers, and molded objects of all types.

The first synthetic polymers were obtained as by-products of various organic reactions and were generally regarded as unwanted contaminants. Thus the first preparations of many of the polymers now regarded as essential to our modern lifestyle were thrown away in disgust. One chemist who refused to be defeated by the "tarry" products obtained when he combined phenol and formaldehyde was the Belgian-American chemist Leo H. Baekeland (1863–1944). Baekeland's work resulted in the first completely synthetic plastic, called Bakelite, a substance that when molded to a certain shape under high pressure and temperature cannot be softened again or dissolved. Bakelite is a **thermoset polymer**. In contrast, cellulose nitrate is a **thermoplastic polymer**; that is, it can be remelted after it has been molded.

The discovery of Bakelite in 1907 spawned a large plastics industry, producing telephones, billiard balls, and insulators for electrical devices. During the early days of polymer chemistry, there was a great deal of controversy about the nature of these materials. Although the German chemist Hermann Staudinger speculated in 1920 that polymers were very large molecules held together by strong chemical bonds, most chemists of the time assumed that these materials were much like colloids, where small molecules are aggregated into large units by forces weaker than chemical bonds.

One chemist who contributed greatly to the understanding of polymers as giant molecules was Wallace H. Carothers of the DuPont Chemical Company. Among his accomplishments was the preparation of nylon (see Section 22.6). The nylon story illustrates further the importance of serendipity in scientific research. When nylon is made, by the reaction of a dicarboxylic acid and a diamine,



the resulting product is a sticky material with little structural integrity. Because of this, it was initially put aside as having no apparently useful characteristics. However, Julian Hill, a chemist in the Carothers research group, one day put a small ball of this nylon on the end of a stirring rod and drew it away from the remaining sticky mass, forming a string. He noticed the silky appearance and strength of this thread and realized that nylon could be drawn into useful fibers.

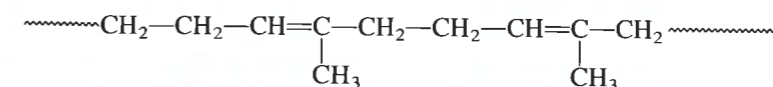
The reason for this behavior of nylon is now understood. When nylon is first formed, the individual polymer chains are oriented randomly, like cooked spaghetti, and the substance is highly amorphous. However, when the substance is



Casting polyurethane plastic.

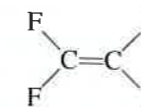
drawn into a thread, the chains tend to line up (the nylon becomes more crystalline), which leads to increased hydrogen bonding between N—H and C=O groups on adjacent chains (see Fig. 22.18). This increase in crystallinity and the accompanying increase in hydrogen-bonding interactions give rise to strong fibers and a highly useful material. Commercially, nylon is produced by forcing the raw material through a *spinneret*, a plate containing small holes, which forces the polymer chains to line up.

Another property that adds strength to polymers is **crosslinking**, the formation of covalent bonds between adjacent chains. The structure of Bakelite is highly cross-linked, which accounts for the strength and toughness of this polymer. Another example of crosslinking occurs in the manufacture of rubber. Raw natural rubber consists of chains of the type



and is a soft, sticky material unsuitable for tires. However, in 1839 Charles Goodyear (1800–1860), an American chemist, accidentally found that if sulfur is added to rubber and the mixture is heated (a process called **vulcanization**) the resulting rubber is still elastic (reversibly stretchable) but much stronger. This change in character occurs through the formation of covalent bonds to sulfur atoms that link the chains.

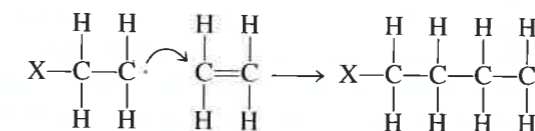
**Polyethylene** and substituted polyethylenes (see Section 22.6) are mainstays of the polymer industry. The discovery of Teflon, a very important substituted polyethylene, is another illustration of the role of chance in chemical research. In 1938 a DePont chemist named Roy Plunkett was studying the chemistry of gaseous perfluoroethylene:



He synthesized about 100 pounds of the chemical and stored it in steel cylinders. When one of the cylinders produced no perfluoroethylene gas after the valve was opened, the cylinder was cut open to reveal a white powder. This powder turned out to be a polymer of perfluoroethylene, which was eventually developed into Teflon.

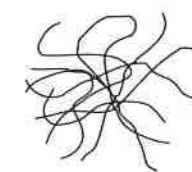
### Polymers Based on Ethylene

A large section of the polymer industry involves the production of macromolecules made from ethylene or substituted ethylenes. As we saw in Section 22.6, ethylene molecules polymerize by addition, after the double bond has been broken by some initiator:

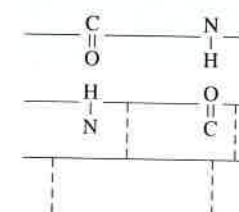


This process continues by adding new ethylene molecules eventually giving polyethylene, a thermoplastic material.

Charles Goodyear tried for many years to change natural rubber into a useful product. In 1839 he accidentally dropped some rubber containing sulfur on a hot stove. Noting that the rubber did not melt as expected, Goodyear pursued this lead and developed vulcanization.



(a)



(b)

Figure 22.18

(a) Raw (amorphous) nylon with random chain orientations.  
(b) Nylon fibers after drawing.



Teflon-coated frying pan. Teflon is a polymer of C<sub>2</sub>F<sub>4</sub>.

## CHEMICAL IMPACT

## Wallace Hume Carothers

Wallace H. Carothers, a brilliant organic chemist who was principally responsible for the development of nylon and the first synthetic rubber (Neoprene), was born in 1896 in Burlington, Iowa. As a youth, Carothers was fascinated by tools and mechanical devices and spent many hours experimenting. In 1915 he entered Tarkio College in Missouri and so excelled in chemistry that even before his graduation he was made a chemistry instructor.

Carothers eventually moved to the University of Illinois at Urbana-

Champaign, where he was appointed to the faculty when he completed his Ph.D. in organic chemistry in 1924. He moved to Harvard University in 1926 and then to DuPont Chemical Company in 1928. At DuPont, Carothers headed the organic chemistry division and during his 10 years there played a prominent role in laying the foundations of polymer chemistry.

By the age of 33, Carothers had become a world-famous chemist whose advice was sought by almost everyone working in polymers. He was the first industrial chemist to be elected to the

prestigious National Academy of Sciences.

Carothers was an avid reader of poetry and a lover of classical music. Unfortunately, he also suffered from severe bouts of depression that finally led to his suicide in 1937 in a Philadelphia hotel room, where he drank a cyanide solution. He was 41 years old. Despite the brevity of his career, Carothers was truly one of the finest American chemists of all time. His great intellect, his love of chemistry, and his insistence on perfection all constituted his special genius.

There are two forms of polyethylene: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The chains in LDPE contain many branches and thus do not pack as tightly as those in HDPE, which consist of mostly straight-chain molecules.

Traditionally, LDPE was manufactured at high pressure (~20,000 psi) and high temperature (500°C). These severe reaction conditions require specially designed equipment, and for safety reasons, the reaction is usually run behind a reinforced concrete barrier. More recently, lower reaction pressures and temperatures have become possible through the use of catalysts. One catalytic system using triethylaluminum [Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>] and titanium(IV) chloride was developed by Karl Ziegler in Germany and Giulio Natta in Italy. Although this is a very efficient catalyst, it catches fire on contact with air and must be handled very carefully. A safer catalytic system was developed at Phillips Petroleum Company. It uses a chromium(III) oxide (Cr<sub>2</sub>O<sub>3</sub>) and aluminosilicate catalyst and has become the dominant process in the United States. The product of the catalyzed reaction is highly linear (unbranched) and is often called **linear low-density polyethylene**. It is very similar to HDPE.

The major use of LDPE is for manufacturing the tough transparent film that is used in the packaging for so many consumer goods. Two-thirds of the approximately 10 billion pounds of low-density polyethylene produced annually in the United States is used for this purpose. The major use of HDPE is for blow-molded products such as bottles for consumer products (see Fig. 22.19).

The useful properties of polyethylene are due primarily to its high molecular weight (molar mass). Although the strengths of the interactions between specific points on the nonpolar chains are quite small, the chains are so long that these small attractions accumulate to a very significant value so that the chains stick together very tenaciously. There is also a great deal of physical tangling of the lengthy chains. The combination of these interactions gives the polymer strength and toughness. However, a material like polyethylene can be remelted and formed into a new shape (thermoplastic behavior) because in the melted state the molecules can readily flow past one another.

psi is the abbreviation for pounds per square inch; 15 psi = 1 atm.

The term *molecular weight* is used in this section rather than *molar mass* because the former remains the common terminology in the polymer industry.

