

## Experiment 26E

FV-4-13-09

### LINEAR AND CROSSLINKED POLYMERS

**MATERIALS:** Resorcinol, 3 M NaOH, formalin, phthalic anhydride, anhydrous sodium acetate, ethylene glycol, glycerol, corn starch, Nylon 6,10 demo, ring stand, Bunsen burner or hot plate, 2 clamps, test tube (20 x 150 mm), 2 test tubes (16 x 125 mm), applicator sticks, weighing boat, polyvinyl alcohol solution, sodium borate solution, stirring rod, 20 mL graduated cylinder, 10 mL graduated cylinder, 2 beakers, 2 plastic beakers, thermometer.

**PURPOSE:** The purpose of this experiment is to study the properties of polymers.

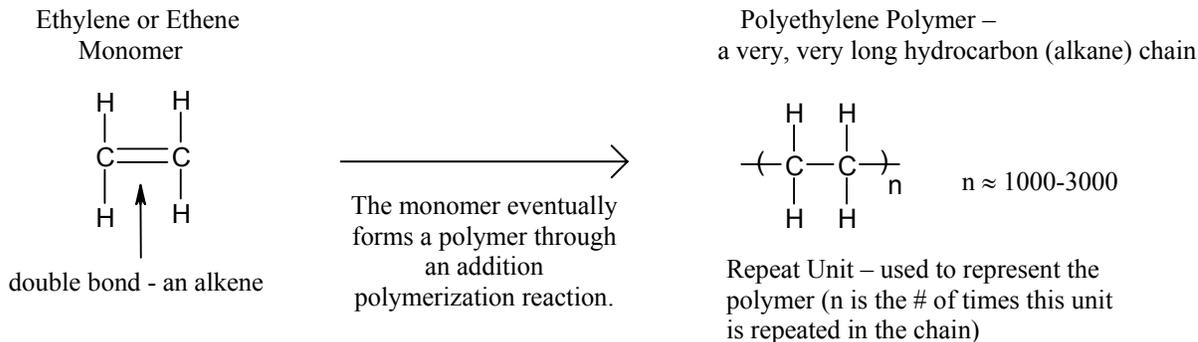
**LEARNING OBJECTIVES:** By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Understand the differences between linear and crosslinked polymers.
2. Compare and contrast the properties of polyester fibers.
3. Define the following terms: polymer, monomer, repeat unit, crosslinking, biopolymer.

**PRE-LAB:** Complete the Pre-lab assignment **before** lab.

#### DISCUSSION:

Polymers are extremely large molecules (molar masses from 1000 to greater than  $10^6$  g/mole) which result from chemically linking thousands of relatively small molecules called monomers. Dramatic changes in physical properties accompany this process. Monomers, due to their weak intermolecular forces, are either gases, liquids or structurally weak molecular solids. In a polymerization reaction, these are joined together to form larger molecules. As the intermolecular forces between the molecules increase, the mixture becomes more viscous. Eventually the molecules become so large that their chains become entangled. It is this entanglement of the individual polymer chains that gives polymeric materials their characteristic properties. A classic example of the changes accompanying polymerization is given by the conversion of ethylene to polyethylene (PE). Ethylene,  $\text{CH}_2\text{CH}_2$ , is a gas at room temperature while polyethylene is a rigid plastic used widely as storage containers.



While chain entanglement is a common structural feature in all polymeric materials, other structural features give different polymers their unique properties (Figure 1). These include: 1) the flexibility and microstructure of individual polymer chains, 2) the strength of interchain forces and, most importantly, 3) the presence of crosslinks (usually covalent bonds) between the polymer chains. Crosslinking restricts the ability of individual polymer chains to slide past each other. The result is a polymer with a three-dimensional network

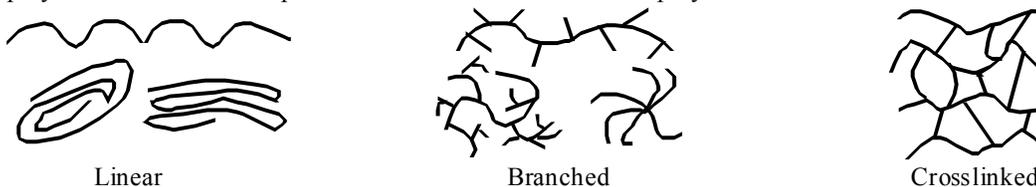


Figure 1: Types of polymer chain structures.

structure. Depending on the degree and type of crosslinking, various properties can be obtained. Low crosslink density materials, such as elastomers (e.g., rubber bands), are elastic and deformable. Highly crosslinked materials, such as Bakelite (used in pot handles and billiard balls), are more rigid and brittle. Temporarily crosslinked materials behave as viscous, liquid-like gels.

