Synthetic Condensation Polymers

2.4

A firefighter entering a burning building must be protected from intense heat. Imagine a fabric that could withstand the extreme temperatures of an industrial fire. That fabric is likely to be knitted with Nomex fibres. Nomex is a polymer made from amide monomers. It is used to make flame-resistant clothing, electrical insulation, industrial filters, and aircraft parts. Race-car drivers, firefighters, fighter pilots, and astronauts all wear clothing that incorporates this polymer (**Figure 1**). Nomex is a condensation polymer, formed when two monomers bond together with the elimination of a small molecule.

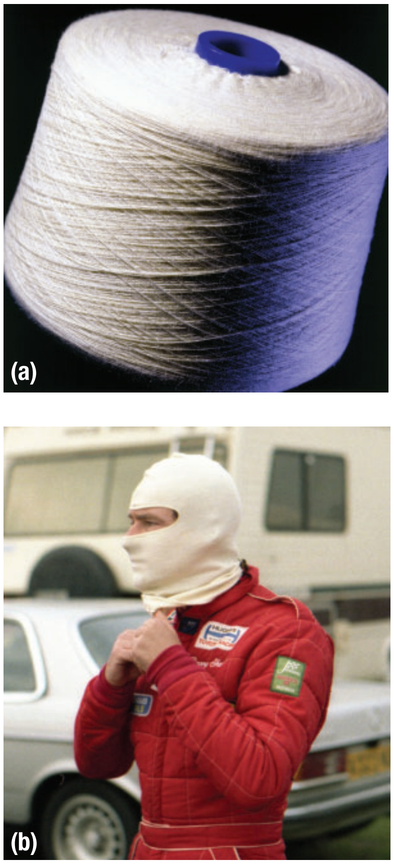
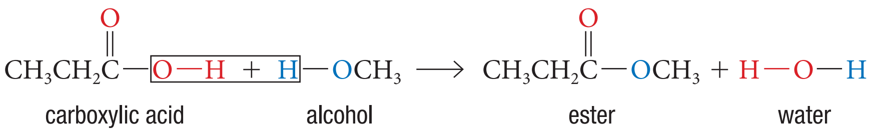


Figure 1 (a) Nomex is a flame-resistant material that can be formed into fine thread. This thread is then woven or knitted into safety clothing. (b) Race-car drivers wear balaclavas made of Nomex.

Producing Condensation Polymers

In Section 2.2, you studied polymers that were made by addition reactions of unsaturated monomers. There are many molecules without carbon–carbon double bonds that can also react to form polymers. What type of reaction can join these monomers together?

Recall what you know about reactions that take place between two organic compounds, resulting in the formation of a larger compound and a small molecule such as water. This type of reaction is called a condensation reaction (Section 1.4). For example, an alcohol reacts in a condensation reaction with a carboxylic acid to form an ester.



Condensation reactions can also be used to produce condensation polymers. A **condensation polymer**, like an addition polymer, is composed of repeating groups of monomers. These monomers, unlike those in addition polymers, have two reactive functional groups involved in the polymerization reaction. They do not necessarily have any carbon double bonds.

The two most common types of condensation polymers have either ester linkages or amide linkages. Esters have a carboxyl functional group joining the monomers (R–COOR′); amides have a carbonyl group, –C=O, connected to a nitrogen atom, –N–, joining the monomers (R–CONR′). Let us look at these two types of polymers in more detail.

condensation polymer a very long organic molecule formed as a result of condensation reactions between monomers with two functional groups

Polyesters

A **polyester** is a polymer formed by a series of esterification reactions between monomers. Monomers with two functional groups, an –OH (hydroxyl) group and a –COOH (carboxyl) group, form chains by undergoing condensation reactions at both ends. As each monomer molecule is added to the chain, the condensation reaction produces a small by-product molecule, such as water.

polyester a polymer formed by a condensation reaction that results in ester linkages between monomers

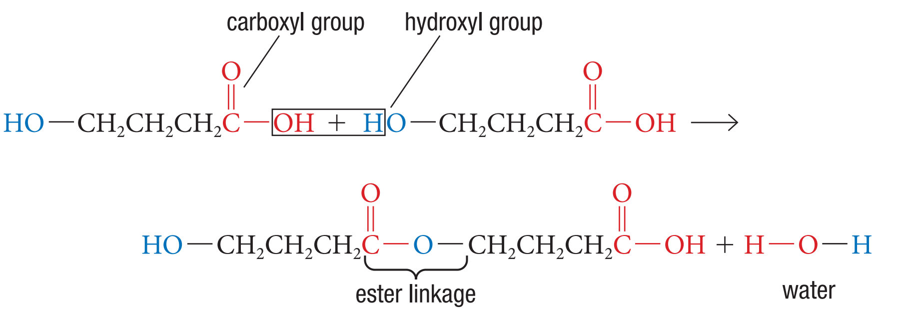
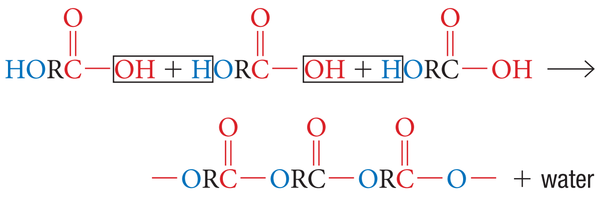


Figure 2 Clothes that are made of polyester are washable and durable.

