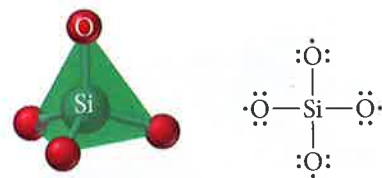


Nanotubes are 100 times stronger than steel and only 1/16 as dense. Consequently, we use carbon nanotubes commercially for lightweight applications that require strength, such as golf clubs and bicycle frames. When the nanotubes are lined up parallel to one another, a bundle of the tubes forms a “wire” with very low electrical resistance. These tiny wires raise the possibility of making incredibly small electronic devices.

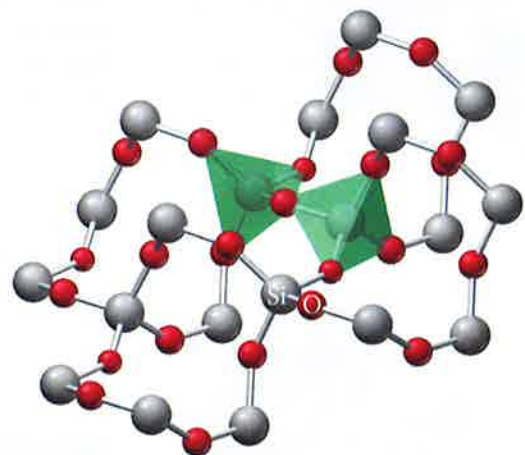
## Silicates

The **silicates** (extended arrays of silicon and oxygen) are the most common network covalent atomic solids. Geologists estimate that 90% of Earth’s crust is composed of silicates. Silicon and oxygen form a network covalent structure in which a silicon atom bonds to four oxygen atoms, assuming a tetrahedral shape with the silicon atom in the middle and the four oxygen atoms at the corners of the tetrahedron (Figure 12.21 ▶).

In this structure, the silicon atom bonds to each oxygen atom with a single covalent sigma bond. In contrast to carbon, which often bonds to oxygen with a double bond (one sigma and one pi bond), silicon typically forms only a single bond with oxygen because the silicon atom is too large to allow substantial overlap between the *p*-orbitals on the two atoms. The silicon atom in this structure, by bonding to four oxygen atoms, obtains a complete octet. However, each oxygen atom is one electron short of an octet. Therefore, each O atom forms a second covalent bond to a different Si atom, resulting in the three-dimensional structure of **quartz**. Quartz has a formula unit of  $\text{SiO}_2$  and is generally called **silica**. In silica, each Si atom is in a tetrahedron surrounded by four O atoms, and each O atom acts as a bridge connecting the corners of two tetrahedrons (Figure 12.22 ▶). See Section 23.3 for a more extended discussion of silicate structures.



▲ **FIGURE 12.21**  $\text{SiO}_4$  Tetrahedron In an  $\text{SiO}_4$  tetrahedron, silicon occupies the center of the tetrahedron, and one oxygen atom occupies each corner.



▲ **FIGURE 12.22** Structure of Quartz In the quartz structure, each Si atom is in a tetrahedron surrounded by four O atoms, and each O atom is a bridge connecting the corners of two tetrahedrons.

## 12.7 Ceramics, Cement, and Glass

The silicate structures we examined in Section 12.6 are common in ceramics, cement, and glass. These substances are used in buildings, electrical devices, pottery, and kitchenware. If you look around wherever you are sitting at this moment, you are likely to see examples of these materials. In this section of the chapter, we examine each of these amazing classes of materials individually.

### Ceramics

**Ceramics** are traditionally defined as inorganic nonmetallic solids that are prepared from powders usually mixed with water, formed into the desired shape and then heated. Ceramics are extensively used to make bricks, tiles, pottery, dishware, and insulating elements in electrical devices. They display a range of properties but are usually hard, strong, nonconductive, and brittle. The word “ceramics” originates from the Greek *keramikos*. *Keramikos* is an area of Athens that was the potters’ quarter of the city, and the Greeks were among the first accomplished potters. However, pottery itself predates recorded history. The oldest known example is the Venus of Dolni, a figurine that dates to 29,000–25,000 BCE. Ceramics can be categorized into three types: silicate, oxide, and nonoxide.

### Silicate Ceramics

Many ceramics are composed of aluminosilicates, a class of minerals in which some of the silicon atoms in the silicate structure are replaced by aluminum (see Section 23.3). The weathering of naturally occurring aluminosilicates produces **clays**, which are essentially powdered forms of the minerals mixed with water. When heated, reactions occur that transform the clay into the ceramic substance.

