Experiment 26Dx

FV 11/22/03

LINEAR AND CROSSLINKED POLYMERS

MATERIALS: Polymer demos (sodium polyacrylate, polyurethane, silicone polymer, happy/sad balls, beads), 4% polyvinyl alcohol solution, 4% sodium borate solution, wooden stick, 50 mL disposable beaker, 5 mL disposable beaker, cross polarizers, acetate film, cellophane tape, plastic bag, polymer examples, trash bag.

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

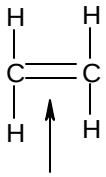
LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Understand the differences between linear and crosslinked polymers, and their properties.
2. Define the following terms: polymer, repeat unit, crosslinking.

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 attractive 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 give 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.

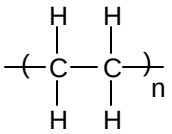
Ethylene or Ethene Monomer



double bond - an alkene

The monomer eventually forms a polymer through a polymerization reaction.

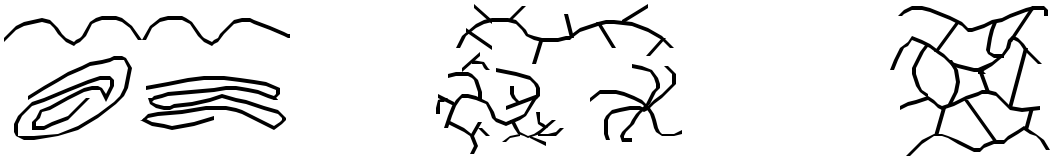
Polyethylene Polymer – a very, very long hydrocarbon chain



$n \approx 1000\text{-}3000$

Repeat Unit – used to represent the polymer (n is the # of times this unit is repeated in the chain)

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. Temporarily crosslinked materials behave as viscous, liquid-like gels.



Linear Branched Crosslinked

Figure 1: Types of polymer chain structures.

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 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 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.

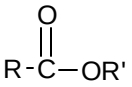


Figure 2: Ester functional group.

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).

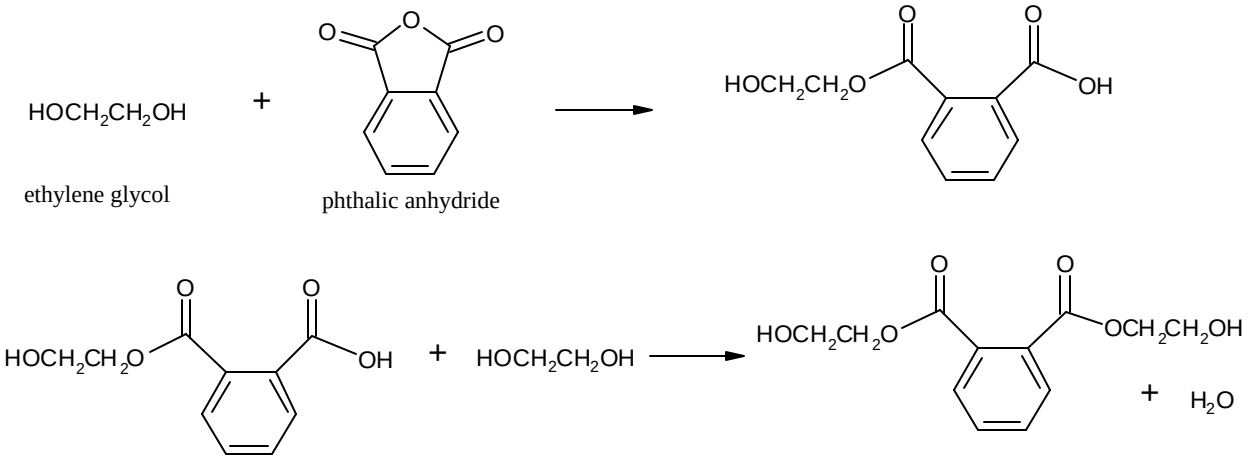


Figure 3: Initial reactions leading to the formation of linear polyester.

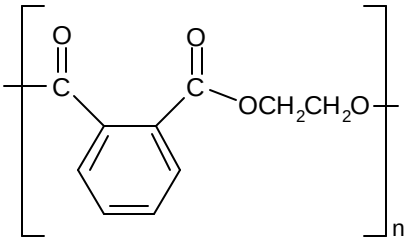


Figure 4: Repeat unit for linear polyester.

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), $HOCH_2CH(OH)CH_2OH$, can used to form the crosslinked polyester (Figure 5).