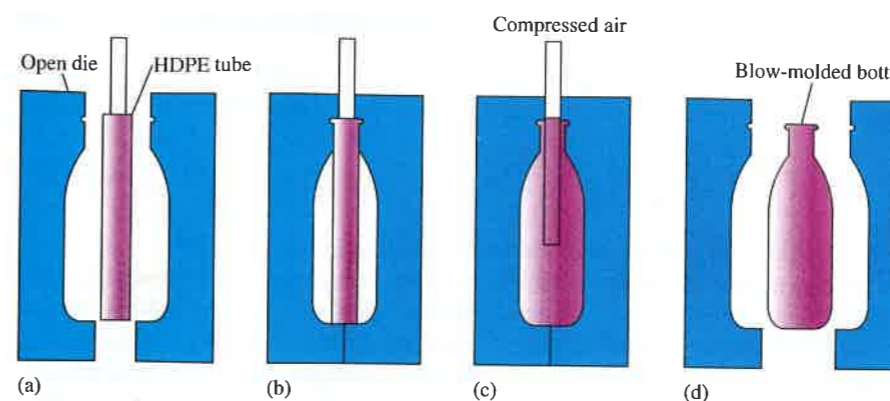


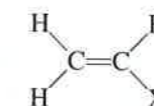
Figure 22.19

A major use of HDPE is for blow-molded objects such as bottles for soft drinks, shampoos, bleaches, and so on. (a) A tube composed of HDPE is inserted into the mold (die). (b) The die closes, sealing the bottom of the tube. (c) Compressed air is forced into the warm HDPE tube, and it expands to take the shape of the die. (d) The molded bottle is removed from the die.

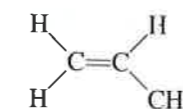
Since a high molecular weight gives a polymer useful properties, one might think that the goal would be to produce polymers with chains as long as possible. However, this is not the case—polymers become much harder to process as the molecular weights increase. Most industrial operations require that the polymer flow through pipes as it is processed. However, as the chain lengths increase, viscosity also increases. In practice, the upper limit of a polymer's molecular weight is set by the flow requirements of the manufacturing process. Thus the final product often reflects a compromise between the optimal properties for applications and those that allow ease of processing.

Although many polymer properties are greatly influenced by molecular weight, other important properties are not. For example, chain length does not affect a polymer's resistance to chemical attack. Physical properties such as color, refractive index, hardness, density, and electrical conductivity are also not greatly influenced by molecular weight.

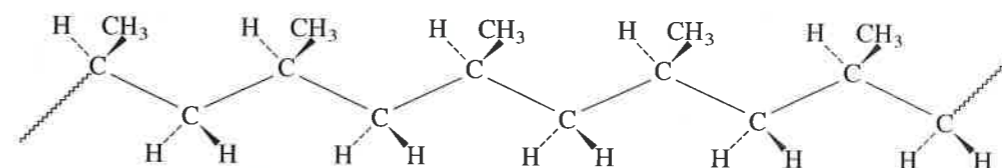
We have seen that one way to change the strength of a polymeric material is to vary the chain length. Another method for modifying polymer behavior is to vary the substituents. For example, if we use a monomer of the type



the properties of the resulting polymer depend on the identity of X. The simplest example is polypropylene, whose monomer is



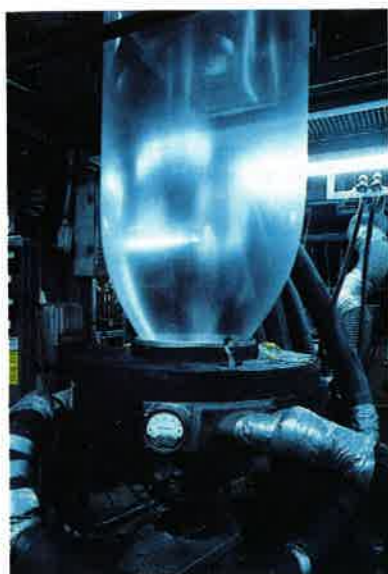
and that has the form



The CH<sub>3</sub> groups can be arranged on the same side of the chain (called an **isotactic**

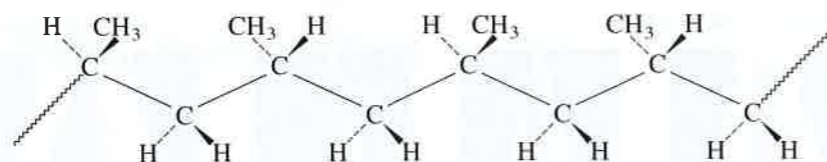


Two polyethylene bottles. The one on the left is made with high-density polyethylene, while the one on the right is made with low-density polyethylene.



Plastic films made from ethylene and its derivatives are used to package most consumer products. This photo shows molten plastic being formed into a bag.

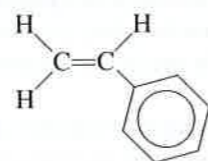
chain) as shown above, can alternate (called a **syndiotactic chain**) as follows:



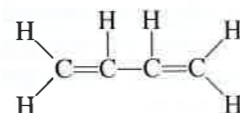
or can be randomly distributed (called an **atactic chain**).

The chain arrangement has a significant effect on the polymer's properties. Most polypropylene is made by using the Ziegler-Natta catalyst,  $\text{Al}(\text{C}_2\text{H}_5)_3 \cdot \text{TiCl}_4$ , which produces highly isotactic chains that pack together quite closely. As a result, polypropylene is more crystalline, and therefore stronger and harder, than polyethylene. The major uses of polypropylene are for molded parts (40%), fibers (35%), and packaging films (10%). Polypropylene fibers are especially useful for athletic wear because they do not absorb water from perspiration as cotton does. Rather the moisture is wicked away from the skin to the surface of the polypropylene garment, where it can evaporate. The annual U.S. production of polypropylene is about 7 billion pounds.

Another related polymer, **polystyrene**, is constructed from the monomer styrene:

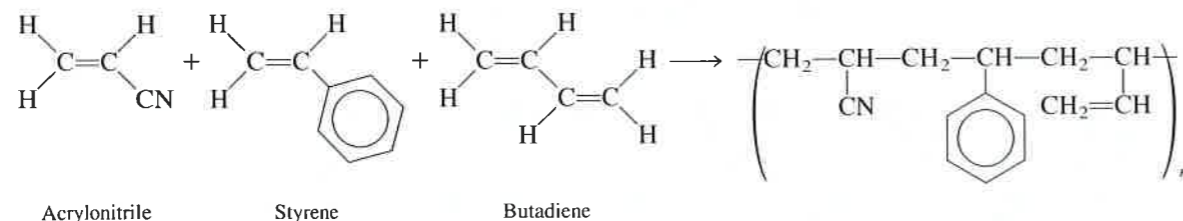


Pure polystyrene is too brittle for many uses, so most polystyrene-based polymers are really *copolymers* of styrene and butadiene,



thus incorporating bits of butadiene rubber into the polystyrene matrix. The resulting polymer is very tough and is often used in furniture as a substitute for wood.

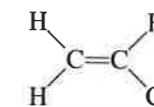
Another polystyrene-based product is acrylonitrile-butadiene-styrene (ABS), a tough, hard, and chemically resistant plastic used for pipes and items such as radio housings, telephone cases, and golf club heads for which shock resistance is an essential property. Originally, ABS was produced by copolymerization of the three monomers:



However, it is now prepared by a special process called **grafting**, in which butadiene is polymerized first, and then the cyanide and phenyl substituents are added chemically.

### PVC: Additives Make the Difference

Another high-volume polymer, **polyvinyl chloride (PVC)**, is constructed from the monomer vinyl chloride:

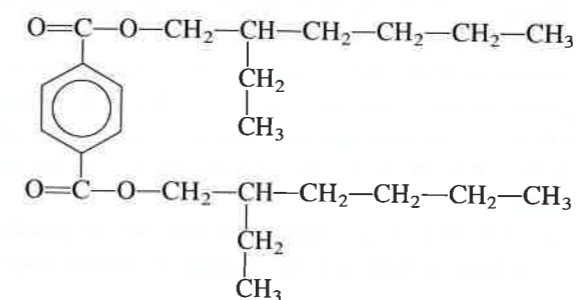


The production of this polymer is quite representative of the processes used in the polymer industry and will be discussed in detail.

In pure form, PVC is a hard, brittle substance that decomposes easily at the temperatures necessary to process it, making it almost useless. That it has become a high-volume plastic (~10 billion pounds per year produced in the United States by the late 1980s) is a tribute to chemical innovation. By use of the proper additives, PVC can be made rigid or highly flexible, and it can be tailored for use in inexpensive plastic novelty items or for precision engineering applications. PVC is used extensively in modern buildings for floor, wall, and window coverings; waste water pipes; exterior trim; insulation for electrical wiring; and a myriad of other applications. PVC is also widely used for clothing, upholstery, automobile bumpers, packaging materials, and credit cards.

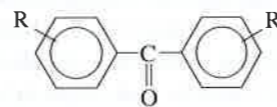
The development of PVC illustrates the interplay of logic and serendipity and also the optimization of properties for processing and for applications. PVC production has been beset with difficulties from the beginning, but a solution has been found for each problem by a combination of chemical deduction and trial and error. For example, many additives have been found that provide temperature stability so that PVC can be processed as a melt and so that PVC products can be used at high temperatures. However, there is still controversy among chemists about exactly how PVC decomposes thermally, and thus the reason that these stabilizers work is not well understood. Also, there are approximately a hundred different plasticizers available for PVC, but the theory of its plasticization is too primitive to predict accurately what compounds might work even better.