To illustrate the effect of crosslinking, consider linear and crosslinked polyesters. These polymers consist of ester functional groups (Figure 2) along the backbone chain. Examples of linear polyesters you may recognize include Dacron (fabric), Mylar (transparent sheet plastic), Kodel ("blister" packaging material), and Lexan (bullet-proof glass). Interestingly, the linear polyester (polyethylene terephthalate or PET) used to make Dacron fabric is also used to make 2-liter soft drink containers. Crosslinked polyesters with which you may be familiar include glyptal resins. These are present in adhesives, paints, and serve as binding agents in composite materials.

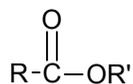


Figure 2: Ester functional group.

One chemical reaction which can be used to prepare polyesters is the condensation reaction of a carboxylic acid with an alcohol. In Figure 3, the initial reaction between one hydroxyl (OH) group on the dialcohol (ethylene glycol) and phthalic anhydride produces a molecule containing a carboxylic acid, an ester and an alcohol group. The carboxylic acid portion of this molecule can then react with another ethylene glycol molecule to produce a diester and a water molecule through a condensation reaction. The hydroxyl groups on the diester may react with more anhydride to extend the polymer chain. By repeating this process, a linear polyester is formed (Figure 4).

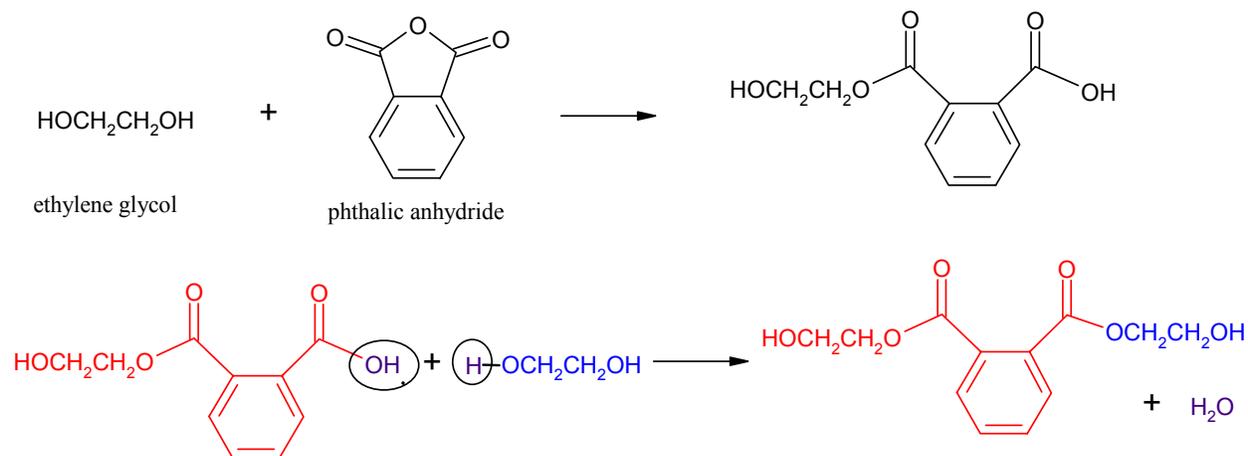


Figure 3: Initial reactions which eventually lead to the formation of linear polyester.

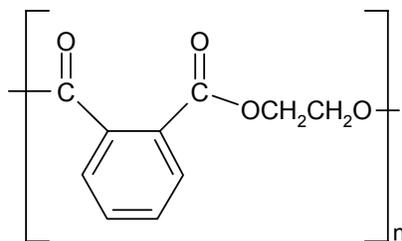


Figure 4: Repeat unit for linear polyester.

Crosslinked polyesters are formed by a similar process except that a molecule containing three or more hydroxyl (-OH) groups is used instead of a molecule containing two hydroxyl groups. The result is that even after two hydroxyl groups react to form the linear polyester, one hydroxyl group remains. Reaction of these remaining hydroxyl groups, from different polymer chains, with phthalic anhydride forms the covalent crosslinks between the polymer chains. Glycerol (which is also known as glycerine and shown in Figure 5), HOCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH, can be used to form the crosslinked polyester.

