Objectives

After completing this section, you should be able to

1. write an equation to represent the formation of nylon 66 from adipic acid and hexamethylenediamine.
2. write an equation to represent the formation of nylon 6 from caprolactam.
3. predict the structure of the step-growth polymer formed from the reaction of two given monomers.
4. identify the monomers needed to prepare a step-growth polymer of a given structure.
5. write an equation to describe the formation of a polyester, such as poly(ethylene terephthalate), from a given diol and diester.
6. write an equation to describe the formation of a polycarbonate from a carbonate and a bisphenol.

Key Terms

Make certain that you can define, and use in context, the key terms below.

- chain-growth polymer
- polyamide
- polyester
- step-growth polymer

Study Notes

You may wish to review chain-growth polymerization in Section 8.10 and Section 14.6. In this section we discuss another important class of polymerization known as step-growth polymerization.

As you can see from the equation given in the discussion on forming condensation polymers, Dacron is formed from two monomers, one of which possesses two carboxylate groups and the other two hydroxyl groups.

It is also possible to form a polyester using two monomers that each posses one carboxyl group and one hydroxyl group. An example is the polymer formed between lactic acid and glycolic acid. This polymer has been used to produce absorbable staples that provide surgeons with a convenient method of closing incisions made during operations on the bladder or intestines, or during hysterectomies. Two advantages of this polyester in such applications are, first, that it begins to hydrolyze in the body after six to eight weeks, and then, that the products of the hydrolysis are both compounds normally present in the body.

\[
\begin{align*}
\text{HO-CH-CO} & \quad \text{HO-CH-CO} \\
\text{CH} & \quad \text{CH} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{O} & \quad \text{O} \\
\text{glycolic acid} & \quad \text{glycolic acid} \\
\text{2-hydroxypropionic acid} & \quad \text{2-hydroxypropionic acid}
\end{align*}
\]
Polyamides

Edit section

Just as the reaction of a diol and a diacid forms a polyester (Section 15.8), the reaction of a diacid and a diamine yields a polyamide. The two difunctional monomers often employed are adipic acid and 1,6-hexanediamine. The monomers condense by splitting out water to form a new product, which is still difunctional and thus can react further to yield a polyamide polymer.

\[
\begin{align*}
    n\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + n\text{HOOCCH}_2\text{CH}_2\text{CH}_2\text{COOH} & \quad \rightarrow \\
    1,6\text{-Hexanediamine} & \quad \text{Adipic acid} \\
    \text{HN}[\text{COCH}_2\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}]_{n}\text{CO} + 2n\text{H}_2\text{O} & \\
    \text{Nylon 66 (a polyamide)}
\end{align*}
\]

Some polyamides are known as nylons. Nylons are among the most widely used synthetic fibers—for example, they are used in ropes, sails, carpets, clothing, tires, brushes, and parachutes. They also can be molded into blocks for use in electrical equipment, gears, bearings, and valves.

Polyesters

Edit section

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:

\[
\begin{align*}
    n\text{HOCH}_2\text{CH}_2\text{OH} + n\text{HOOC}-\text{COOH} & \quad \rightarrow \\
    \text{Ethylene glycol} & \quad \text{Terephthalic acid} \\
    \left[\text{CO}-\text{COOCH}_2\text{CH}_2\text{O}\right]_{n} + n\text{H}_2\text{O} & \\
    \text{Polyethylene terephthalate}
\end{align*}
\]
Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

Condensation Polymers

A large number of important and useful polymeric materials are not formed by chain-growth processes involving reactive species such as radicals, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as step-growth polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

Examples of naturally occurring condensation polymers are cellulose, the polypeptide chains of proteins, and poly(β-hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria. Formulas for these will be displayed below by clicking on the diagram.

Characteristics of Condensation Polymers

Condensation polymers form more slowly than addition polymers, often requiring heat, and they are generally lower in molecular weight. The terminal functional groups on a chain remain active, so that groups of shorter chains combine into longer chains in the late stages of polymerization. The presence of polar functional groups on the chains often enhances chain-chain attractions, particularly if these involve hydrogen bonding, and thereby crystallinity and tensile strength. The following examples of condensation polymers are illustrative.

Note that for commercial synthesis the carboxylic acid components may actually be employed in the form of derivatives such as simple esters. Also, the polymerization reactions for Nylon 6 and Spandex do not proceed by elimination of
water or other small molecules. Nevertheless, the polymer clearly forms by a step-growth process. Some Condensation Polymers

<table>
<thead>
<tr>
<th>Formula</th>
<th>Type</th>
<th>Components</th>
<th>Tm/°C</th>
<th>Tg/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyester</td>
<td>HO₂C-(CH₂)₃-CO₂H</td>
<td>&lt; 0</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HO-CH₂CH₂-OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyester</td>
<td>para HO₂C-C₆H₄-CO₂H</td>
<td>70</td>
<td>262</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dacon, Mylar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyester</td>
<td>meta HO₂C-C₆H₄-CO₂H</td>
<td>50</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HO-CH₂CH₂-OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polycarbonate</td>
<td>(HO₂C-C₆H₄)- (Bisphenol A)</td>
<td>150</td>
<td>267</td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyamide</td>
<td>X₂O (X = OH₂ or CO₂)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyamide</td>
<td>HO₂C-(CH₂)₃-CO₂H</td>
<td>45</td>
<td>265</td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyamide</td>
<td>H₂N(C₆H₄)₃N₂</td>
<td>53</td>
<td>223</td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyamide</td>
<td>Kevlar</td>
<td></td>
<td>300</td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyamide</td>
<td>para HO₂C-C₆H₄-CO₂H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“COCOCOOCOOCOOCO”</td>
<td>polyamide</td>
<td>meta HO₂C-C₆H₄-CO₂H</td>
<td>273</td>
<td>300</td>
</tr>
</tbody>
</table>

Contributors

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Jim Clark (Chemguide.co.uk)