PVC was discovered by a German chemical company in 1912, but its brittleness and thermal instability proved so problematical that in 1926 the company stopped paying the fees that maintained its patents. That same year Waldo Semon, a chemist at B. F. Goodrich, found that PVC could be made flexible by the addition of phosphate and phthalate esters. Semon also found that white lead,  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$ , provided thermal stability. These advances led to the beginning of significant U.S. industrial production of PVC (~4 million pounds per year by 1936). In an attempt to further improve PVC, T. L. Gresham (also a chemist at B. F. Goodrich) tried approximately a thousand compounds, searching for a better plasticizer, and found that bis-(2-ethylhexyl) phthalate



A *plasticizer* is a compound added to a polymer to soften it. The type and amount of plasticizer determine the pliability of the final product. One theory suggests that plasticizers cause softening by insertion between polymer chains, where they are held in place only by London dispersion forces. This lessens polymer-polymer interactions and softens the material.

Type of Additive	Effect	Examples
Plasticizer	Softens the material	Bis-(2-ethylhexyl) phthalate
Heat stabilizer	Increases resistance to thermal decomposition	Lead salts, tin compounds, antimony compounds
Ultraviolet absorber	Prevents damage by sunlight	Titanium(IV) oxide (TiO <sub>2</sub> ), substituted benzophenones
Flame retardant	Lowers flammability	Antimony(III) oxide (Sb <sub>2</sub> O <sub>3</sub> )
Biocide	Prevents bacterial or fungal attack	Arsenic and tin compounds



Recently, there has been concern about the carcinogenicity of di-2-ethylhexyl phthalate, and other phthalate esters are being studied as possible replacements.

gave the best results. This compound remains the most common plasticizer for PVC. Table 22.9 lists the types of additives commonly used in the production of PVC.

Although the exact mechanism of the thermal decomposition of PVC remains unknown, most chemists agree that the chlorine atoms play an important role. Compounds such as lead phosphite, lead sulfate, or lead phthalate are added to PVC to provide anions less reactive than chloride and to provide lead ions to combine with the released chloride ions. As a beneficial side effect, the lead chloride formed gives the PVC added electrical resistance, making lead stabilizers particularly useful in producing PVC for electric wire insulation.

One major use of PVC is for pipes in plumbing systems. Here, even though the cheap lead stabilizers would be preferred from an economic standpoint, the possibility that the toxic lead will be leached from the pipes into the drinking water necessitates the use of more expensive tin and antimony compounds as thermal stabilizers. Because 45% of the annual production of PVC goes into piping, the PVC formulation used for pipes represents a huge market for companies that manufacture additives, and the competition is very intense. The most recently developed low-cost PVC thermal stabilizer is a mixture of antimony and calcium salts. This mixture has replaced stabilizers containing tin compounds that have become increasingly costly in recent years. (The price for tin rose from less than \$2 per pound in the early 1970s to about \$4 in the 1980s.)

Outdoor applications of PVC often require that it contain ultraviolet light absorbers to protect against damage from sunlight. For pigmented applications such as vinyl siding, window frames, and building panels, titanium(IV) oxide is usually used. For applications where the PVC must be transparent, various aromatic organic compounds are added.

The additives used in PVC in the largest amounts are the plasticizers, but one detrimental effect of these additives is an increase in flammability. Rigid PVC,

which contains little plasticizer, is quite flame-resistant because of the high average chloride content. However, as more plasticizer is added for flexibility, the flammability increases to the point where fire retardants must be added, the most common being antimony(III) oxide (Sb<sub>2</sub>O<sub>3</sub>). As the PVC is heated, this oxide forms antimony(III) chloride (SbCl<sub>3</sub>), which migrates into the flame, where it inhibits free radicals (see the discussion of flame retardancy later in this section). However, because antimony(III) oxide is a white salt, it cannot be used for transparent or darkly colored PVC. In these cases sodium antimonate (Na<sub>3</sub>SbO<sub>4</sub>), a transparent salt, is used.

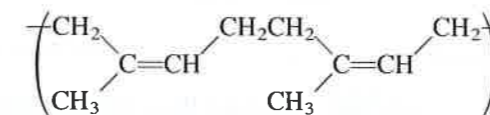
Once the additives have been chosen for a particular PVC application, the materials must be blended. This is often done in a dry-blending process producing a powder that is then used for fabrication of the final product. The powdered mixture also can be melted and formed into pellets, which are easily shipped to manufacturers, where they are remelted and formed into the desired products.

The production of PVC provides a good case study of an industrial process. It illustrates many of the factors that must be taken into account when any product is manufactured: effectiveness of the product, cost, ease of production, safety, and environmental impact.

### Elastomers: Stretchable Polymers

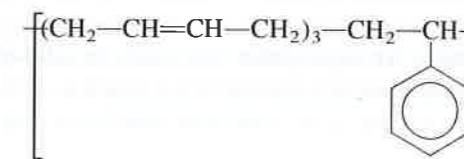
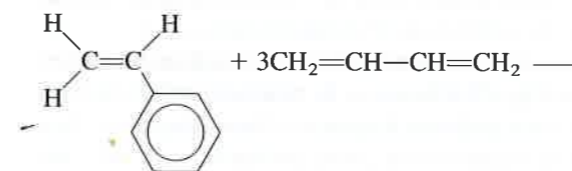
**Elastomers** are materials that recover their shape after a deforming force. The fundamental elastomer is natural rubber, obtained as a latex from a tree native to tropical America but now grown primarily in the tropical Orient. When the Japanese conquered the major rubber-growing areas at the start of World War II, a crash program was undertaken in the United States to develop a suitable substitute. The results of this program were phenomenal; the U.S. production of synthetic rubber increased from none in 1940 to ~800,000 tons in 1944.

Natural rubber is primarily *cis*-polyisoprene,



which, after crosslinking by vulcanization, is especially useful for tires because of its unusual resistance to heat.

Synthetic rubber, which currently accounts for approximately 50% of the total market, is primarily made from copolymerization of styrene (one part) and butadiene (three parts):



The term *rubber* was apparently coined by Joseph Priestley, best known for the discovery of oxygen, because of its ability to rub out pencil marks.

Table 22.10 Common Elastomers		
Type	Monomer(s)	Uses
Polychloroprene (Neoprene)	$\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{CH}=\text{CH}_2$	Wire covering, automotive drive belts
Polyisoprene	$\text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$	Tires
Nitrile	$\text{CH}_2=\overset{\text{CN}}{\text{CH}} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	Automotive hoses and gaskets
Polybutadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	Tires

This polymer, called **SBR rubber**, was developed during World War II and is used principally (75%) for the manufacture of tires. Other types of synthetic elastomers are shown in Table 22.10.

Elastomers are characterized by a highly random (noncrystalline) arrangement of the chains in the relaxed state. When the material is stretched, the chains become more ordered. The tendency to snap back to the original state can be described in terms of entropy. Because the energy of interaction between the nonpolar chains is relatively small, the change in free energy is dominated by the positive  $\Delta S$  term when the elastomer goes from the stretched, relatively ordered state to the relaxed random state. The positive  $\Delta S$  term results in a negative value for  $\Delta G$ , making the relaxing process spontaneous.

$$\Delta G = \Delta H - T\Delta S$$

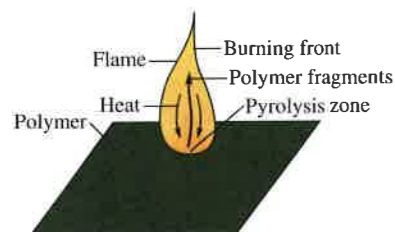


Figure 22.20

The combustion of a polymer. In the pyrolysis zone, the polymer is broken into small fragments as bonds are disrupted by the thermal energy. These fragments then migrate into the higher-temperature flame zone, where they react with oxygen by free-radical chain reactions. The heat from these exothermic reactions is fed down to the polymer surface to provide energy for more pyrolysis.

### Flammability of Polymers

One important property of polymers, especially those used for fabrics and construction materials, is flammability. The United States has a serious problem with domestic fires, which cause thousands of deaths and billions of dollars in property damage each year. One way to combat this problem is to make synthetic materials flame retardant. To see how this might be done, we must first understand what happens when something burns. A relatively simple combustion process, that between methane and oxygen, is illustrated in the following Chemical Impact feature. Note that the process takes place via a free-radical chain reaction.