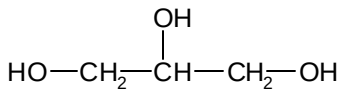
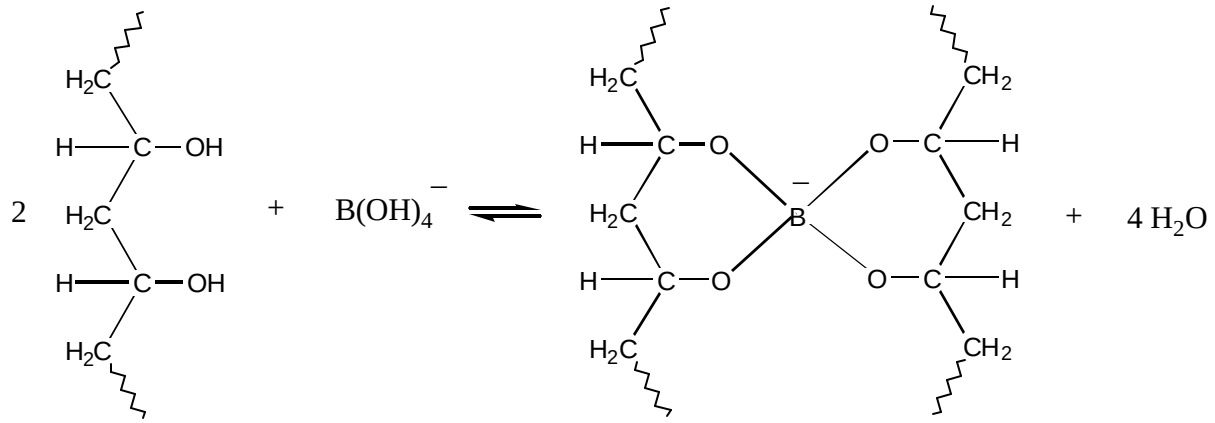


Figure 5: Structure of glycerol (with three hydroxyl groups, sites for crosslinking).

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.



PVA

Figure 6: Crosslinking of polyvinyl alcohol with tetrahydroxyborate ion.

Permanently crosslinked polymers are also known as thermosets. Once formed, thermosets will not remelt upon heating and will decompose at high 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.

PROCEDURE:

Part A. Polymer Demonstrations

1. Your instructor will demonstrate some polymer properties for you (sodium polyacrylate, polyurethane, silicone polymer, rubber balls). Pay attention, then answer Questions #1 and #2 on page E26D-5.

Part B. Preparation of a Temporary Crosslinked Polymer

** Work with a lab partner for Parts B, C, and D.*

1. To a 50 mL disposable beaker, carefully add 20 mL of the polyvinyl alcohol (PVA) solution. Use the graduations on the side of the beaker to measure the amount.
2. Answer Question #3 on page E26D-5.
3. To a small disposable beaker, carefully add 5 mL of the sodium borate solution (crosslinking agent). This amounts to almost filling the small beaker (about 4/5 full).
4. Add the sodium borate to the PVA in the large beaker. Mix the solution with a wooden stick. What happens? You've just prepared a crosslinked polymer which is sometimes known as "slime".
5. Answer Question #4 on page E26D-5.
6. All materials can be disposed in the trash bag provided.

Part C. Optical Properties of Polymers

1. Obtain an acetate sheet and a piece of a plastic bag from your instructor.
2. Using the shared rolls of cellophane tape, add pieces of tape (up to 5 strips) to the top of the acetate sheet to form a pattern (different directions, different thicknesses, layers).
3. There are 2 sets of polarizers for your class. You might have to wait until a set is available (or do Part D first). Obtain a set of polarizers (2 squares). Polarizers allow light of a certain orientation (or directionality) through them. Layer the 2 polarizers and rotate them. Notice when the two polarizers are aligned (maximum light passes) and when the polarizers are crossed (minimum light passes).
4. Put your acetate sheet <u>between</u> the crossed polarizers and view them with a light source behind. Rotate the polarizers. What do you observe?
5. View a piece of a plastic bag through the crossed polarizers <u>as</u> you stretch the bag. You may need more than one set of hands to accomplish this. What do you observe? If you have other clear plastics, you might see stress lines or areas of polymer chain orientation when placed between crossed polarizers.
6. Answer Question #5 on page E26D-5.
7. The acetate sheet and bag can be thrown away. Return the polarizers to your instructor.

Part D. Polymers and Recycling

1. Obtain the bag of polymer examples. Look at each of the materials carefully and notice the recycling code on the bottom of each piece (usually a triangle with a number in it, sometimes accompanied with an abbreviation).
2. Each of these numbers refers to the type of plastic that was used to manufacture the piece. It helps in recycling since processing common materials is more cost effective than mixtures.
3. Answer Question #6 on page E26D-5.

Name _____ Section _____

Partner _____ Date _____

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IN-LAB QUESTIONS

1. Gardeners sometimes add a superabsorber (polyacrylamide spikes) to soil in their gardens. Why do you think this is done?

2. Explain why one ball bounces and the other one does not.

3. In your beaker, you have an aqueous solution of polyvinyl alcohol (PVA), a linear polymer. Describe the properties of this solution of linear polymer. Write out the structure for the repeat unit for PVA.

   Observations: Repeat Unit for PVA :

4. Describe the properties of the temporary crosslinked polymer you created. Is it elastic, stretchy, bouncy? How is it different from the linear polymer? You may touch the gel, but wash or wipe your hands after handling (it doesn't contain toxic materials).

   Observations:

   If acid is added to the gel, it will become less viscous and the network disappears somewhat. If base is added, the network will reform. Explain why this occurs.

5. The effect you saw is known as birefringence (or double refraction) and it is observed when polymer chains align. Materials that have aligned domains will rotate polarized light.

   With the acetate sheet with tape, how many different colors did you observe as you rotated the polarizers?

   Why were different colors seen?

6. Identify one of the polymer products based on its recycling code and abbreviation.

   Describe the product: Recycling code or abbreviation:

   What is the polymer?

   In general, what can be recycled, thermoplastics or thermosets? Explain why.