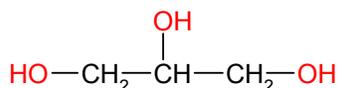


Figure 5: Structure of glycerol (with three hydroxyl groups, three sites for crosslinking).

Permanently crosslinked polymers are also known as thermosets. Once formed, thermosets do not remelt upon heating but can decompose at higher temperatures. In contrast, thermoplastics are polymers that may be softened by heat, reshaped, and cooled in a reversible physical process. They are typically linear or branched polymers with no crosslinks. In general, thermoplastics can be recycled.

Although permanent covalent crosslinks can form during a polymerization reaction to produce a network polymer, intermolecular forces can also link individual polymer chains to form a crosslinked system. For example, when a solution containing tetrahydroxyborate ion, B(OH)<sub>4</sub><sup>-</sup>, is added to an aqueous solution containing polyvinyl alcohol, (-CH<sub>2</sub>CHOH-)<sub>n</sub>, the borate ion forms crosslinks between the alcohol groups on adjacent chains (Figure 6). These crosslinks look like chemical bonds, but they are labile (temporary) polar covalent interactions. They are continually and rapidly breaking and reforming, so the viscous gel exhibits unusual properties intermediate of a solid and liquid.

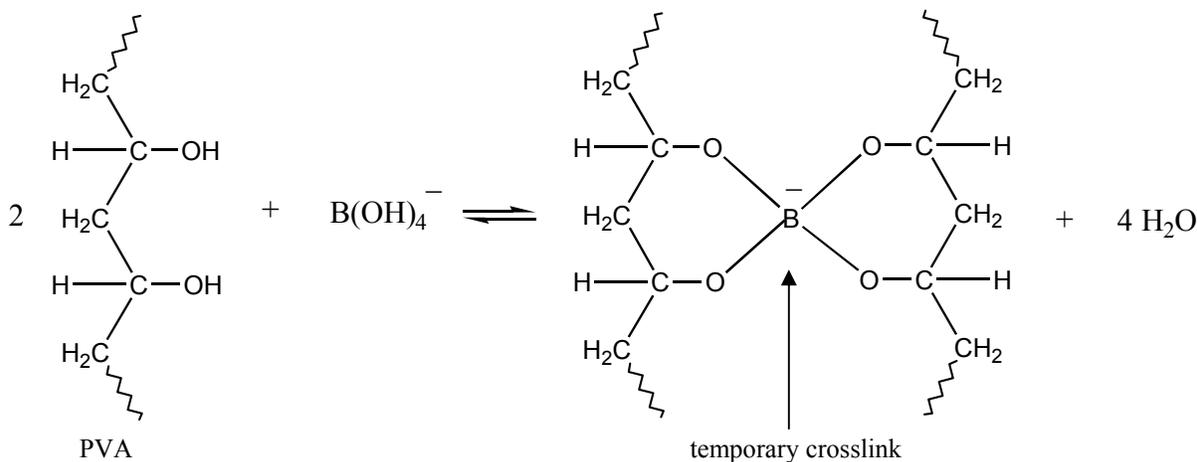


Figure 6: Crosslinking of polyvinyl alcohol with tetrahydroxyborate ion.

While many polymers are man-made (synthetic), including polyethylene, Teflon, Kevlar, and nylon, many natural polymers, or biopolymers, also exist. Biopolymers include fibers such as cotton, wool, and spider silk, as well as proteins, polysaccharides, and DNA in our bodies. Like polymers, biopolymers consist of many repeating units however these are not always the exact same unit. For example, proteins are made up of different amino acids connected together to form a long chain. In this experiment, you will observe the unusual properties of a mixture of corn starch and water. At an appropriate concentration, this mixture behaves quite differently than other solutions. Starch is a complex carbohydrate composed of polysaccharides (long chains of glucose units) and is typically used as a thickening agent in cooking and in the manufacturing of adhesives, paper, and textiles.

## PROCEDURE:

### Part A. Synthesis of a Linear Polymer - Nylon 6,10

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1. Your instructor will demonstrate the synthesis of Nylon 6,10 which is a linear polymer that can be “drawn” (or pulled) into a fiber. As your instructor performs the demonstration, answer Question #1 on page E26E-7.

