POLYMERS - LINEAR AND CROSSLINKED POLYESTERS

MATERIALS: Phthalic anhydride, anhydrous sodium acetate, ethylene glycol, glycerol, ring stand, Bunsen burner, 2 clamps, 2 test tubes (16 x 125), applicator sticks, weighing boat.

PURPOSE: The purpose of this experiment is to study the properties of polyester fibers.

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

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

DISCUSSION:

Polymers are extremely large molecules (molar masses can be > 1,000,000 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. As these are joined together into intermediate-sized molecules, attractive forces between the molecules grow and the mixture becomes more viscous. Eventually the molecules become so large that they become entangled. It is this entanglement of the individual polymer chains that give polymeric materials their characteristic properties. A classic example of the changes accompanying polymerization is given by the conversion of vinyl chloride to polyvinyl chloride (PVC). Vinyl chloride, CH_2CHCl, is a gas at room temperature while polyvinyl chloride is a rigid plastic used widely in household plumbing.

While chain entanglement is a common structural feature in all polymeric materials, other structural features give different polymers their unique properties. 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 (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 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 crosslinked polyesters, are more rigid than linear samples.

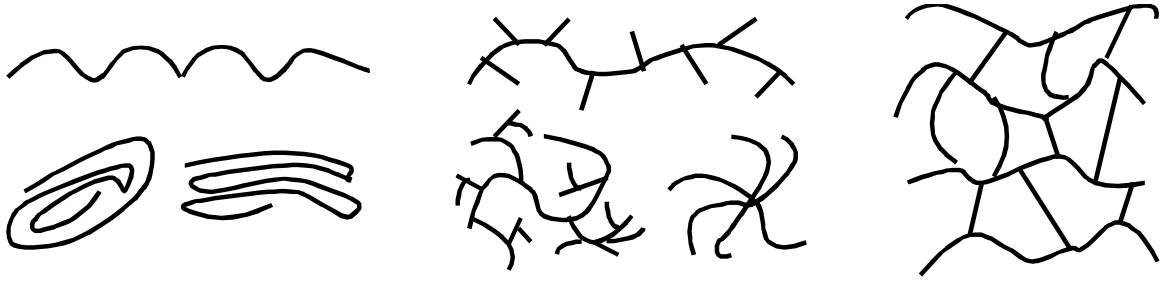


Figure 1: Types of polymer chain structures

In this experiment, linear and crosslinked polyesters will be prepared and compared. A polyester is a polymer with an ester functional group (Figure 2) in its backbone chain. Examples of linear polyesters with which you may be familiar include Dacron (fabric), Mylar (transparent sheet plastic), Kodel ("blister" packaging material), and Lexan (bullet-proof glass). Interestingly, the linear polyester (polyethylene terephthalate) used to make Dacron fabric is also used to make 2-liter soft drink containers. Crosslinked polyesters with which you may be familiar include the glyptal resins. These are present in adhesives, paints, and serve as binding agents in composite materials.

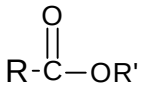
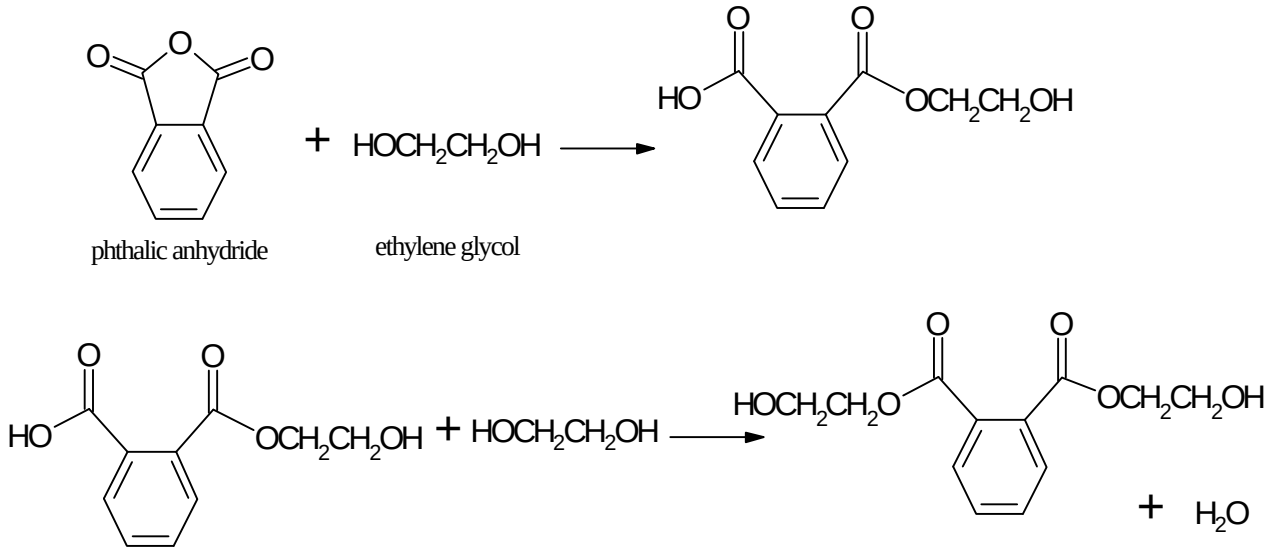


Figure 2: Ester functional group

One chemical reaction which can be used to prepare polyesters is the condensation of a carboxylic acid anhydride with a polyalcohol. This is illustrated for the reaction between phthalic anhydride and ethylene glycol in Figure 3. Initial reaction between one hydroxyl (OH) group on the dialcohol (ethylene glycol) and the 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 an H_2O molecule. The hydroxyl groups on the diester may react with more anhydride to extend the polymer chain. By this process, linear polyesters are formed.