Polymer combustion, although a more complicated process, still involves free radicals. The burning of a polymer (Fig. 22.20) is a cyclic process in which thermal energy is used to break bonds to form polymer fragments. These fragments then react exothermically with oxygen by a free-radical chain mechanism and thus furnish energy to sustain combustion. The polymer can be made flame retardant by providing some means of interrupting this cycle. This is done by solid-phase inhibition or by vapor-phase inhibition. In **solid-phase inhibition** the polymer surface is changed to help prevent fragmentation. If the polymer is extensively crosslinked at the surface, a carbonaceous char forms that insulates the underlying polymer, de-

## CHEMICAL IMPACT

### The Mechanism of Methane Combustion

The reaction between methane and oxygen,

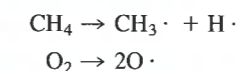


occurs by formation of free radicals (fragments with an unpaired electron) that undergo a series of reactions, producing new radicals in a chain reaction. The radicals are initially formed when energy from an ignition source is fed into the system. The reactions in the chain can be classified into four types: *initiation*, in which radicals are formed; *propagation*, in which one or more radicals react to form a new radical; *branching*, in which one radical

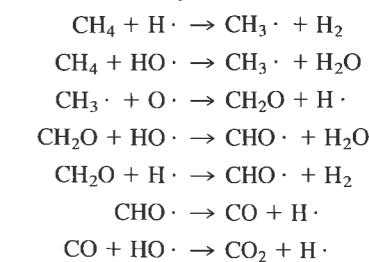
reacts to form two radicals; and *termination*, in which two radicals react to form a nonradical.

Examples of the various types of steps are as follows, where  $\text{R}\cdot$  represents a carbon-containing radical and  $\text{M}$  is a non-reacting substance that absorbs energy to give  $\text{M}^*$  as the  $\text{R}-\text{H}$  bond forms:

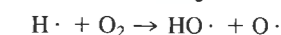
#### Initiation



#### Propagation



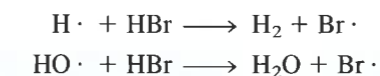
#### Branching



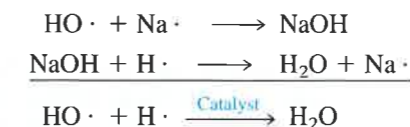
#### Termination



priving the combustion process of its fuel. As a result, the flame cools, and the fire goes out. **Vapor-phase inhibition** involves changing the chemistry of the combustion process. Substances called **free-radical inhibitors** are built into the polymer. They migrate into the flame to produce additional radical-termination steps or to replace highly reactive radicals with less active radicals. Their effect is to greatly decrease the combustion rate either by radical scavenging:



or by radical recombination:



Many polymers have natural flame retardancy. For example, a polymer containing halogen atoms or aromatic groups burns less readily because large quantities of energy are required to break the bonds in these substances and because these substances tend to char naturally.

Polymers that are naturally flammable have flame retardants either built into the polymer itself or added as separate molecules. The most common additives are phosphorus compounds, which retard flames by solid-phase inhibition as a result of the formation of acids that promote char formation.

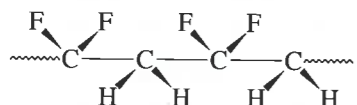
Halogens are the substances most often used to modify the polymer itself to decrease flammability. The carbon-halogen bonds break in the flame, releasing the halogen atoms which can then form hydrogen halides that behave as free-radical inhibitors. For example, styrene becomes less flammable if halogens are substituted for hydrogen atoms on the phenyl ring.



## CHEMICAL IMPACT

## Plastic that Talks and Listens

Imagine a plastic so "smart" that it can be used to sense a baby's breath, measure the force of a karate punch, sense the presence of a person 100 ft away, or make a balloon that sings. There is a plastic film capable of doing all these things. It's called **polyvinylidene difluoride (PVDF)**, which has the structure



When this polymer is processed in a particular way, it becomes piezoelectric and pyroelectric. A *piezoelectric* substance produces an electric current when it is physically deformed or alternately when it undergoes a deformation caused by the application of a current. A *pyroelectric* material is one that develops an electrical

potential in response to a change in its temperature.

Because PVDF is piezoelectric, it can be used to construct a paper-thin microphone; it responds to sound by producing a current proportional to the deformation caused by the sound waves. A ribbon of PVDF plastic one quarter of an inch wide could be strung along a hallway and used to listen to all the conversations going on as people walk through. On the other hand, electric pulses can be applied to the PVDF film to produce a speaker. A strip of PVDF film glued to the inside of a balloon can play any song stored on a microchip attached to the film—hence a balloon that can sing happy birthday at a party. The PVDF film also can be used to construct a sleep apnea monitor, which, when placed beside the mouth of a sleeping infant, will set off an alarm if the

breathing stops, thus helping to prevent sudden infant death syndrome (SIDS). The same type of film is used by the U.S. Olympic karate team to measure the force of kicks and punches as the team trains. Also, gluing two strips of film together gives a material that curls in response to a current, creating an artificial muscle. In addition, because the PVDF film is pyroelectric, it responds to the infrared (heat) radiation emitted by a human as far away as 100 ft, making it useful for burglar alarm systems.

Making the PVDF polymer piezoelectric and pyroelectric requires some very special processing, which makes it costly (\$10 per square foot), but this seems a small price to pay for its near-magical properties.

## FOR REVIEW

## Summary

The study of carbon-containing compounds and their properties is called organic chemistry. Most organic compounds contain chains or rings of carbon atoms. The organic molecules responsible for maintaining and reproducing life are called biomolecules.

Hydrocarbons are organic compounds composed of carbon and hydrogen. Those which contain only C—C single bonds are saturated and are called alkanes. All alkanes can be represented by the general formula  $C_nH_{2n+2}$ .

Methane ( $CH_4$ ) is the simplest alkane, and the next three in the series are ethane ( $C_2H_6$ ), propane ( $C_3H_8$ ), and butane ( $C_4H_{10}$ ). In a saturated hydrocarbon, each carbon atom is bonded to four other atoms and is described as being  $sp^3$  hybridized. Alkanes containing long chains of carbon atoms are called normal, or straight-chain, hydrocarbons.

Structural isomerism in alkanes involves formation of branched structures. Specific rules for systematically naming alkanes indicate the point of attachment of any substituent group, the length of the root chain, and so on.

Alkanes can undergo combustion reactions to form carbon dioxide and water or substitution reactions in which hydrogen atoms are replaced by other atoms. Al-

kanes also can undergo dehydrogenation to form unsaturated hydrocarbons. Cyclic alkanes are saturated hydrocarbons with ring structures.

Hydrocarbons with carbon-carbon double bonds are called alkenes and are said to be unsaturated. The simplest alkene is ethylene ( $C_2H_4$ ), which is described in terms of  $sp^2$  hybridized carbon atoms. Because the  $p$  orbitals on the carbon atoms in ethylene form a  $\pi$  bond, free rotation of the two  $CH_2$  groups relative to each other does not occur (as it does in alkanes). This restriction means that alkenes exhibit *cis-trans* isomerism.

Alkynes are unsaturated hydrocarbons with a triple carbon-carbon bond. The simplest in the series is acetylene ( $C_2H_2$ ), which is described as containing  $sp$  hybridized carbon atoms.

Unsaturated hydrocarbons undergo addition reactions such as hydrogenation (addition of hydrogen) and halogenation (addition of halogen atoms). Ethylene and substituted ethylene molecules can undergo polymerization, a process by which many molecules (monomers) are joined together to form a large chainlike molecule.

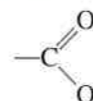
Aromatic hydrocarbons, such as benzene, are stable ring compounds with delocalized  $\pi$  electron systems. They undergo substitution reactions rather than the addition reactions characteristic of typical alkenes.

Organic molecules that contain elements in addition to carbon and hydrogen can be viewed as hydrocarbon derivatives: hydrocarbons with functional groups. Each functional group exhibits characteristic chemical properties.

Alcohols contain the —OH group and tend to have strong hydrogen bonding in the liquid state. Aldehydes and ketones contain the carbonyl group:



In aldehydes this group is bonded to at least one hydrogen atom. Carboxylic acids are characterized by the carboxyl group:



They can react with alcohols to form esters. Amines can be thought of as derivatives of ammonia in which one or more N—H bonds have been replaced by an N—C bond.

Polymers can be formed by addition polymerization in which monomers add together via a free radical mechanism. Polymers also can be formed by condensation polymerization, which involves the splitting out of a small molecule (often water) between two monomers to form a dimer, which then undergoes further condensation.

## Key Terms

biomolecule  
organic chemistry  
Section 22.1  
hydrocarbons  
alkanes

normal (straight-chain or unbranched) hydrocarbons  
structural isomerism  
combustion reaction  
substitution reaction  
dehydrogenation reaction  
cyclic alkanes

Section 22.2  
alkenes  
*cis-trans* isomerism  
alkynes  
addition reaction

hydrogenation reaction	alcohols	dimer
halogenation	phenol	polyester
polymerization	carbonyl group	<i>Section 22.7</i>
<i>Section 22.3</i>	ketones	thermoset polymer
aromatic hydrocarbons	aldehydes	thermoplastic polymer
phenyl group	carboxylic acids	crosslinking
<i>Section 22.4</i>	carboxyl group	vulcanization
petrochemicals	esters	polyethylene
cracking	amines	isotactic chain
polymerization	<i>Section 22.6</i>	syndiotactic chain
feedstock	polymers	atactic chain
steam cracking	addition polymerization	polystyrene
<i>Section 22.5</i>	free radical	polyvinylchloride (PVC)
hydrocarbon derivatives	condensation polymerization	elastomers
functional group	copolymer	inhibition
	homopolymer	

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the Solutions Guide.

