

Experiment 26F

FV 1/8/08

PREPARATION AND RECYCLING OF LINEAR AND CROSSLINKED POLYMERS

MATERIALS: Resorcinol, 3 M NaOH, formalin, phthalic anhydride, anhydrous sodium acetate, ethylene glycol, Nylon 6,10 demo, fabric demo, ring stand, Bunsen burner, hot plate, test tube clamp, 2 test tubes (16 x 125 mm), applicator sticks, weighing boat, 10 mL graduated cylinder, beaker, thermometer, samples of PET, HDPE, LDPE and PS foam, glass microscope slides (2), polyvinyl alcohol solution, sodium borate solution, stirring rod, 20 mL graduated cylinder, 2 plastic beakers, thermometer

PURPOSE: The purpose of this experiment is to synthesize and study the properties of polymers, particularly as related to recycling.

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 recycling properties of linear and crosslinked polymers.
3. Compare the combustion properties of various types of material.
4. 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, CH_2CH_2 , is a gas at room temperature while polyethylene is a rigid plastic used widely as storage containers.

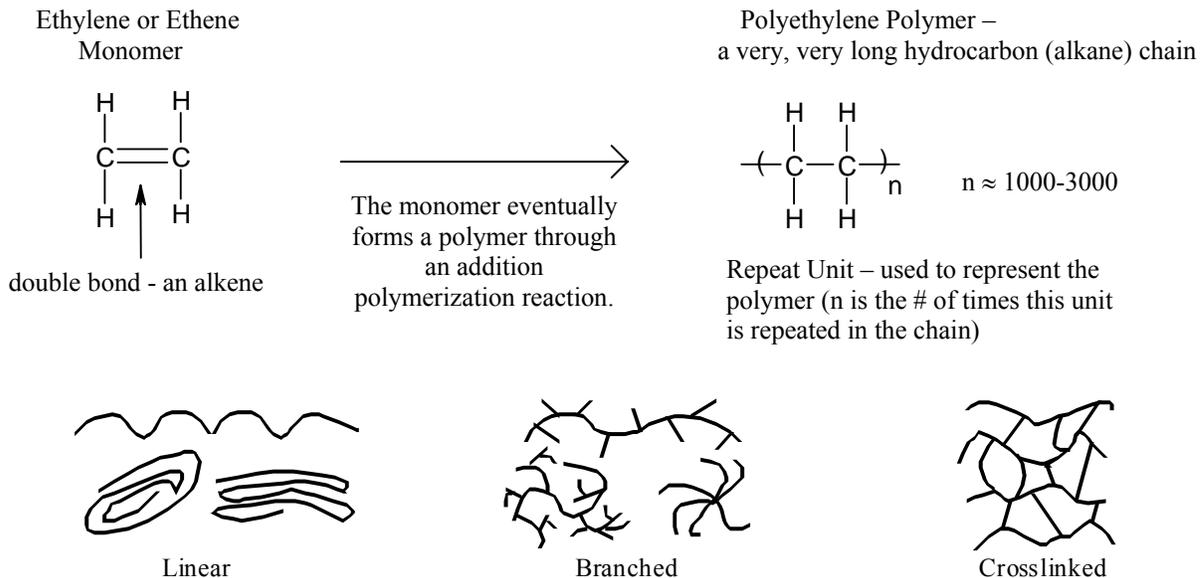


Figure 1: Types of polymer chain structures.

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 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.

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.

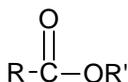


Figure 2: Ester functional group.

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).