### Part B. Synthesis of Bakelite-type Plastic

1. Place about 5 g of resorcinol in a **large** test tube. Set the test tube in a beaker or Erlenmeyer flask to assist in adding the solids to the test tube.
2. Add 1 ml of 3 M NaOH and mix.
3. Add 5 ml of formalin and mix thoroughly.
4. For a water bath, place a beaker of water on a ring stand with wire gauze. Use a Bunsen burner to heat the water to 45-50°C. Check the bath temperature with a thermometer. Alternately, a hot plate could be used.
5. Place the test tube in the 45-50°C water bath and swirl the tube until all of the crystals dissolve. If swirling is insufficient, use a disposable wooden stick to carefully mix the contents. Do not leave the stick in the test tube while heating. When checking the temperature of the *water bath*, DO NOT place the thermometer in the test tube, only into the water.
6. When the solution is homogeneous, raise the temperature of the bath to 55°C and maintain this temperature for at least 10 minutes. Record your observations of this reaction in the table on page E26E-6.
7. Turn off the burner and allow the solution to cool within the water bath. The polymer must cool slowly to prevent cracking.
8. You have just prepared a highly crosslinked polymer similar to Bakelite. After it has cooled completely, your instructor can remove the solid by breaking the tube. Examine the material and record your observations. While you are waiting for the material to cool, start the next part of the experiment.

### Part C. Synthesis of Polyester Fibers

1. Label 2 **small** test tubes #1 and #2.
2. To *each* test tube, add 2.00 g phthalic anhydride and 0.10 g anhydrous sodium acetate. Set the test tube in a beaker or flask to aid in adding the solids.
3. To test tube #1, add 1.00 g ethylene glycol.
4. To test tube #2, add 0.90 g glycerol.
5. Clamp the 2 test tubes to the same ring stand to heat them simultaneously. Do not use clamps with rubber grips since they might melt or burn. Point the test tubes away from people.
6. Using a Bunsen burner, slowly heat the test tubes to a gentle boil. Continuously move the flame as you heat the test tubes until the solids melt and the solutions are homogenous. Do NOT heat the tubes too quickly as the solutions may boil over or escaping gases may ignite.
7. Stop heating when the solution in test tube #1 turns a pale yellow color and the solution in test tube #2 just turns light orange. The heating times should be approximately 3 minutes for test tube #1 and 5 minutes for test tube #2 but these times will depend on the heat of the flame. Carefully observe the properties of each solution. Record your observations in the table on page E26E-6.



Answer Question #2 on page E26E-8.

8. Let the polyester samples cool and thicken for a few minutes. “Draw” a polyester fiber from each tube by using an applicator stick to obtain a drop of liquid from the tube. Touch another stick to the drop and then *slowly* pull the two sticks apart. You should be able to make a fiber at least 1 meter long. This process is similar to what is done in industry to make fibers. If your cooled solutions aren’t viscous enough, heat them a few minutes longer and try it again.
9. Experiment with drawing fibers. What method produces the longest fibers? Compare the fibers prepared from each test tube. Which one gave longer, stronger fibers? Which was more brittle? Record your observations.



Answer Questions #3 and #4 on page E26E-8.

#### Part D. Preparation of a Temporary Crosslinked Polymer

1. Using a graduated cylinder, add 20 mL of the Polyvinyl alcohol (PVA) solution to a small beaker.
2. Add 2-3 drops of methyl red indicator to the beaker. The indicator will be pink in the presence of excess acid and yellow in the presence of excess base.
3. To the beaker, add 5 mL of the sodium borate solution and mix the solution with a stirring rod. What happens? You've just prepared a crosslinked polymer which is sometimes known as "slime".
4. Pour off any excess liquid from the gel. Study the properties of this gel. Is it elastic? Does it stretch? Does it bounce? Record your observations in the table on page E26E-6.
5. To a small portion of the gel (about 2-3 mL) in a beaker, add 2 M HCl dropwise until the indicator turns pink. Mix well. What happens?
6. To the acidified gel, add 2 M NaOH dropwise and mix until the gel reforms. What color is the indicator?
7. Dispose of the gel in the proper waste container.



Answer Question #5 on page E26E-8.