For example, the clay kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , undergoes irreversible chemical and structural changes when heated (or fired) above 1500 °C. These changes transform the clay into a white ceramic solid containing an extended network of Si-O and Al-O tetrahedra. Kaolinite is the most important component of porcelain, a ceramic substance that



▲ The Venus of Dolni, the oldest known ceramic object, dates to 29,000–25,000 BCE. It was discovered in 1925 in the Czech Republic.



▲ Ceramic electrical insulator



▲ Aluminum oxide crucible, a container in which substances can be subjected to high temperatures.

originated in China during the Han dynasty about 2000 years ago. Chinese porcelain was superior to previous ceramics and became highly valued and prized for its beauty and durability, especially when formed into cups for drinking tea. The Chinese profitably exported their porcelain wares to the Middle East and the West and kept their recipe for making it a secret for hundreds of years. The term *china* today still refers to the fine plates, saucers, and cups made from porcelain and related ceramic materials. Silicate ceramics also find extensive use as insulators in electrical applications.

### Oxide Ceramics

Among the most common oxide ceramics are  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . These materials demonstrate the advantages and disadvantages of ceramic materials compared to metals.  $\text{Al}_2\text{O}_3$  melts at  $2072^\circ\text{C}$ , compared to aluminum metal, which melts at  $660^\circ\text{C}$ .  $\text{MgO}$  melts at an even higher temperature ( $2852^\circ\text{C}$ ). Both are physically and chemically stable at high temperatures. The high melting point and chemical stability make  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  outstanding *refractory materials*—materials that can be used in high-temperature applications.

For example, aluminum oxide and magnesium oxide are used in industrial furnaces, high-speed cutting tools, crucibles, heating elements, and fire proofing. Engineers have long desired to take advantage of the high-temperature stability of ceramics to make ceramic engines. A ceramic engine can run at a higher temperature, which makes it more efficient and would require less cooling. However, certain less desirable characteristics of ceramics have made that pursuit difficult. Ceramic materials tend to be brittle and subject to thermal shock (they can crack upon fast changes in temperature). Metals can bend and stretch under stress, but ceramics break. Even though ceramics have found some limited use as components of engines, a completely ceramic mass-produced engine remains elusive.

### Nonoxide Ceramics

The nonoxide ceramics include substances such as  $\text{Si}_3\text{N}_4$ , BN, and SiC. Silicon nitride is a network covalent solid with a structure similar to silica; the silicon atoms sit in the center of nitrogen tetrahedra that are linked. Silicon nitride is used extensively in engine parts and nonmetallic ball bearings. Boron nitride is isoelectronic with  $\text{C}_2$  (BN and  $\text{C}_2$  have the same number of valence electrons) and forms structures similar to carbon. For example, BN can form layered sheets (similar to graphite), which are covalently bound within the sheets but with only dispersion forces between the sheets. As a result, this form of BN makes a good high-temperature lubricant. Another form of boron nitride has the diamond structure, which results in a hard, strong substance similar to diamond. This form of boron nitride is used as an abrasive and to make cutting tools. Boron nitride can even form nanotubes similar to those formed by carbon. Silicon carbide also has a diamond structure, but in silicon carbide, half of the carbon atoms are replaced by silicon atoms. It too finds applications as an abrasive, and it is also used as a refractory material and an additive to steel.

### Cement

Cement was first discovered by the Romans, who used lime, volcanic ash, and clay to make a pourable slurry that hardened into a rocklike substance. The Romans used cement to construct the 43.3-m-diameter dome of the Pantheon, a 2000-year-old edifice. This dome remains the largest unreinforced concrete dome in existence.

The majority of the cement used today is Portland cement. **Portland cement** is a powdered mixture consisting mostly of limestone ( $\text{CaCO}_3$ ) and silica ( $\text{SiO}_2$ ), with smaller amounts of alumina ( $\text{Al}_2\text{O}_3$ ), iron(III) oxide ( $\text{Fe}_2\text{O}_3$ ), and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The powdered mixture reacts with water in a number of complex reactions that produce a final rocklike substance. Unlike clays, which lose water upon setting, Portland cement reacts *with* water as it hardens. The hardening process involves the formation of Si-O-Si bridges that produce fibrous structures. These structures bond strongly to each other (and most other substances). The original Portland cement was patented in 1824 by an English bricklayer named Joseph Aspidin (1788–1855). The hardened cement resembles a prestigious building stone from the Isle of Portland in Southwest England and derives its name from this resemblance.