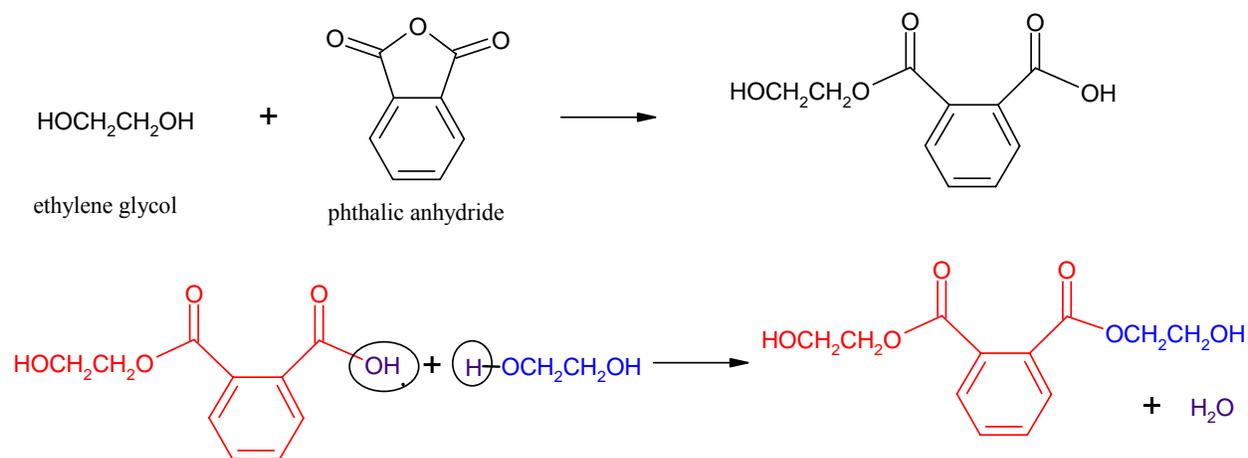


Figure 3: Initial reactions which eventually lead to the formation of linear polyester.

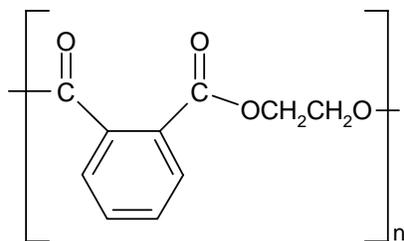


Figure 4: Repeat unit for linear polyester.

For a polymeric material to be easily recycled, it must be capable of one of two behaviors. The most easily recycled polymers can be softened by heat, reshaped, and cooled in a reversible physical process. They are called thermoplastics and are typically linear or branched polymers with no crosslinking between the individual chains. Some plastics can also be recycled by reversing the reaction used to form them, regenerating the monomers. This type of recycling applies primarily to polyesters and polyamides but is more costly than heating and reshaping. Permanently crosslinked polymers are also known as thermosets. Once formed, thermosets do not remelt upon heating but can decompose at higher temperatures. This is because the chains are joined by covalent bonds which cannot easily be broken.

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, $B(OH)_4^-$, is added to an aqueous solution containing polyvinyl alcohol, $(-CH_2CHOH-)_n$, 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.

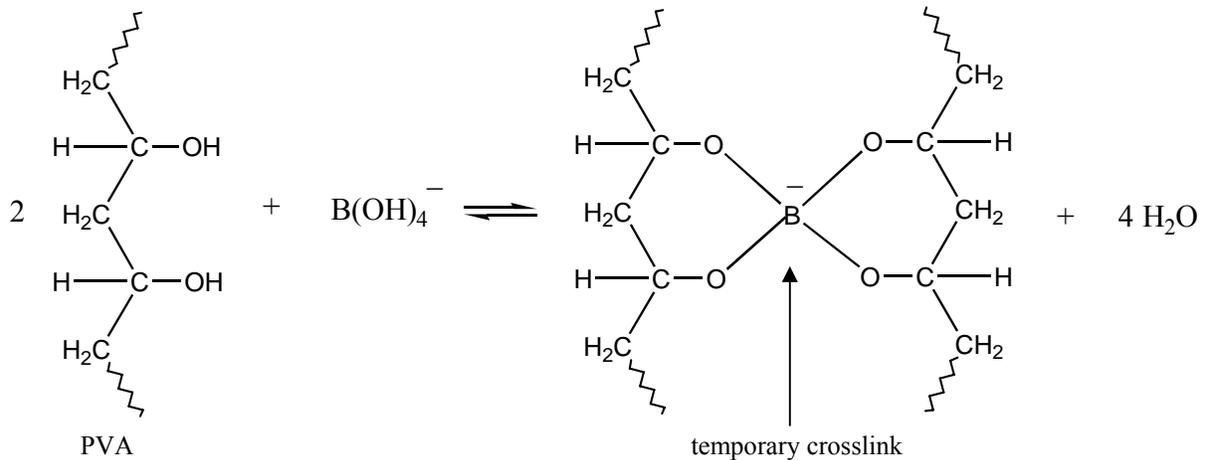


Figure 6: Crosslinking of polyvinyl alcohol with tetrahydroxyborate ion.