To form a polymer chain, a monomer must attach to one end of the chain, either with its carboxyl group reacting with the hydroxyl group on the chain, or with its hydroxyl group reacting with the carboxyl group on the chain. Either way, it forms an ester linkage and eliminates a water molecule. Each end of the growing chain can then react with another monomer, and this process continues until a long polyester polymer is formed. Synthetic condensation polymers are widely used in consumer and industrial textiles (**Figure 2**).

The general reaction equation for the formation of a polyester is

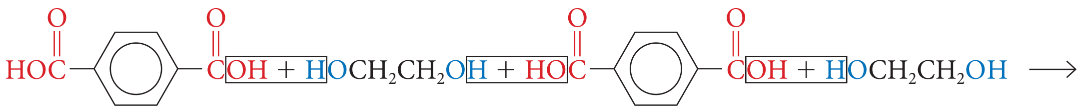


a polyester

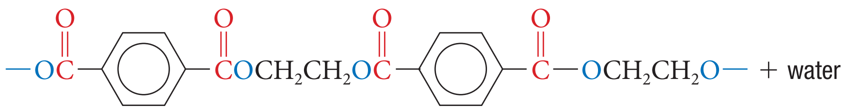
Polyesters can also be formed from two different monomers. One monomer must have two hydroxyl groups (a diol) and the other must have two carboxylic acid groups (a dicarboxylic acid). In this case, the polyester is a copolymer formed with alternating monomers diol and dicarboxylic acid. CAREER LINK

Dacron

Dacron is the brand name for polyethene terephthalate (PET). It is a condensation copolymer formed by the reaction of ethane-1,2-diol (ethene glycol) and benzene-1,4-dicarboxylic acid (terephthalic acid). Ester linkages join the monomers together.

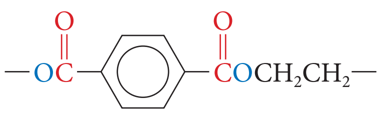


benzene-1,4-dicarboxylic acid (terephthalic acid) | ethane-1,2-diol (ethene glycol) | benzene-1,4-dicarboxylic acid (terephthalic acid) | ethane-1,2-diol (ethene glycol)



polyethene terephthalate (PET)

The repeating unit of Dacron is



Polyamides

Recall from Section 1.7 that, in the formation of an amide, a carboxylic acid reacts with ammonia or with a primary or secondary amine. The resulting functional group is an amide group consisting of a carbonyl group, –C–O, in which the carbon atom is bonded to a nitrogen atom.

A **polyamide** is a polymer formed by a condensation reaction resulting in amide linkages between monomers. Amide linkages are formed by a condensation reaction between an amine and a carboxylic acid (just as ester linkages are formed by

polyamide a polymer formed by condensation reactions resulting in amide linkages between monomers a condensation reaction between an alcohol and a carboxylic acid). The second product of the amide reaction is usually water. (In some polyamide reactions a dicarbonyl chloride is used in place of a dicarboxylic acid. In this case, a molecule of hydrogen chloride is eliminated.)

The carboxyl groups allow many hydrogen bonds to form between polymer chains. Together, these hydrogen bonds make polyamides exceptionally strong. Polyamides are also resistant to damage from insects and heat. Kevlar is a polyamide used in body armour (**Figure 3**). Nomex, described above, is valued for its heat resistance.

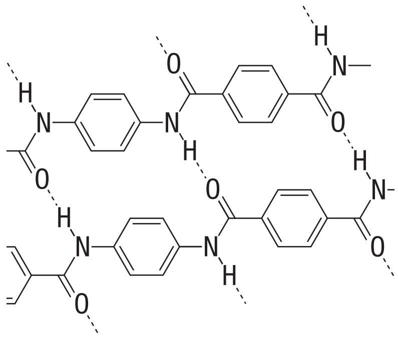
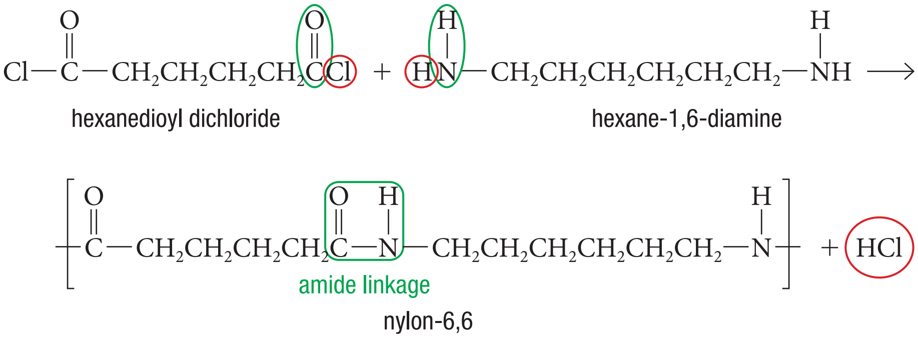