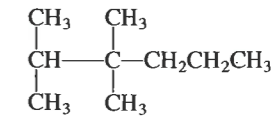
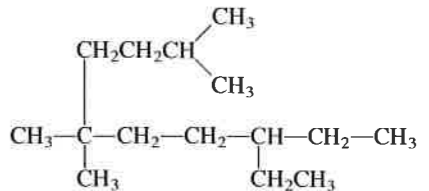
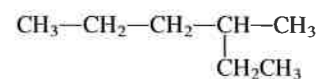
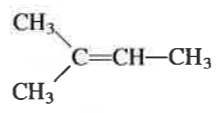
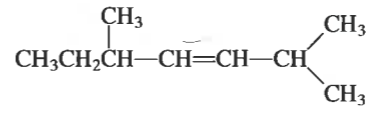
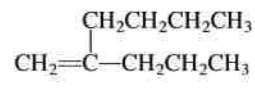
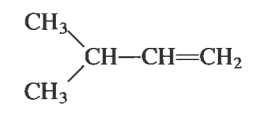
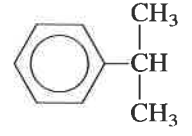
### Questions

- The normal (unbranched) hydrocarbons are often referred to as the *straight-chain hydrocarbons*. What does this name refer to? Does this mean that the carbon atoms in a straight-chain hydrocarbon really have a linear arrangement? Explain.
- Distinguish between structural and geometric isomerism.
- Distinguish between isomerism and resonance.
- Distinguish between substitution and addition reactions. Give an example of each type.
- Define and give an example of each of the following.
  - Addition polymer
  - Condensation polymer
  - Copolymer
- Define and give an example of each of the following.
  - Free-radical polymerization
  - Addition polymerization
  - Condensation polymerization
- Distinguish between a thermoset polymer and a thermoplastic polymer.
- How do the physical properties of polymers depend on chain length and extent of chain branching?
- Explain how plasticizers and crosslinking agents are used to change the physical properties of polymers.
- Isotactic polypropylene is harder than atactic polypropylene. Explain.
- Explain why each of the following changes in a polymer will lead to decreased flammability.
  - Replacing hydrogen atoms with halogen atoms
  - Replacing carbon atoms singly bonded to each other in the polymer chain with aromatic rings
  - Highly crosslinking a polymer
- How does crosslinking affect the elasticity of an elastomer?
- Nylon is named according to the number of C atoms between the N atoms in the chain. Nylon-46 has 4 C atoms then 6 C atoms, and this pattern repeats. Nylon-6 always has 6 atoms in a row. Speculate as to why nylon-46 is stronger than nylon-6. (*Hint*: Consider the strengths of interchain forces.)
- In which polymer, polyethylene or polyvinyl chloride, would you expect to find the stronger intermolecular forces (assuming the average chain lengths are equal)?

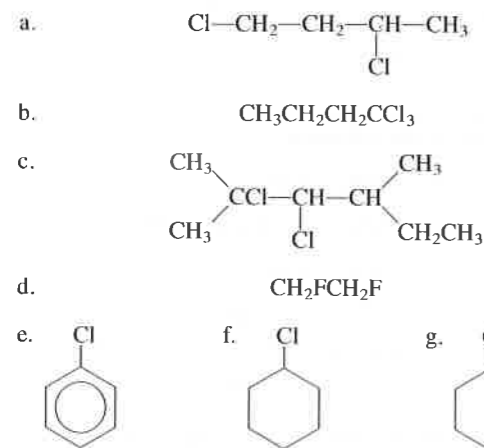
### Exercises

In this section similar exercises are paired.

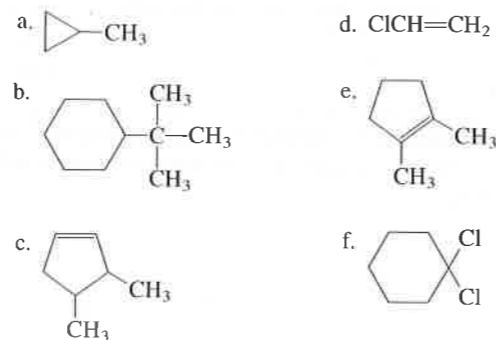
#### Hydrocarbons

- Draw and name the five structural isomers of hexane (C<sub>6</sub>H<sub>14</sub>). Which isomer would you expect to have the highest boiling point? Why?
- Name each of the following:
  - 
  - 
  - 
- Draw the structural formula for each of the following.
  - 2-Methylpentane
  - 2,2,4-Trimethylpentane, also called isooctane. This substance is the reference (100 level) for octane ratings.
  - 2-*tert*-Butylpentane
  - The name given in part c is incorrect. Give the correct name for this hydrocarbon.
- Draw the structure for 2-ethyl-3-methyl-5-isopropylhexane. This name is incorrect. Give the correct systematic name.
- Name each of the following alkenes.
  - $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$
  - 
  - 
- Name each of the following alkenes.
  - $\text{CH}_2=\text{C}-\text{CH}_3$   
|  
CH<sub>2</sub>CH<sub>3</sub>
  - 
  - 
- Give the structure for each of the following.
  - 3-Hexene
  - 2,4-Heptadiene
  - 2-Methyl-3-octene
- Give the structure for each of the following.
  - 4-Methyl-1-pentene
  - 2,3,3-Trimethyl-1-hexene
  - 3-Ethyl-4-decene
- Give the structure of each of the following aromatic hydrocarbons.
  - o*-Xylene
  - p*-Di-*tert*-butylbenzene
  - m*-Diethylbenzene
- Cumene is the starting material for the industrial production of acetone and phenol. The structure of cumene is . Give the systematic name for cumene.

25. Name each of the following.



26. Name each of the following.

**Isomerism**27. Draw all the structural and geometric isomers of  $\text{C}_3\text{H}_4\text{Cl}_2$ .

28. Draw all the structural and geometric isomers of bromochloropropene.

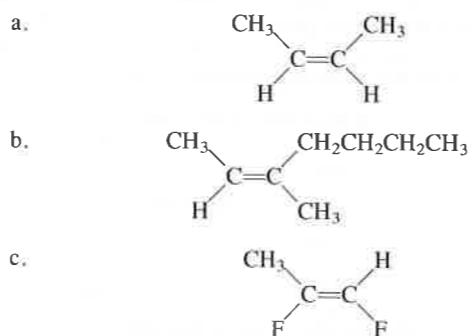
29. Draw all the isomers of dimethylnaphthalene.

30. Draw all the isomers of difluoroethene and indicate which ones are polar.

31. Draw the following.

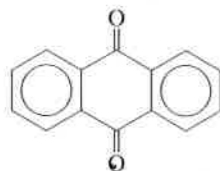
- a. *cis*-2-Hexene  
 b. *trans*-2-Butene  
 c. *cis*-2,3-Dichloro-2-pentene

32. Name the following.

**Functional Groups**

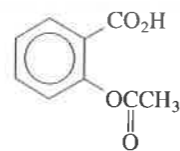
33. Identify each of the following compounds as a carboxylic acid, ester, ketone, aldehyde, or amine.

- a. Anthraquinone, an important starting material in the manufacture of dyes:

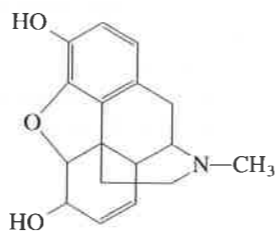


34. Identify the functional groups present in the following pharmaceuticals.

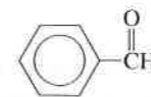
a. Aspirin



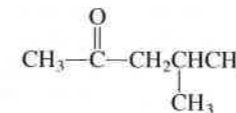
b. Morphine



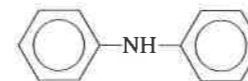
b.



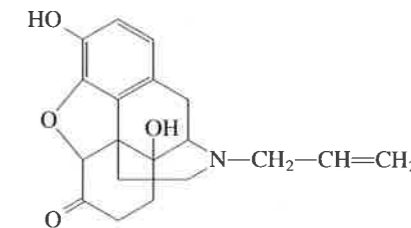
c.



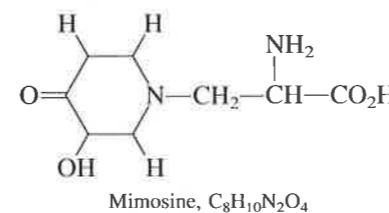
d.



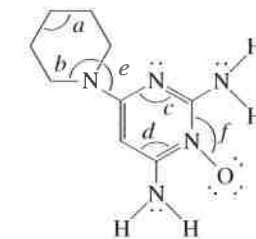
c. Naloxone (a narcotic antagonist)



35. Mimosine is a natural product found in large quantities in the seeds and foliage of some legume plants and has been shown to cause inhibition of hair growth and hair loss in mice.