▲ The Roman Pantheon, still a popular tourist attraction, sits in the center of the ancient heart of Rome.

Portland cement is combined with sand and pebbles to make **concrete**, the most widely used building material in the world. Concrete dramatically revolutionized construction. Before concrete, buildings were made exclusively by arranging the materials piece by piece. With the development of concrete, buildings could literally be poured into place. Concrete is used extensively to make foundations, walls, buildings, bridges, aqueducts, roads, and dams. About half of all the structures humans construct are made of concrete.

## Glass

Silica melts when heated above 1500 °C. After melting, if cooled quickly, silica does not crystallize back into the quartz structure. Instead, the Si atoms and O atoms form a randomly ordered amorphous structure called a **glass**. Silicate glass is transparent, impervious to water, and an **outstanding** material for making windows and drinking vessels. The Egyptians and Greeks likely made glass objects; however, the Romans in the first century BCE were the first to extensively develop glass making. They discovered that adding sodium carbonate to silica dramatically lowers its melting point, allowing glass to form at much lower temperatures. In addition, they developed glass-blowing, which involves melting glass and then using a tube to blow the glass into spherical shapes.

When  $\text{SiO}_2$  is made into a glass, the result is called **vitreous silica** or **fused silica**. This type of glass is hard, resists high temperatures, has a low thermal expansion, and is transparent to both visible light and ultraviolet light. Vitreous silica (because of the high temperatures required to produce it) is too expensive for most common applications. The most common modern glass is **soda-lime glass**, which is also referred to as *window glass*. Soda-lime glass is about 70%  $\text{SiO}_2$ ; the balance is mostly  $\text{Na}_2\text{O}$  and  $\text{CaO}$ . This type of glass is transparent to visible light (not ultraviolet) and has a high thermal expansion, but it is less expensive to make and form into desired shapes than vitreous silica.

One disadvantage of soda-lime glass is its tendency to crack under thermal shock. Adding boric oxide ( $\text{B}_2\text{O}_3$ ) to the glass mixture instead of  $\text{CaO}$  produces **borosilicate glass** (also known as **Pyrex**<sup>®</sup>), which expands less when heated. As a result, vessels made of Pyrex<sup>®</sup> can withstand heating and cooling cycles that would shatter soda-lime glass. The beakers, flasks, and other glassware found in most chemistry labs are made of borosilicate glass.

**Leaded glass** (often called *crystal*, even though it is not a crystal) results when  $\text{PbO}$  is mixed with  $\text{SiO}_2$  and a couple of other minor components. This type of glass has a higher index of refraction (it bends light more than ordinary glass), which results in glassware with a more brilliant appearance than soda-lime glass. It also makes a ringing sound when tapped, which is a common test to distinguish lead crystal from ordinary glass. Recent concerns about the toxicity of lead in leaded glass have led to the development of lead-free alternatives (often called lead-free crystal) for stemware and drinking glasses, which has properties similar to those of leaded glass, but without the negative health risks.

## 12.8 Semiconductors and Band Theory

Recall that in Section 12.4 we discussed a model for bonding in metals called the *electron sea model*, which we first introduced and explained in Section 9.11. We now turn to a model for bonding in solids that is both more sophisticated and more broadly applicable—it applies to both metallic solids and covalent solids. The model is **band theory**, and it grows out of molecular orbital theory, first discussed in Section 10.8.

### Molecular Orbitals and Energy Bands

Recall that according to molecular orbital theory, the atomic orbitals of the atoms combine within a molecule to form molecular orbitals. These molecular orbitals are not localized on individual atoms but *delocalized over the entire molecule*. Similarly, in band theory, the atomic orbitals of the atoms within a solid crystal combine to form orbitals that are not localized on individual atoms, but delocalized over the entire *crystal*. In some sense, the crystal is like a very large molecule, and its valence electrons occupy the molecular orbitals formed from the atomic orbitals of each atom in the crystal.