Figure 3 Hydrogen bonds between polymer chains give Kevlar its amazing strength.

Nylon 6,6

Perhaps the most familiar condensation polymer is nylon. Nylon is a copolymer, with two different types of monomers. One common form of nylon is produced when hexane-1,6-diamine (hexamethylenediamine) and hexanedioyl dichloride (adipoyl chloride) react, resulting in the formation of a C–N bond and a hydrogen chloride molecule:



As the polymer grows, both ends are free to react with another monomer. Repetition of this process leads to a long chain of the units shown in square brackets.

There are several types of nylon, depending on the particular diamine and dicarboxylic acid or dicarbonyl chloride used. The reaction to form nylon occurs quite readily under laboratory conditions (**Figure 4**).

Figure 4 The reaction to form nylon occurs at the interface of two liquid layers in a beaker. The bottom layer is hexanedioyl dichloride dissolved in carbon tetrachloride, CCl_4. The top layer is hexane-1,6-diamine dissolved in water. A molecule of hydrogen chloride is produced as each C–N bond forms.

Tutorial 1 Drawing Condensation Polymers

In this tutorial, you will learn how to draw condensation polymers given the names of the monomers, and how to draw and classify monomers given the structure of the polymer.

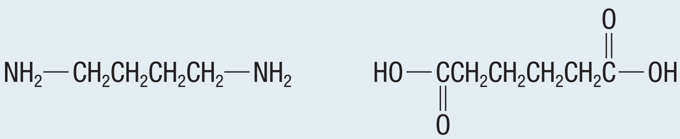
Sample Problem 1: Drawing Polymers from Monomers

Draw a condensed structural diagram of the polymer made from repeating units of a 4-carbon diamine and a 6-carbon dicarboxylic acid.

Solution

The first monomer is butane-1,4-diamine. The second monomer is hexane-1,6-dicarboxylic acid. These monomers are typical of nylon.

Draw the structure of each monomer.

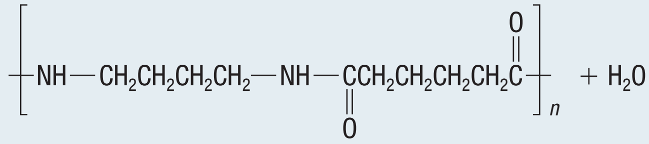


Combine the structures so that an amide linkage is formed between the two molecules. A molecule of water will be produced during the reaction.

> **LEARNING TIP**
>
> **Stereochemical Formulas**
> To represent three-dimensional shapes on paper, we need to be able to show which bonds, and hence atoms, are closer to us and which are farther away. Diagrams called stereochemical formulas were developed to do this. They use the following conventions: a solid line — is a bond in the plane of the page, and a wedged line is a bond to an atom in front of the plane of the page (toward the viewer).

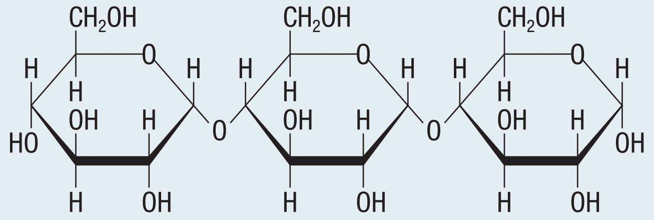
> **Investigation 2.4.1**
>
> **Preparation of a Polyester (page 106)**
> You have learned about properties of polyesters, polyamides, and condensation reactions. In this observational study, you will perform a condensation reaction and explore the characteristics of the resulting polymer.

Show that the polymer is continuous by adding bond lines at each end, drawing square brackets around the structure, and writing the subscript *n* to indicate many repeats.



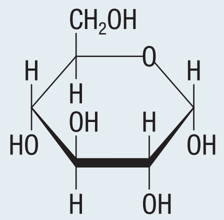
Sample Problem 2: Drawing and Classifying Monomers from a Polymer

Starch is a polymer formed in a condensation reaction in which molecules of water are eliminated from the new bonds. Draw the monomer that makes up starch.