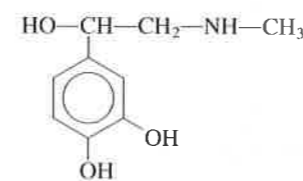


- a. What functional groups are present in mimosine?  
 b. Give the hybridization of the eight carbon atoms in mimosine.  
 c. How many  $\sigma$  and  $\pi$  bonds are found in mimosine?

36. Minoxidil ( $\text{C}_9\text{H}_{15}\text{N}_5\text{O}$ ) is a compound, produced by the Upjohn Company, that has been approved as a treatment of some types of male pattern baldness.

- a. Would minoxidil be more soluble in acidic or basic aqueous solution? Explain.  
 b. Give the hybridization of the five nitrogen atoms in minoxidil.  
 c. Give the hybridization of each of the nine carbon atoms in minoxidil.  
 d. Give approximate values of the bond angles marked *a*, *b*, *c*, *d*, *e*, and *f*.  
 e. Including all the hydrogen atoms, how many  $\sigma$  bonds exist in minoxidil?  
 f. How many  $\pi$  bonds exist in minoxidil?

37. The structure of ephedrine (adrenaline) is



What functional groups are present?

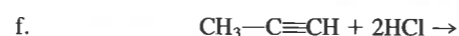
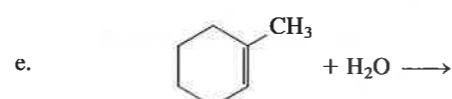
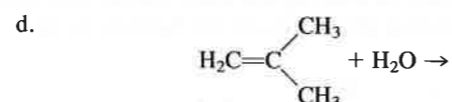
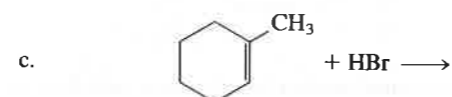
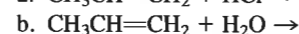
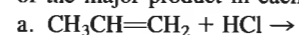
38. Menthol has the systematic name 2-isopropyl-5-methylcyclohexanol. Draw the structure of menthol.

## Reactions of Organic Compounds

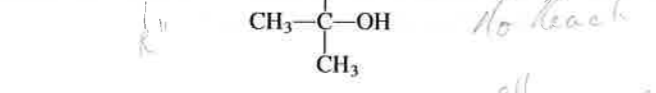
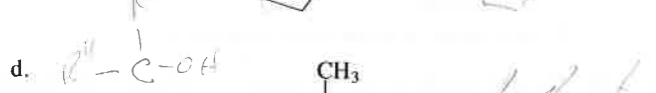
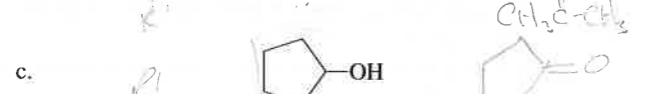
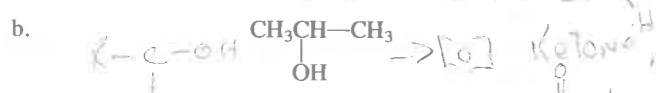
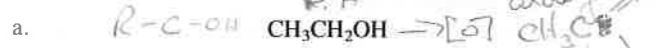
39. Complete the following reactions.



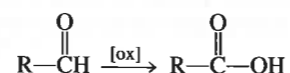
40. Reagents such as HCl, HBr, and HOH can add across carbon-carbon double bonds. The addition occurs so that the hydrogen atom in the reagent attaches to the carbon atom in the double bond that already has the greater number of hydrogen atoms bonded to it. With this rule in mind, draw the structure of the major product in each of the following reactions.



41. Give the structure of the product resulting from the oxidation of each of the following alcohols.

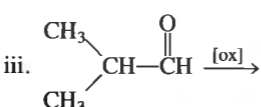
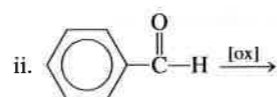
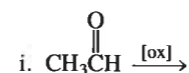


42. Oxidation of an aldehyde yields a carboxylic acid.



Thus it is very difficult to get only the pure aldehyde from the oxidation of a primary alcohol.

a. Draw the structures for the products of the following oxidations.



b. Which of the reactions in Exercise 41 would result in a mixture of an aldehyde and an acid as products? Draw the structures of the acids formed.

43. How would you synthesize each of the following?

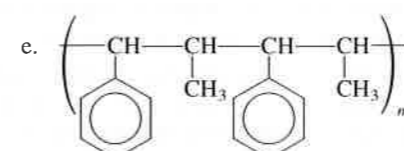
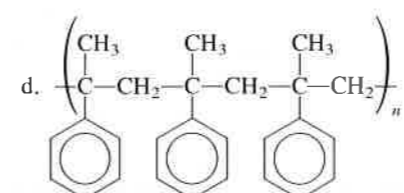
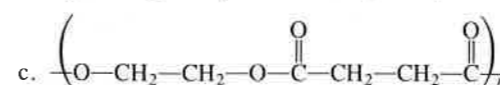
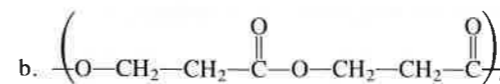
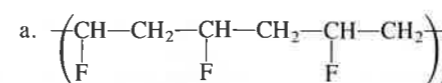
- 1,2-Dibromopropane from propene
- 1,2-Dibromopropane from propyne
- Butyl acetate

44. How would you synthesize each of the following?

- Ethylbutyrate
- Acetone from an alcohol
- t*-Butylalcohol (2-methyl-2-propanol)

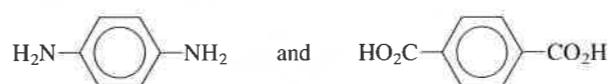
## Polymers

45. What monomer(s) must be used to produce the following polymers?



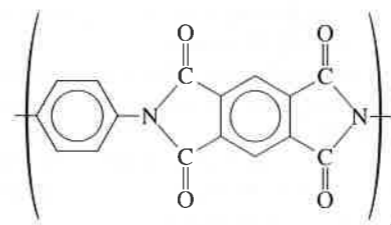
Classify these polymers as condensation or addition polymers. Which are copolymers?

47. Kevlar, used in bulletproof vests, is made by the condensation copolymerization of the monomers

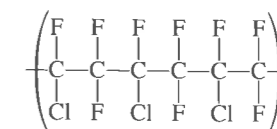


Draw the structure of a portion of the Kevlar chain.

49. Polyimides are polymers that are tough and stable at temperatures of up to 400°C. They are used as a protective coating on the quartz fibers used in fiber optics. What monomers were used to make the following polyimide:

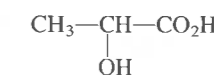


46. Kel-F is a polymer with the structure

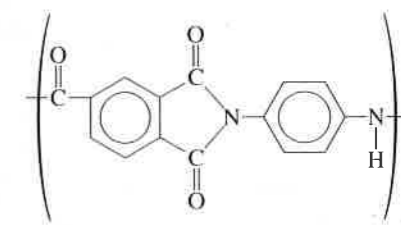


- What is the monomer for Kel-F?
- Would you expect Kel-F to be more or less reactive than Teflon?

48. The polyester formed from lactic acid,

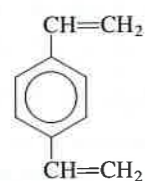


is used for tissue implants and surgical sutures that will dissolve in the body. Draw the structure of a portion of this polymer.

50. The Amoco Chemical Company has successfully raced a car with a plastic engine. Many of the engine parts, including piston skirts, connecting rods, and valve-train components, were made of a polymer called *Torlon*:

What monomers are used to make this polymer?

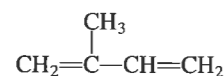
51. Polystyrene can be made more rigid by copolymerizing styrene with divinylbenzene:



How does the divinylbenzene make the copolymer more rigid?

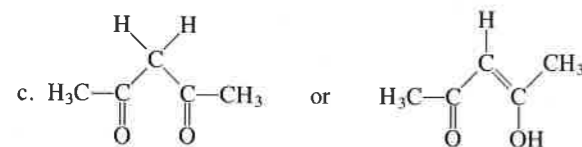
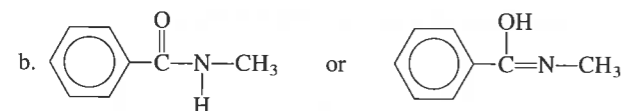
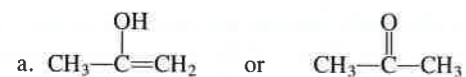
### Additional Exercises

53. Isoprene, the repeating unit in natural rubber, has the structure



Give the systematic name for isoprene.