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 E26F-7.

Part B. Combustion of Polymeric Fabrics

1. Your instructor will burn several fabrics made from polymeric fibers. As your instructor performs the demonstration, make careful observations, including whether the flame was self-sustaining or self-extinguishing and whether the polymer melted during combustion. Record your observations on page E26F-6

Part C. Synthesis of Bakelite-type Plastic (One member of the group should carry out this reaction, while the other member prepares polyester.)

1. Place 2.5 g of resorcinol in a test tube.
2. Set the test tube in a 400 mL beaker containing 100 mL of water. This beaker serves as a water bath, cooling or heating the test tube as appropriate.
3. Add 10 drops of 3 M NaOH and mix, using a wooden stick.
4. Add 2.5 mL of formalin and mix.
5. Place the water bath and test tube on a ring stand equipped with wire gauze. Use a Bunsen burner to heat the water to 45-50°C. Check the bath temperature with a thermometer.
6. Mix the contents with the wooden stick until all the resorcinol dissolves.
7. When the solution is homogeneous, raise the temperature of the bath to 55°C and maintain this temperature until the mixture begins to thicken, approximately five to ten minutes. The mixture should reach about the consistency of molasses.
8. Quickly place a dollop of the thick mixture onto a microscope slide. If possible, pour the remainder into a small weighing boat.
9. Allow the Bakelite to cool until it hardens completely, fifteen minutes or more.
10. Examine the material and record your observations on page E26F-6.

Part D. Synthesis of a Linear Polyester

1. To a 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.
2. Add 20 drops of ethylene glycol and a boiling chip.
3. Clamp the test tube to a ring stand. Do not use clamps with rubber grips since they might melt or burn. Point the test tube away from people.
4. Using a Bunsen burner, slowly heat the test tube to a gentle boil. Continuously move the flame as you heat the test tubes until the solid melts and the solution is homogenous. Do NOT heat the tubes too quickly as the solution may boil over or escaping gases may ignite.
5. Heat gently for 8-10 minutes, keeping the solution at a low boil.
6. Let the sample cool for a few minutes, until it thickens to about the consistency of molasses. Transfer a dollop of the mixture to the same microscope slide as used in Part C. Keep the two samples from touching.
7. As the polyester cools, try drawing a fiber, using two wooden sticks.
8. Record your observations in the table on page E26F-6.



Answer Question #2 on page E26F-8.

Part E. Properties of Polymers

1. Cut small, about 5 mm square, samples of HDPE (high density polyethylene), LDPE (low density polyethylene), PS (polystyrene) and PET (polyethylene terephthalate ester). Place the samples on a clean microscope slide. Label the samples.
2. Place the microscope slide with the four samples AND the microscope slide containing the cooled Bakelite and polyester samples onto a cold hot plate.
3. Heat the hot plate to 100°C. Record your observations in the table on page E26F-6. After the hot plate has

- been at 100°C for 2 minutes, raise the temperature 25°C. Keep the temperature there for two minutes and record your observations. These observations may include changes in shape, color, phase, etc. Use a wooden stick to touch the samples and see how their properties are changing.
4. Continue to heat the samples, in 25 degree increments, until the hot plate is at 250°C. Record observations at each temperature.

Part F. 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 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 #4 on page E26F-8.

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 26F

Part B. Combustion of polymeric fabrics

Sample	Rayon	Acrylic	Vinyl	Nylon	Polyester
Observations					

Part C. Synthesis of Bakelite-type Plastic

<p>Observations during reaction:</p> <p>Properties of the final product:</p>

Part D. Synthesis of Polyester Fibers

<p>Observations during reaction:</p> <p>Properties of the final product:</p>

Part E. Recycling of Polymers

Sample/ Temperature	HDPE	LDPE	PS	PET	Polyester	Bakelite
100°C						
125°C						
150°C						
175°C						
200°C						
225°C						
250°C						

Part F. Preparation of a Temporary Crosslinked Polymer

Observations:

Name _____

Section _____

Partner _____

Date _____

Experiment 26F**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.