Solution

There is only one repeating unit, so starch is a homopolymer. The repeating units are based on ring structures. Adding the components of a water molecule to either end of each monomer gives the following structure:



Practice

1. Draw a structural diagram of the polymer formed by the reaction of
   (a) propane-1,3-diol and pentanedioic acid
   (b) butanedioic acid and a 5-carbon diamine
   (c) hexanedioic acid and a 3-carbon diamine K/U C

Unwanted Plastic

As the quantity of plastics and other polymers used by people around the world grows, disposal of unwanted materials has become a major problem. Polymers in landfills do not degrade and are expected to remain unchanged for centuries—and perhaps even longer. Polyethene and polystyrene packaging materials are particularly long-lived and widely used. In one vast region of the Pacific Ocean, the water near the surface is clogged with floating or partially submerged plastic garbage. This waste is hazardous to marine organisms. Because each addition polymer is essentially a massive alkane molecule, the plastic garbage is very stable chemically: it does not degrade.

Condensation polymers, unlike addition polymers, can be made biodegradable. Certain bacteria can hydrolyze the amide or ester linkages between monomers, chopping up the polymer chain into smaller pieces. Micro-organisms can then consume and digest many of the resulting fragments. Although biodegradable polymers are preferable to plastics that do not break down, they are not a perfect solution to the garbage problem. The most effective solution is to reduce the production of plastics in the first place. We can do this by reducing, reusing, recycling, and using alternative materials.

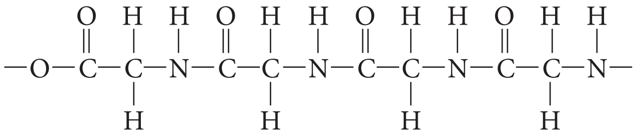
2.4 Review

Summary

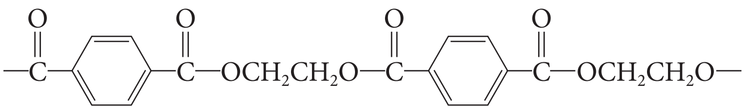
- Condensation polymers are polymers formed when monomers join during condensation reactions. A small molecule, such as water or hydrogen chloride, is also produced during the reaction.
- Polyesters are formed by condensation reactions between carboxylic acids and alcohols that result in ester linkages. Polyamides are formed by condensation reactions between carboxylic acids and amines that result in amide linkages.
- Plastic garbage is a serious environmental problem. The most effective solution is to reduce the quantity of waste produced.

Questions

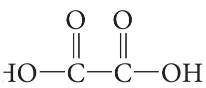
1. Draw the structure of the monomer that forms this homopolymer by condensation: K/U C



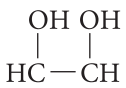
2. Draw the structures of the monomers that react to form this polyester copolymer: K/U C



3. A condensation polymer can be formed between propane-1,3-diol and 1,4-diaminobutane. K/U C
   (a) Draw the structures of both reactants, circling the functional groups that are involved with the polymerization.
   (b) Draw the structure of the polymer that is produced.
4. Describe the similarities and differences between polyesters and polyamides. Provide examples. K/U
5. Ethanedioic (oxalic) acid is found in certain vegetables, such as spinach. Ethane-1,2-diol is a toxic synthetic compound better known as ethylene glycol.

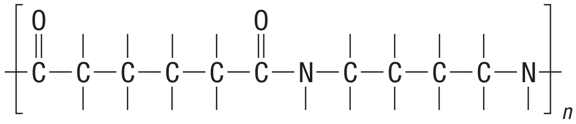


ethanedioic acid



ethane-1,2-diol

   Draw three units of the polymer made from ethanedioic acid and ethane-1,2-diol. K/U C
6. Write the names and draw the structural formulas for the reactants that form this polyamide: T/I C



7. Sodium polymethacrylate can absorb many times its own mass in water. This property makes the polymer ideal for use in hygiene products and baby diapers. What else do you think this polymer would be suitable for? T/I A
8. Many monomers can form long polymer chains, but some can also form bonds with neighbouring polymer chains, resulting in cross-linking. K/U T/I C
   (a) What properties or structure would such a monomer need?
   (b) Draw an example of a monomer that may be able to form cross-links. Circle any functional groups.
   (c) Draw the resulting polymer before cross-linking has taken place. Circle any functional groups that could be involved in cross-linking.
   (d) Draw the resulting polymer after cross-linking has taken place.
9. You have invented two polymers for use as potting-soil supplement material for plants. T/I C A
   (a) What properties would the polymers need to have?
   (b) Plan an investigation to compare two polymers for the characteristics you listed in (a). Briefly describe the materials, equipment, and procedure, as well as how you could interpret the data.