54. Draw structures for each of the following.  
 a. Difluoromethane  
 b. 1-Bromo-1,2-dichloropropane  
 c. *m*-Difluorobenzene
55. *Cis-trans* isomerism is also possible in molecules with rings. Draw the *cis* and *trans* isomers of 1,2-dimethylcyclohexane.
56. There is only one compound that is named 1,2-dichloroethane, but there are two distinct compounds that can be named 1,2-dichloroethene. Why?
57. Tautomers are molecules that differ in the position of a hydrogen atom. Use bond energies (Table 8.4) to predict which tautomer in each of the following tautomeric pairs is more stable.



58. Draw the isomer specified.  
 a. An aldehyde that is an isomer of acetone  
 b. An ether that is an isomer of 2-propanol

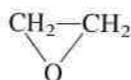
52. Polyesters containing double bonds are often crosslinked by reacting the polymer with styrene.  
 a. Draw the structure of the copolymer of  
 $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$  and  $\text{HO}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{H}$   
 b. Draw the structure of the crosslinked polymer (after the polyester has been reacted with styrene).

- c. A geometric isomer of *cis*-2-butene  
 d. A primary amine that is an isomer of trimethylamine  
 e. A secondary amine that is an isomer of trimethylamine  
 f. A primary alcohol that is an isomer of 2-propanol

59. Drugs such as morphine (see Exercise 34) are often treated with strong acids. The most commonly used form of morphine is morphine hydrochloride. Draw the structure of morphine hydrochloride. Why are drugs treated in this way?

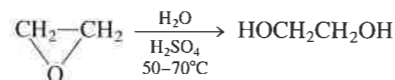
60. Consider the reaction of propane with chlorine.  
 a. How many monochloro products are formed? Draw their structures.  
 b. How many dichloro products can be formed? Draw their structures.

61. Ethylene oxide

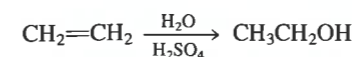


is an important industrial chemical. While most ethers are unreactive, ethylene oxide is quite reactive. It resembles  $\text{C}_2\text{H}_4$  in its reactions in that many addition reactions occur across the C—O bond.

- a. Why is ethylene oxide so reactive? (*Hint*: Consider the bond angles in ethylene oxide as compared with those predicted by the VSEPR model.)  
 b. Ethylene oxide undergoes addition polymerization forming a polymer used in many applications requiring a non-ionic surfactant. Draw the structure of this polymer.  
 c. Ethylene oxide is also an important intermediate in the chemical industry. Its major use is in the production of ethylene glycol for antifreeze.



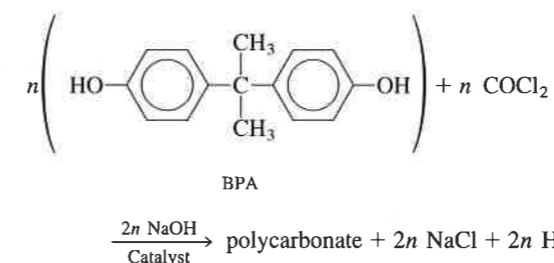
This reaction is similar to the addition reactions of alkenes, for example:



Use bond energies (Table 8.4) to estimate  $\Delta H$  for the above two reactions.

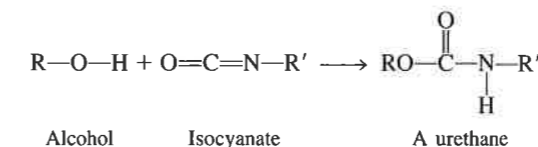
- d. The molecular weight (molar mass) of polymers is often given as part of their trade name by the manufacturers. For example, Carbowax 20M is a polymer of ethylene oxide with an average molar mass of 20,000 g/mol. On average, how many monomer units are in such a polymer? Does this mean that every molecule in a sample of this polymer has the same length? Explain.

62. Polycarbonates are a class of thermoplastic polymers that are used in the plastic lenses of eyeglasses and in the shells of bicycle helmets. A polycarbonate is made from the reaction of bisphenol A (BPA) with phosgene ( $\text{COCl}_2$ ):

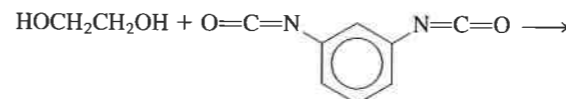


Phenol ( $\text{C}_6\text{H}_5\text{OH}$ ) is used to terminate the polymer (stop its growth).

- a. Draw the structure of the polycarbonate chain formed from the above reaction.  
 b. Is this reaction a condensation or addition polymerization?
63. A urethane linkage occurs when an alcohol adds across the carbon–nitrogen double bond in an isocyanate:



Polyurethanes (formed from the copolymerization of a diol with a diisocyanate) are used in foamed insulation and a variety of other construction materials. What is the structure of the polyurethane formed by the reaction



64. a. Draw the structures of the polymers formed from the monomers listed in Table 22.10.  
 b. These polymers also show geometric isomerism. For example, there are two polymers of isoprene: *cis*-polyisoprene (natural rubber) and *trans*-polyisoprene (gutta per-

cha). Gutta percha, which is not an elastomer, has been used as the center of golf balls. Draw the structures of these polymers.

65. Which of the following polymers would be stronger or more rigid? Explain your choices.  
 a. The copolymer of ethylene glycol and terephthalic acid or the copolymer of 1,2-diaminoethane and terephthalic acid  
 b. The polymer of  $\text{HO}-(\text{CH}_2)_6-\text{CO}_2\text{H}$  or that of



- c. Polyacetylene or polyethylene

66. When acrylic polymers are burned, toxic fumes are produced. For example, in many airplane fires, more passenger deaths have been caused by breathing toxic fumes than by the fire itself. Using polyacrylonitrile as an example, what would you expect to be one of the most toxic, gaseous combustion products created in the reaction?

67. Stretch a rubber band while holding it gently to your lips. Then slowly let it relax while still in contact with your lips.  
 a. What happens to the temperature of the rubber band on stretching?  
 b. Is the stretching an exothermic or endothermic process?  
 c. Explain the above result in terms of interparticle forces.  
 d. What is the sign of  $\Delta S$  and  $\Delta G$  for stretching the rubber band?  
 e. Give the molecular explanation for the sign of  $\Delta S$  for stretching.

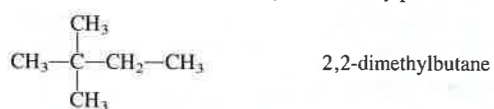
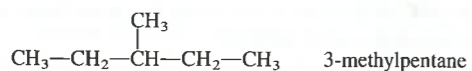
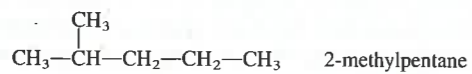
68. All the following observations about the aging of an automobile are related. Explain the relationship among these three observations.  
 i. On hot days a waxy coating may appear on the inside of the glass of a car.  
 ii. The "new car" smell gradually goes away.  
 iii. Vinyl seat covers become brittle and crack.

69. Look up the structures of the following drugs in *The Merck Index*. What functional groups are present? Give a use for each drug.  
 a. Dopa  
 b. Amphetamine  
 c. Ephedrine  
 d. Acetaminophen  
 e. Phenacetin

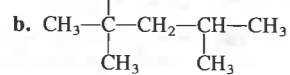
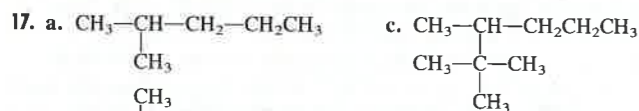
70. Many drugs are sold using trade names or common names. The structures of such substances can be found using the Cross Index of Names at the back of *The Merck Index*. Use *The Merck Index* to find the structure of each of the following and its primary use.  
 a. Ecotrin      d. Keflex  
 b. Tylenol      e. Nalfon  
 c. Lasix      f. Voltaren

5. a. Addition polymer: formed by adding monomer units to a double bond. Teflon  $n \text{CF}_2=\text{CF}_2 \rightarrow -(\text{CF}_2-\text{CF}_2)_n$ ; b. Condensation polymer: two monomers combine, eliminating a small molecule. Nylon and dacron are examples. c. Copolymer: formed from more than one monomer. Nylon and dacron are also copolymers. 7. A thermoplastic polymer can be remelted; a thermoset polymer cannot be softened once it is formed. 9. Plasticizers make a polymer more flexible. Cross-linking makes a polymer more rigid. 11. a. Replacement of hydrogen with halogens results in fewer H and OH radicals in the flame, reducing flame temperature. b. With aromatic groups present, it is more difficult to "chip off" pieces of the polymer in pyrolysis zone. c. It is more difficult to "chip off" fragments of the polymer in the pyrolysis zone. The polymer chars instead of burning. 13. For a given chain length, there are more hydrogen bonding sites in Nylon-6 compared to Nylon-6.

15.  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$  hexane or n-hexane (highest b.p., least branched)



n-Hexane should have the highest boiling point. It is the least branched and, therefore, there will be the strongest dispersion forces between hexane molecules.