#### Part E. Observing the Properties of a Biopolymer

1. Fill a plastic beaker approximately 1/4 full with corn starch (about 12 grams). Make a small well in the middle of the corn starch using a plastic stirrer.
2. Slowly pour about 10 mL of distilled water into the center of the corn starch and mix.
3. Carefully stir the mixture until it is uniform. The mixture should be quite viscous (and resist the forces of mixing). Add a little more water if undissolved solid still remains.
4. Observe the properties of this unique fluid. What happens when you mix the fluid quickly? What happens when you mix it slowly? Try tapping the top of the mixture with the stirrer; can you easily break through the surface? Apply more or less force and observe how the fluid reacts.
5. Move to a sink, and pour some of the fluid into the palm of your hand. How easily does it pour? Can it be rolled into a ball (this must be done quickly)? What happens after you roll a ball, then leave it alone? Why do you think this fluid is called a shear-thickening fluid?
6. Rinse the corn starch mixture down the sink with plenty of water. CLEAN UP YOUR MESS! Rinse out all glassware and *wash your hands before leaving lab.*

#### Clean-up:

1. Dispose of test tubes in the broken glassware container. Do not place paper towels in this container.
2. Wash all glassware. Return all equipment to their proper locations.
3. Wipe down your lab benches with a sponge to remove any spilled polymer.
4. Wash your hands before leaving lab.

Name \_\_\_\_\_

Section \_\_\_\_\_

Partner \_\_\_\_\_

Date \_\_\_\_\_

**DATA SECTION**  
**Experiment 26E**

**Part B. Synthesis of Bakelite-type Plastic**

Observations during reaction:
Properties of the final product:

**Part C. Synthesis of Polyester Fibers**

	Observations	
	Test Tube #1 - Linear Fiber	Test Tube #2 - Crosslinked Fiber
After heating:		
After drawing the fiber:		
After cooling the solid:		

**Part D. Preparation of a Temporary Crosslinked Polymer**

Observations/Properties of the gel:
Properties of the gel after adding HCl:
Properties of the gel after adding NaOH:

Name \_\_\_\_\_

Section \_\_\_\_\_

Partner \_\_\_\_\_

Date \_\_\_\_\_

**Experiment 26E****IN-LAB QUESTIONS**

1. Your instructor will demonstrate the synthesis of Nylon 6,10 for you. Write down your observations at the following points of the demonstration, then answer the questions that follow.

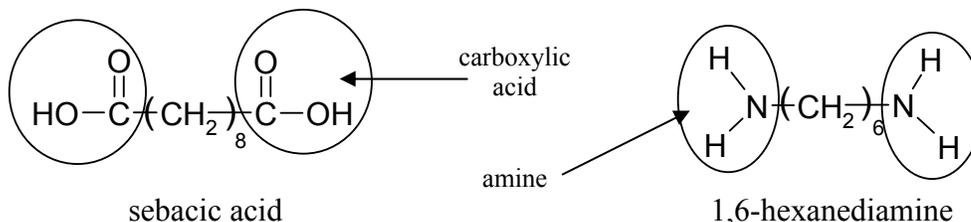
a. A solution containing 1,6-hexanediamine and a solution containing sebacic acid are carefully added to each other. Do these 2 solutions mix homogeneously? Are they miscible?

Observations:

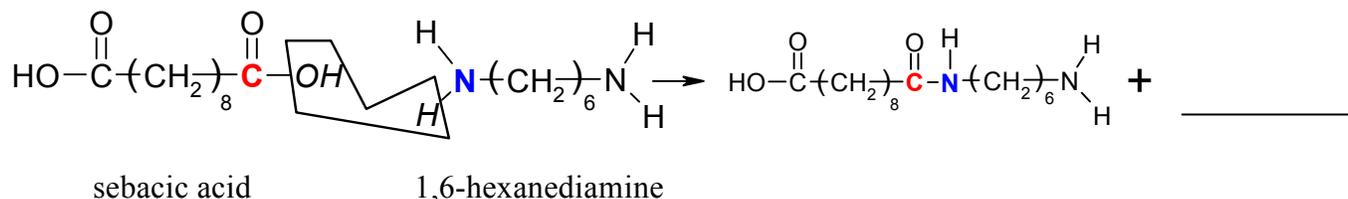
b. When the white material at the interface is grabbed by a pair of forceps, explain what happens.

Observations:

c. This reaction involves sebacic acid and 1,6-hexanediamine. Their structures are shown below with their organic functional groups labeled.



The reaction used to form Nylon 6,10 is known as a condensation reaction. Below is one step in the condensation process (the process repeats many times until a long polymer chain is eventually formed). What is the other product formed in this reaction?



d. Nylon 6,10 is one type of Nylon polymer. Nylon fibers are strong and used in clothing, ropes, and parachutes. List all the intermolecular forces present between the molecules of Nylon 6,10.