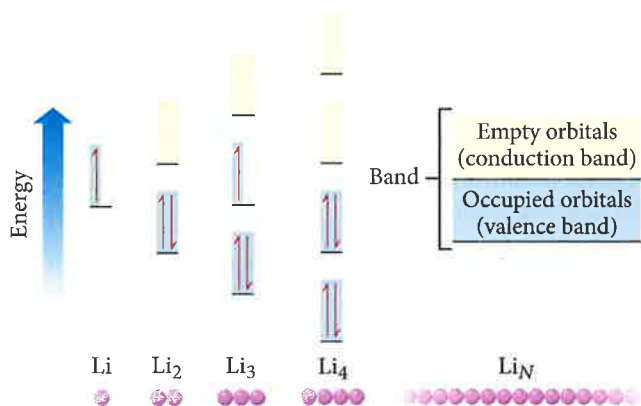


▲ Glass blowing involves blowing air into a hot piece of glass to form spherical shapes.



▲ Leaded glass has a higher index of refraction than ordinary glass, making it appear more brilliant.

The amount of lead that leaches into a drink from leaded glass over a short period of time is likely inconsequential. However, storing drinks in leaded glass for long periods of time can lead to elevated lead levels in the liquid.



**▲ FIGURE 12.23 Energy Levels of Molecular Orbitals in Lithium Molecules** When many Li atoms are present, the energy levels of the molecular orbitals are so closely spaced that they fuse to form a band. Half of the orbitals are bonding orbitals and contain valence electrons; the other half are antibonding orbitals and are empty.

Consider a series of molecules constructed from individual lithium atoms. The energy levels of the atomic orbitals and resulting molecular orbitals for Li, Li<sub>2</sub>, Li<sub>3</sub>, Li<sub>4</sub>, and Li<sub>N</sub> (where *N* is a large number on the order of 10<sup>23</sup>) are shown in Figure 12.23. The lithium atom has a single electron in a single 2s atomic orbital. The Li<sub>2</sub> molecule contains two electrons and two molecular orbitals. The electrons occupy the lower-energy bonding orbital—the higher-energy, or antibonding, molecular orbital is empty. The Li<sub>4</sub> molecule contains four electrons and four molecular orbitals. The electrons occupy the two bonding molecular orbitals—the two antibonding orbitals are completely empty.

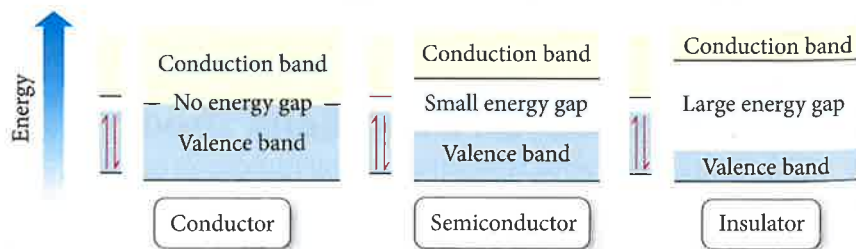
The Li<sub>N</sub> molecule contains *N* electrons and *N* molecular orbitals. However, because there are so many molecular orbitals, the energy spacings between them are infinitesimally small; they are no longer discrete energy levels, but rather they form a *band* of energy levels. One half of the orbitals in the band (*N*/2) are bonding molecular orbitals, and (at 0 K) these orbitals contain the *N* valence electrons; this band is called the **valence band**. The other *N*/2 molecular orbitals are antibonding and (at 0 K) are completely empty; this band is called the **conduction band**. If the atoms composing a solid have *p* orbitals available, then the same process leads to another set of bands at higher energies.

In lithium metal, the highest occupied molecular orbital lies in the middle of a band of orbitals, and the energy difference between it and the next higher-energy orbital is infinitesimally small. Therefore, above 0 K, electrons can easily make the transition from the valence band to the conduction band. Because electrons in the conduction band are mobile, lithium, like all metals, is a good electrical conductor. Mobile electrons in the conduction band are also responsible for the thermal conductivity of metals. When a metal is heated, electrons are excited to higher-energy molecular orbitals. These electrons quickly transport the thermal energy throughout the crystal lattice.

In metals, the valence band and conduction band are energetically continuous—the energy difference between the top of the valence band and the bottom of the conduction band is infinitesimally small. In semiconductors and insulators, however, an energy gap, called the **band gap**, exists between the valence band and conduction band as shown in Figure 12.24. Band gaps are usually specified in units of electron volts abbreviated as eV (1 eV = 1.602 × 10<sup>-19</sup>J). In insulators, the band gap is large, and electrons are not promoted into the conduction band at ordinary temperatures, resulting in no electrical conductivity. In semiconductors, the band gap is smaller. As a result, the conductivity of semiconductors increases with increasing temperature because heat allows a greater number of electrons to be thermally promoted into the conduction band.