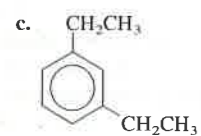
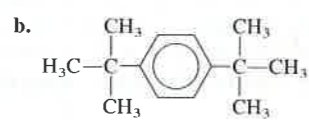
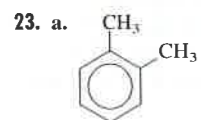


d. 2,2,3-trimethylhexane

19. a. 1-butene; b. 2-methyl-2-butene; c. 2,5-dimethyl-3-heptene

21. a.  $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$ ; b.  $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_2\text{CH}_3$ ;

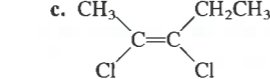
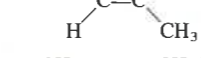
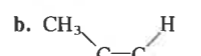
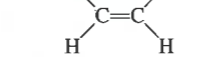
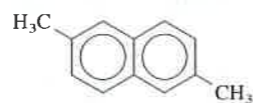
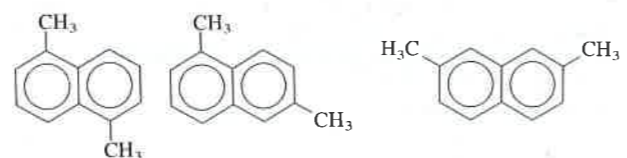
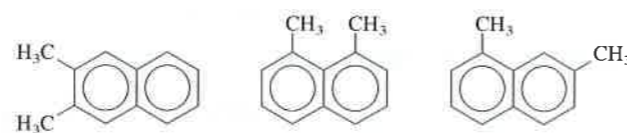
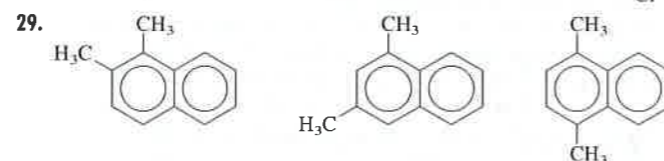
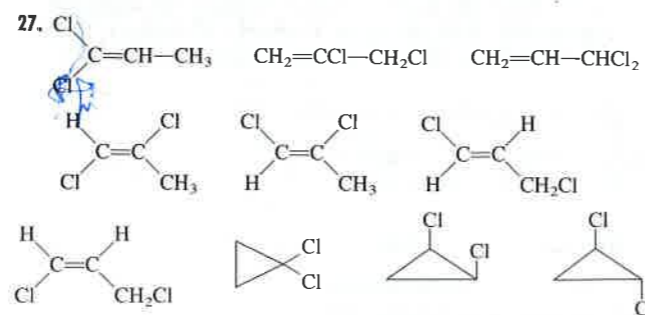
c.  $\text{CH}_3\text{CHCH}=\text{CHCH}_2\text{CH}_2\text{CH}_3$



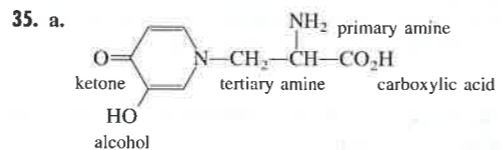
25. a. 1,3-dichlorobutane; b. 1,1,1-trichlorobutane;

c. 2,3-dichloro-2,4-dimethylhexane; d. 1,2-difluoroethane;

e. chlorobenzene; f. chlorocyclohexane; g. 3-chlorocyclohexene

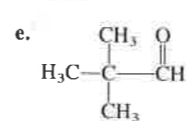
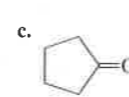
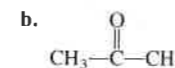
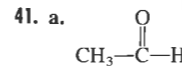
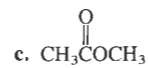


33. a. ketone; b. aldehyde; c. ketone; d. amine



b. 5 carbons in ring and in  $-\text{CO}_2\text{H}$ ;  $sp^2$ ;  $-\text{CH}_2-$  and  $-\text{CH}-\text{NH}_2$ ;  $sp^3$ ; c. 4  $\pi$ -bonds and 24  $\sigma$ -bonds

37. 3 alcohol groups and an amine 39. a.  $\text{CH}_2\text{BrCH}_2\text{Br}$ ;  
b.  $\text{C}_6\text{H}_5\text{Br} + \text{HBr}$



d. No reaction

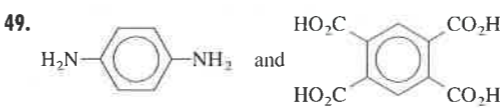
43. a.  $\text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$ ;

b.  $\text{CH}_3\text{C}\equiv\text{CH} + \text{H}_2 \xrightarrow{\text{catalyst}} \text{CH}_3\text{CH}=\text{CH}_2 + \text{Br}_2 \rightarrow \text{CH}_3\text{CHBrCH}_2\text{Br}$

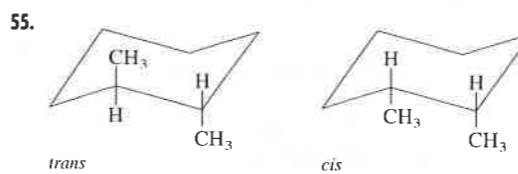
c.  $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \rightarrow$   
 $\text{CH}_3\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$

45. a.  $\text{CHF}=\text{CH}_2$  (addition); b.  $\text{HOCH}_2\text{CH}_2\text{CO}_2\text{H}$  (condensation);  
c. copolymer of  $\text{HOCH}_2\text{CH}_2\text{OH}$  and  $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H}$  (condensation)

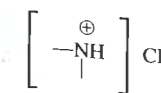
d.  $\text{CH}_3\text{CH}=\text{CH}_2$  (addition)      e.  $\text{CH}=\text{CHCH}_3$  (addition)



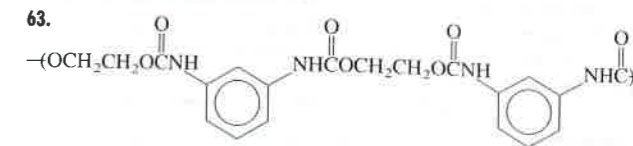
51. divinyl benzene acts as a crosslinking agent, making the polymer more rigid 53. 2-methyl-1, 3-butadiene



57. a. ketone; b. amide with  $\text{C}=\text{O}$ ; c. structure with two  $\text{C}=\text{O}$   
59. The amine group is protonated



Morphine hydrochloride is ionic and thus more soluble in water.  
61. a. The bond angles in the ring are about  $60^\circ$ . VSEPR predicts bond angles close to  $109^\circ$ . The bonding electrons are close together and electron-electron repulsions are high.  
b.  $-(\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2)_n$ ; c.  $\approx 0$ ,  $-37 \text{ kJ}$ ;  
d.  $\approx 450$ , No. The molar mass is an average of a large number of chains with varying lengths.



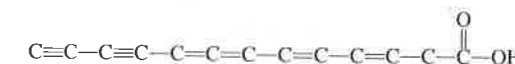
65. a. The polyamide from 1,2-diaminoethane and terephthalic acid is stronger because of the possibility of hydrogen bonding between chains. b. The polymer of



because the chains are stiffer. c. Polyacetylene is  $n \text{HC}\equiv\text{CH} \rightarrow -(\text{CH}=\text{CH})_n$ . Polyacetylene is stronger, because the double bonds in the chain make the chains stiffer.

67. a. The temperature increases on stretching. b. exothermic;  
c. As the chains of the polymer are stretched they line up with each other resulting in stronger forces between chains. d.  $\Delta G(+)$ ,  $\Delta S(-)$ ;  
e. The structure of the stretched polymer is more ordered.

69. Compounds are numbered in *The Merck Index*. The number and page for each compound is given for the 10th edition. a. dopa, 3427, p. 497; b. amphetamine, 606, p. 84; c. ephedrine, 3558, p. 520; d. acetaminophen, 39, p. 7; e. phenacetin, 7064, p. 1035  
71.



73. No, it would be a different molecule with two 4-membered rings.  
75. a. 43%; b.  $1.00 \times 10^3 \text{ kg}$  (theoretical), 430 kg (actual);  
c. i.  $\$1.58/\text{lb}$ ; ii.  $\$0.63/\text{lb}$ ; d. The disposal of  $\text{AlCl}_3$  and  $\text{H}_2\text{SO}_4$  in i. would be a major problem. e. iii.  $\$0.57/\text{lb}$  using benzene or  $\$2.63/\text{lb}$  using benzophenone. iv.  $\$0.20/\text{lb}$ ; f. Process iv. is most economical.

### Chapter 23

1. Primary: amino acid sequence; covalent bonds; Secondary: features such as  $\alpha$ -helix, pleated sheets: H-bonding; Tertiary: three dimensional shape: hydrophobic and hydrophilic interactions, salt linkages, hydrogen bonds, disulfide linkages, dispersion forces 3. Both denaturation and inhibition reduce the catalytic activity of an enzyme. Denaturation changes the structure of an enzyme. Inhibition involves the attachment of an incorrect molecule at the active site, preventing substrate from interacting with the enzyme. 5. hydrogen bonding 7. nitrogen atoms with lone pairs of electrons 9. A deletion may change the entire code for a protein. A substitution will change only one single amino acid in a protein. 11. a triglyceride containing more than one carbon-carbon