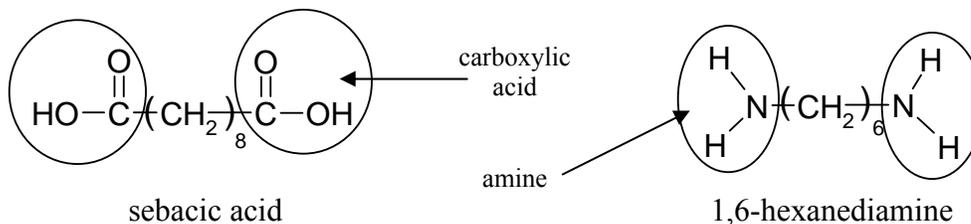
a. A solution containing 1,6-hexanediamine and a solution containing sebacic acid are carefully added to each other. Do these 2 solutions mix homogeneously? Are they miscible?

Observations:

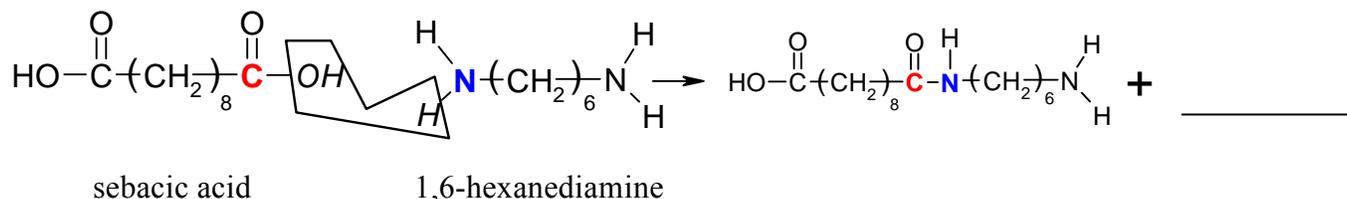
b. When the white material at the interface is grabbed by a pair of forceps, explain what happens.

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.

2. As the samples in Parts B and C were heated, you should observe the solutions becoming more viscous. Explain why this happens.

3. Linear polymers are usually thermoplastics. This means that they may be formed, melted and reformed any number of times. Crosslinked polymers, on the other hand, are thermosets; they retain the shape in which they were originally formed. Heating a thermoset will only cause it to burn (decompose), it will not melt or become malleable. From your observations in Part C, answer the following:

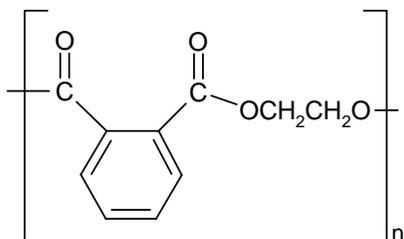
a. Which of the polymers tested are thermosets and which are thermoplastics?

b. Most soda bottles are made from PET (polyethylene terephthalate ester). Why are these bottles not re-used by sterilizing and refilling?

c. Why is HDPE a better choice for a milk bottle, which is filled with hot liquid, than PET?

d. From an environmental point of view, which are better, thermoplastics or thermosets? Explain why.

e. Polyesters, such as the one you prepared in Part C and PET, can be recycled by reacting the polymer with an alcohol, such as methanol. Write the products of this process.



Polyester

4. Why is this “slime” considered a *temporary* crosslinked system? Why do acid and base affect the properties of the gel?

For more information about polymers, go to <http://www.pslc.ws/macrog/maindir.htm>

Name _____

Section _____

Date _____

PRE-LAB QUESTIONS
Experiment 26F

Complete these questions prior to attending lab. Some of the results will be useful in conducting the experiment, so you should record those results in the appropriate section of the lab as well.

1. Which of the following are considered polymers or biopolymers? Select all that apply.

Glycerol

Teflon

Bakelite

Rubber Bands

Polyester

Proteins

Thermoplastics

DNA

2. How is polyethylene $(-\text{CH}_2-\text{CH}_2-)_n$ formed?

3. What is the difference between HDPEs and LDPEs?

4. For polymeric materials to be easily recycled, they must be capable of one of two behaviors. List the two required behaviors.

5. In this experiment, you will be synthesizing a linear polyester fiber using *phthalic anhydride* and *ethylene glycol*. Draw and label each of the structures below.