28.6 Step-Growth Polymers

Step-growth polymers are formed by the intermolecular reaction of bifunctional molecules (molecules with two functional groups). When the functional groups react, in most cases a small molecule such as H_2O, alcohol, or HCl is lost. This is why these polymers are also called *condensation polymers.*

There are two types of step-growth polymers. One type is formed by the reaction of a single monomer that possesses two different functional groups A and B. Functional group A of one monomer reacts with functional group B of another monomer.

$$\text{A—B} \quad \text{A—B} \longrightarrow \text{A—X—B}$$

The other type of step-growth polymer is formed by the reaction of two different bifunctional monomers. One monomer contains two A functional groups and the other monomer contains two B functional groups.

Step-growth polymers are made by combining molecules with reactive groups at each end.

$$\text{A—A} \quad \text{B—B} \longrightarrow \text{A—X—B}$$

The formation of step-growth polymers, unlike the formation of chain-growth polymers, does not involve chain reactions. Any two monomers (or short chains) can react. The progress of a typical step-growth polymerization is shown schematically in Figure 28.3. When the reaction is 50% complete (12 bonds have formed between 25 monomers), the reaction products are primarily dimers and trimers. Even at 75% completion, no long chains have been formed. This means that if step-growth polymerization is to lead to long-chain polymers, very high yields must be achieved.

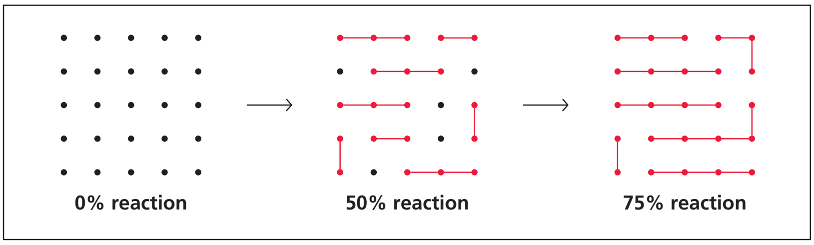
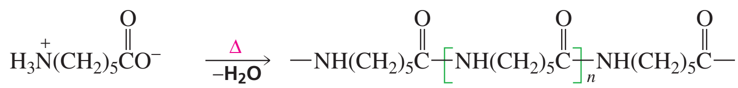


Figure 28.3
Progress of a step-growth polymerization.

Polyamides

Nylon is the common name of a synthetic **polyamide**. Nylon 6 is an example of a step-growth polymer formed by a monomer with two different functional groups. The carboxylic acid group of one monomer reacts with the amino group of another monomer, resulting in the formation of amide groups. Structurally, the reaction is similar to the polymerization of α-amino acids to form proteins (Section 23.7). This particular nylon is called nylon 6 because it is formed from the polymerization of 6-aminohexanoic acid, a compound that contains six carbons.

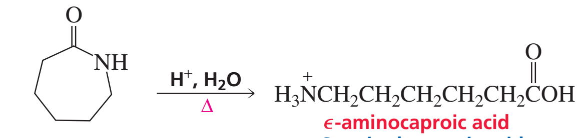
Nylon was first synthesized in 1931 by **Wallace Carothers (1896–1937)**. *He was born in Iowa and received a Ph.D. from the University of Illinois. He taught there and at Harvard before being hired by DuPont to head its program in basic science. Nylon was introduced to the public in 1939, but its widespread use was delayed until after World War II because all nylon produced during the war was used by the military. Carothers died unaware of the era of synthetic fibers that dawned after the war.*



6-aminohexanoic acid

nylon 6
a polyamide

The starting material for nylon 6 is ε-caprolactam. The lactam is opened by hydrolysis.



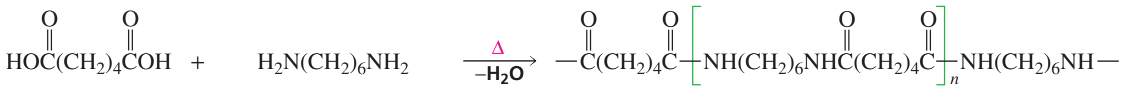
ε-caprolactam

ε-aminocaproic acid

6-aminohexanoic acid

3-D Molecules: ε-Caprolactam; Nylon 6; Nylon 66

Nylon 66 is an example of a step-growth polymer formed by two different bifunctional monomers: adipic acid and 1,6-hexanediamine. It is called nylon 66 because it is a polyamide formed from a six-carbon diacid and a six-carbon diamine.



adipic acid

1,6-hexanediamine

nylon 66

▲ Nylon is pulled from a beaker of adipoyl chloride and 1,6-hexanediamine.

Nylon first found wide use in textiles and carpets. Because it is resistant to stress, it is now used in many other applications, such as mountaineering ropes, tire cords and fishing lines, and as a substitute for metal in bearings and gears. The extended applications of nylon precipitated a search for new "super fibers" with super strength and super heat resistance.

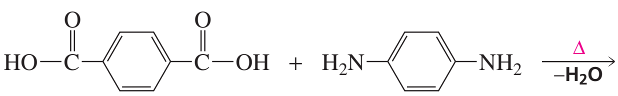
PROBLEM 15◆

a. Draw a short segment of nylon 4.
b. From what lactam is nylon 4 synthesized?
c. Draw a short segment of nylon 44.

PROBLEM 16

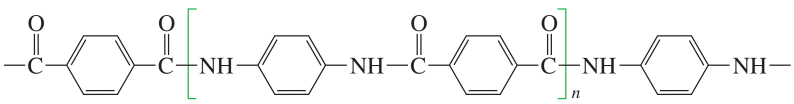
Write an equation that explains what will happen if a scientist working in the laboratory spills sulfuric acid on her nylon 66 hose.

One super fiber is Kevlar®, a polymer of 1,4-benzenedicarboxylic acid and 1,4-diaminobenzene. The incorporation of aromatic rings into polymers has been found to result in polymers with great physical strength. Aromatic polyamides are called **aramides**. Kevlar® is an aramide with a tensile strength greater than that of steel. Army helmets are made of Kevlar®, which is also used for lightweight bulletproof vests and high-performance skis. Because it is stable at very high temperatures, it is used in the protective clothing worn by firefighters.



1,4-benzenedicarboxylic acid

1,4-diaminobenzene



Kevlar®
an aramide

Kevlar® owes its strength to the way in which the individual polymer chains interact with each other. The chains are hydrogen bonded, causing them to form a sheetlike structure.