Recall from Section 2.7 that a semiconductor is a substance of intermediate (and highly temperature-dependent) electrical conductivity.

**► FIGURE 12.24 Band Gap** In a conductor, there is no energy gap between the valence band and the conduction band. In semiconductors there is a small energy gap, and in insulators there is a large energy gap.



The Group 4A elements exhibit a range of band gaps as shown in Table 12.2.

**TABLE 12.2 Band Gap of Group 4A Elements**

Group 4A Element	Atomic Radius (pm)	Band Gap	Classification
Carbon (diamond)	77	5.5 eV	Insulator
Silicon	118	1.11 eV	Semiconductor
Germanium	122	0.67 eV	Semiconductor
Tin	140	0.08 eV	Metal
Lead	180	none	Metal

Notice that the band gap decreases as you move down the column of elements. Why? We know from our discussion of periodic properties (see Section 8.6) that atomic radius increases as we move down a column in the periodic table. The increasing radius reduces the overlap between orbitals on neighboring atoms, which in turn reduces the energy difference between the antibonding orbitals (the conduction band) and the bonding orbitals (the valence band). This results in a decreasing band gap as you move down the column of elements.

## Doping: Controlling the Conductivity of Semiconductors

Doped semiconductors contain minute amounts of impurities that result in additional electrons in the conduction band or electron “holes” in the valence band. For example, silicon is a group 4A semiconductor. Its valence electrons just fill its valence band. The band gap in silicon is large enough that only a few electrons are promoted into the conduction band at room temperature; therefore, silicon is a poor electrical conductor. However, silicon can be doped with phosphorus, a group 5A element with five valence electrons, to increase its conductivity. The phosphorus atoms are incorporated into the silicon crystal structure, and each phosphorous atom brings with it one additional electron. Since the valence band is completely full, the additional electrons must go into the conduction band. These electrons are then mobile and can conduct electrical current. This type of semiconductor is an **n-type semiconductor** because the charge carriers are *negatively* charged electrons in the conduction band.

Silicon can also be doped with a group 3A element, such as gallium, which has only three valence electrons. When gallium is incorporated into the silicon crystal structure, gallium atoms trap some of the electrons in silicon’s valence band, resulting in electron “holes,” or empty molecular orbitals, in the valence band. The presence of holes also allows for the movement of electrical current because electrons in the valence band can move between holes. In this way, the holes move in the opposite direction as the electrons. This type of semiconductor is a **p-type semiconductor** because each hole acts as a *positive* charge.

At the heart of most modern electronic devices are silicon chips containing millions of **p-n junctions**, tiny spots that are p-type on one side and n-type on the other. These junctions can serve a number of functions, including acting as **diodes** (circuit elements that allow the flow of electrical current in only one direction) or **amplifiers** (elements that amplify a small electrical current into a larger one).

**Semiconductor Type** Which element would you dope into germanium to create a p-type semiconductor?

- (a) indium                      (b) tin                              (c) arsenic



CONCEPTUAL  
CONNECTION 12.5

## 12.9 Polymers and Plastics

**Polymers** are long, chainlike molecules composed of repeating units called **monomers**. In Chapter 22, we discuss natural polymers such as starches, proteins, and DNA, which play important roles in living organisms. In this section, we learn about synthetic polymers, which we encounter daily in plastic products such as PVC tubing, styrofoam coffee cups, nylon rope, and plexiglass windows. Polymeric materials are common in our everyday lives, found in everything from computers to toys to packaging materials. Most polymers are durable, partly because of the length of their molecules. In general, the longer a molecule, the greater the intermolecular forces between molecules and the higher the melting point and boiling point of the substance. Since breaking or tearing a **polymeric** material involves either overcoming the intermolecular forces between chains or actually breaking the covalent bonds between monomers, polymers tend to be durable materials.