Figure 3: Initial reactions leading to the formation of 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 hydroxyl groups, from different polymer chains, with phthalic anhydride forms the crosslink between the polymer chains. Glycerol (which is also known as glycerine), $HOCH_2CH(OH)CH_2OH$, will be used to form the crosslinked polyester in this experiment.

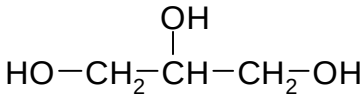


Figure 4: Structure of glycerol

PROCEDURE:

1. Label two test tubes #1 and #2.

2. To <u>each</u> test tube, add 2.00 g phthalic anhydride *and* 0.10 g anhydrous sodium acetate.

3. To test tube #1, add 0.89 g glycerol.

4. To test tube #2, add 0.98 g ethylene glycol.

5. On a ring stand, clamp the test tubes side by side to heat them simultaneously. Do not use clamps with rubber grips since these might melt or burn. Angle the test tubes slightly and point them away from people.

6. Using a Bunsen burner, carefully heat both tubes to a <u>gentle</u> boil. Continuously sweep the flame between the 2 tubes until the solutions are homogenous. Carefully observe the color of each solution. When the solution turns to a pale yellow color, stop heating it. The heating times should be about 3 minutes for test tube #1 and 5 minutes for test tube #2. Record your observations in the table on page E26C-4.

7. Let the polyester samples cool 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 polymer fiber at least 1 meter long! This process is analogous to the process by which polyester fibers are formed industrially.

8. Experiment with your technique of drawing fibers. What procedures result in the longest fibers? Compare similar diameter fibers prepared from the two test tubes. Which polymer gave longer, stronger fibers? Which was more rubbery and which was more brittle? Record your observations.

9. After the tubes have cooled for at least one hour, wrap them in paper towels and gently tap with a hammer to examine the samples. Wash off any glass clinging to the solids. Compare the 2 materials. Which was more rubbery and which was more brittle? Record your observations.

Name _____ Section _____

Partner _____ Date _____

OBSERVATIONS
Experiment 26C

	Material in Test Tube #1	Material in Test Tube #2
After heating:		
After drawing the fiber:		
After cooling the solid:		

(circle your answer)

Test Tube #1 contained:	Linear Polyester	Crosslinked Polyester
Test Tube #2 contained:	Linear Polyester	Crosslinked Polyester

Questions

1. a. As the samples are heated, you should observe vapor escaping from the top of each test tube. What is this vapor?

   b. You should also observe the solutions becoming more viscous. Why?

2. What do you think is happening to the individual polymer chains as the fiber is being drawn?

3. Compare the fibers from test tubes #1 and #2. What difference in the molecular structure of these materials accounts for their different properties?

4. Based on the starting reagents, explain why one of the polyesters synthesized was linear and the other was crosslinked.

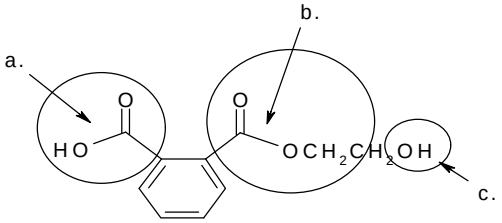
5. Linear polymers are usually thermoplastics. This means that they may be formed, melted and reformed any number of times. Crosslinked polymers, on the other hand, are thermosets; they retain the shape in which they were originally formed. Heating a thermoset will only cause it to burn (decompose),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

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

Name _____ Section _____ Date _____

EXPERIMENT 26C
Prelab Questions

1. Name each of the functional groups circled in the structure below. Refer to page 958 in McMurry & Fay.

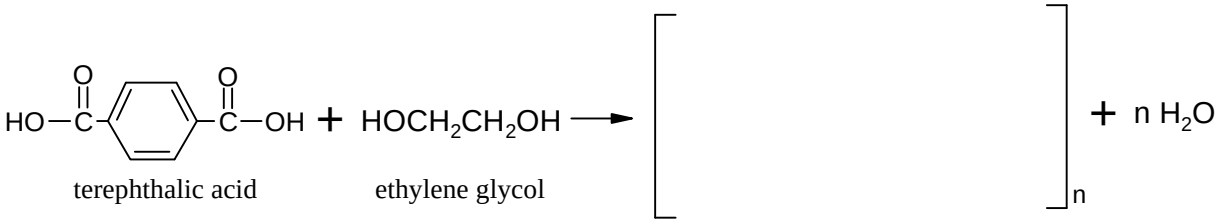


a. _____

b. _____

c. _____

2. Polyethylene terephthalate (PET) is a linear polyester used in the manufacturing of soft drink bottles. If you look on the bottom of your plastic drink bottle, you should see the recycling code for PET (1). Synthesized from terephthalic acid (a diacid) and ethylene glycol (a dialcohol), PET is formed by a number of linkages with water eliminated at each step. This reaction is known as a condensation reaction. Draw the repeat unit for PET below. Refer to page 977 in McMurry & Fay.



terephthalic acid ethylene glycol

Repeat Unit

3. a. Go to the following web site and find 3 uses for polyesters:

http://www.psrc.usm.edu/macrog/index.htm (The Macrogalleria - level 2)

i.

ii.

iii.

b. Why does peanut butter come in shatter-proof jars but jelly usually does not?