One of the simplest synthetic polymers is polyethylene. The polyethylene monomer is ethene (also called ethylene):



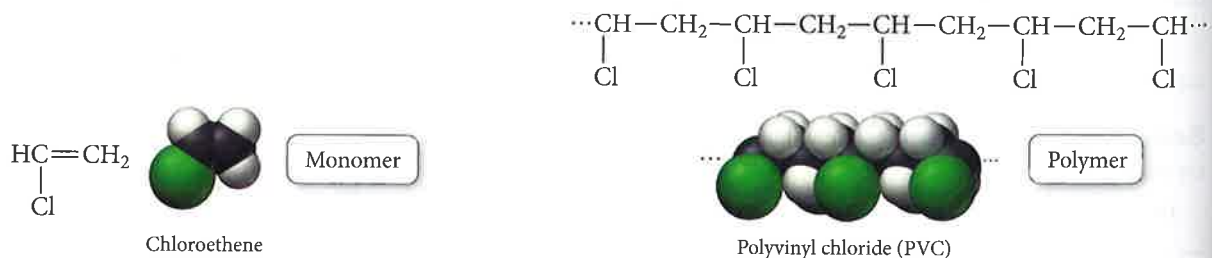
Ethene monomers react with each other, breaking the double bond between carbons and bonding together to form a long polymer chain:



► **FIGURE 12.25 Polyethylene**  
Plastic milk bottles are made from polyethylene.

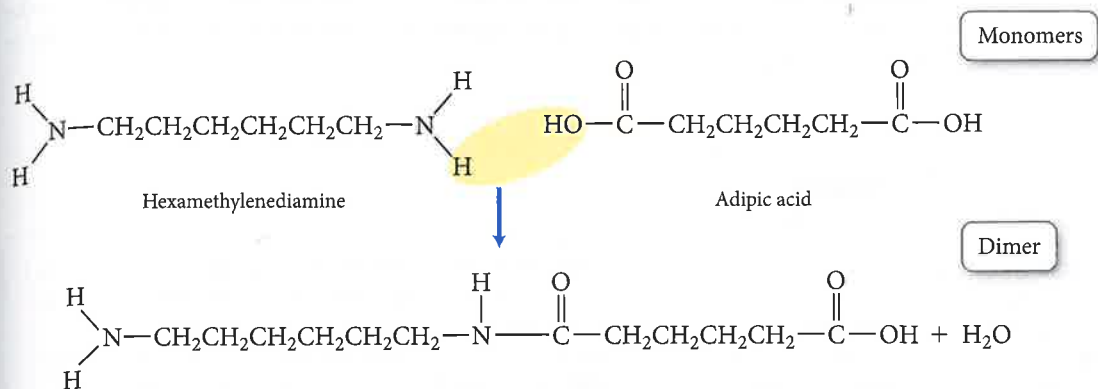
Polyethylene is an **addition polymer**, a polymer in which the monomers link together without the elimination of any atoms. Polyethylene is the plastic that is used for milk jugs, juice containers, and garbage bags. The properties of polyethylene depend on the exact structure of the ethylene chain and the resulting structure of the material. Although polymers are generally amorphous, they can have regions of crystallinity. For polyethylene, the degree of crystallinity depends in part on the degree of branching in the chain. High-density polyethylene (HDPE), for example, has little branching, so that the chains can align closer to one another, resulting in high crystallinity, high density, and good strength and heat resistance. Common plastic milk jugs are made of HDPE (Figure 12.25◀). Low-density polyethylene (LDPE), in contrast, has more highly branched chains. This branching prevents the chains from interacting as efficiently, resulting in lower crystallinity, density, and strength and heat resistance. Many common plastic bags are made of LDPE.

Substituted polyethylenes make up an entire class of polymers (Table 12.3). For example, polyvinyl chloride (PVC)—the plastic used to make certain kinds of pipes and plumbing fixtures—is composed of monomers in which a chlorine atom has been substituted for one of the hydrogen atoms in ethene (Figure 12.26▼). These monomers, which are shown here, react to form PVC:



► **FIGURE 12.26 Polyvinyl Chloride**  
Polyvinyl chloride is used for many plastic plumbing supplies, such as pipes and connectors.

Some polymers—called *copolymers*—consist of two different kinds of monomers. For example, the monomers that compose nylon 6,6 are hexamethylenediamine and adipic acid. These two monomers add together via a condensation reaction as follows:



**TABLE 12.3** Polymers of Commercial Importance

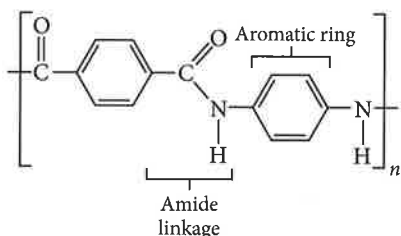
Polymer	Structure	Uses
<b>Addition Polymers</b>		
Polyethylene	$-(\text{CH}_2-\text{CH}_2)_n-$	Films, packaging, bottles
Polypropylene	$\left[ \begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \\ \text{CH}_3 \end{array} \right]_n$	Kitchenware, fibers, appliances
Polystyrene	$\left[ \begin{array}{c} \text{CH}_2-\text{CH} \\   \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Packaging, disposable food containers, insulation
Polyvinyl chloride	$\left[ \begin{array}{c} \text{CH}_2-\text{CH} \\   \\ \text{Cl} \end{array} \right]_n$	Pipe fittings, clear film for meat packaging
<b>Condensation Polymers</b>		
Polyurethane	$\left[ \begin{array}{c} \text{C}-\text{NH}-\text{R}-\text{NH}-\text{C}-\text{O}-\text{R}'-\text{O} \\    \quad    \\ \text{O} \quad \text{O} \end{array} \right]_n$ R, R' = $-\text{CH}_2-\text{CH}_2-$ (for example)	"Foam" furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethylene terephthalate (a polyester)	$\left[ \text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O}) \right]_n$	Tire cord, magnetic tape, apparel, soda bottles
Nylon 6,6	$\left[ \text{NH}-(\text{CH}_2)_6-\text{NH}-\text{C}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O}) \right]_n$	Home furnishings, apparel, carpet fibers, fish line, polymer blends

The product that forms between the reaction of two monomers is a **dimer**. The polymer (nylon 6,6) forms as the dimer continues to add more monomers. Polymers that eliminate an atom or a small group of atoms during polymerization are **condensation polymers**. Nylon 6,6 and other similar nylons are drawn into fibers and used to make consumer products such as panty hose, carpet fibers, and fishing line (see *Chemistry in Your Day: Kevlar*).

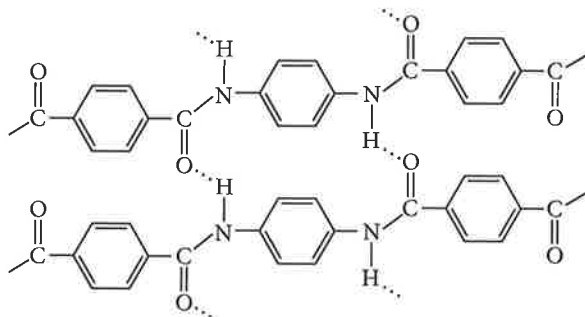
## Chemistry IN YOUR DAY | Kevlar

In 1965, Stephanie Kwolek, working for DuPont to develop new polymer fibers, noticed an odd cloudy product from a polymerization reaction. Some researchers might have rejected the product, but Kwolek insisted on examining its properties more carefully. The results were astonishing—when the polymer was spun into a fiber, it was stronger than any fiber known before. Kwolek had discovered Kevlar, a material that is pound for pound five times stronger than steel.

Kevlar is a condensation polymer featuring aromatic rings and amide linkages:



The polymeric chains within Kevlar crystallize in a parallel arrangement (like dry spaghetti noodles in a box), with strong cross-linking between neighboring chains resulting from hydrogen bonding. The hydrogen bonding occurs between the N—H groups on one chain and the C=O groups on neighboring chains:



This structure is responsible for Kevlar's high strength and its other properties, including fire resistance and chemical resistance (for example, resistance to acids).

Today, DuPont sells hundreds of millions of dollars worth of Kevlar every year. Kevlar is particularly well known for its use in bulletproof vests. This application of Kwolek's discovery has saved thousands of lives. In addition, Kevlar is used to make helmets, radial tires, brake pads, racing sails, suspension bridge cables, skis, and high-performance hiking and camping gear.



▲ Kevlar is used to make bulletproof vests.

## Self-Assessment Quiz

**Q1.** An X-ray beam of  $\lambda = 154 \text{ pm}$  is incident on the surface of an unknown metallic crystal. It produces a maximum diffraction at an angle of  $\theta = 29.1^\circ$ . Assuming  $n = 1$ ,

calculate the separation between layers of metal atoms in the crystal.

- a) 316 pm                      b) 105 pm  
c) 154 pm                      d) 158 pm

**Q2.** How many atoms are in the body-centered cubic unit cell?

- a) 1                      b) 2                      c) 4                      d) 5