EXPERIMENT 10

Formation of Esters and Polymers

INTRODUCTION

Esters are widely distributed in nature and have various functions in the organisms that make them. The fragrant aromas from many fruits and flowers are esters. The aromas may function to attract insects and other animals to promote pollination or distribution of seeds so that plant species may have a wider distribution on earth. The fats and oils stored in plants and animals are also esters. Fragrances in perfumes are often esters synthesized in the laboratory.

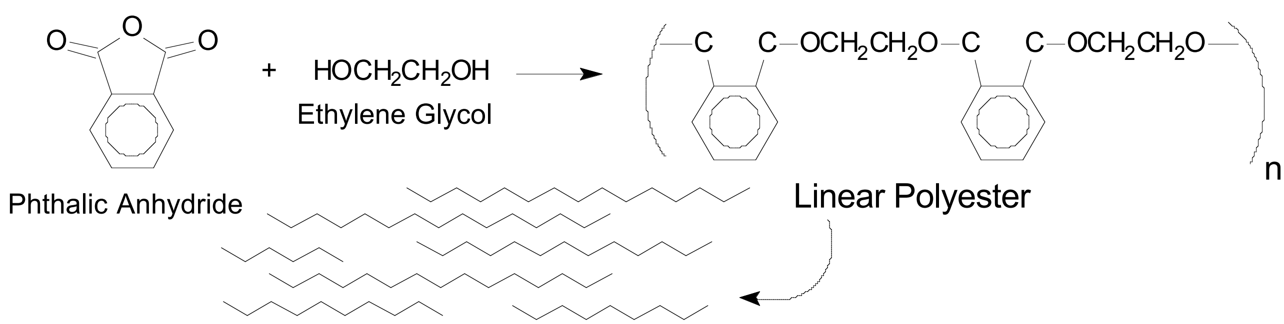
Aspirin is an ester made by combining acetic acid (found in vinegar) with salicylic acid (from willow bark). Salicylic acid has both an acid functional group and an alcohol (or more specifically phenol) functional group. This means the salicylic acid can form esters with either another acid (through combination with the phenol group, as in aspirin) or with another alcohol (through combination with the acid group, as in methyl salicylate). In this experiment you will hydrolyze the aspirin and form a new ester by combining methanol with the acid group to form methyl salicylate or oil of wintergreen, as shown below.

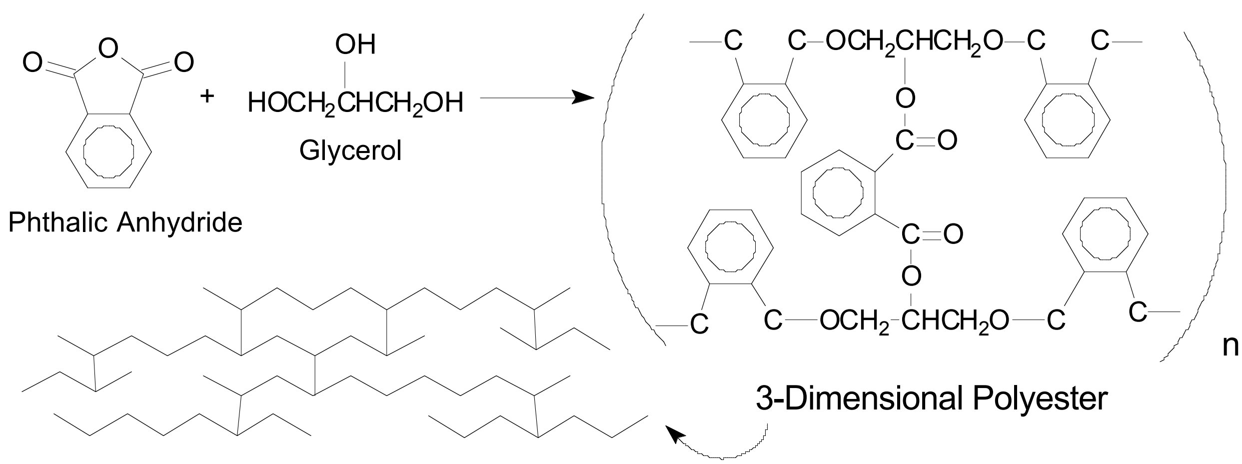
Aspirin doesn't have any particular fragrance, mainly because it doesn't evaporate very well (it decomposes before boiling). The essence (aroma) of wintergreen, or methyl salicylate, is more volatile (evaporates slowly) giving off a characteristic aroma. What commercial products contain methyl salicylate?

Concentrated sulfuric acid is a catalyst in this reaction, acting as a dehydrating agent to remove water.

Polymers are large molecules (macromolecules) that contain multiple units of smaller molecules, or monomers. Polymers may be natural or synthetic. Natural polymers are found in cotton, silk and wool that are processed to make fibers for textiles. In this laboratory you will prepare two synthetic **polyesters**, one a linear polymer and one a three dimensional polymer called glyptal. You will also prepare nylon, a **polyamide**.

Both polyesters are made by combining phthalic anhydride (a dehydrated form of phthalic acid) with a polyalcohol. The combination of an alcohol and an acid produces an ester upon dehydration (removal of water). In this experiment you will use ethylene glycol (a dialcohol) to form a **linear polymer** and glycerol (a trialcohol) to form a branched or **three dimensional polymer**. The reaction for the formation of each polymer is shown.





MATERIALS NEEDED

Aspirin tablets, methanol, concentrated sulfuric acid, phthalic anhydride (solid), sodium acetate (solid), ethylene glycol (liquid), glycerol (or glycerin, liquid), 2 disposable test tubes (ca. 18 x 180 mm), 2 small disposable aluminum cups, copper wire with hook on one end, 0.5 M 1,6-diaminohexane in 0.5 M NaOH, 0.2 M adipoyl chloride solution in hexane, dyes (optional, such as phenolphthalein solution or food coloring), large test tubes, 50 mL graduated cylinder, 400 mL beaker, 50 mL beaker, Bunsen burner.

PROCEDURE

Part 1. Preparation of Wintergreen from Aspirin.

Set up a 400 ml beaker half to two-thirds filled with water and heat it on a hot plate or over a burner with a low flame. Have the water bath hot to the touch, but it should not be near boiling. About 50 to 60°C is good.

Take one aspirin tablet and crush it into a powder with a spatula on a piece of weighing paper. Put the powdered aspirin tablet in a large test tube and add about 2 mL of methanol. Mix well. **Note: All of the aspirin tablet may not dissolve**. Then add several drops (about 8 or 10) of concentrated sulfuric acid to the test tube and mix well.

WARNING!!! Sulfuric Acid Causes Severe Burns

Warm the tube on a hot water bath (but don't boil the methanol) for about 10 minutes and smell the test tube occaisionally by wafting the air above the top of the test tube with your hand toward your nose. It should smell like wintergreen (similar to mint).

Caution: DO NOT stick your nose directly over the end of the test tube. Treat the test tube very carefully - it contains sulfuric acid. Never point the hot test tube toward anyone, including yourself. To smell the mixture in the tube, hold it several inches away from your nose and pass your hand over the top of the test tube, wafting the vapors toward your nose.

The ester vaporizes better if you pour it into a small amount of hot water in a small (50-100 mL) beaker. You can add hot tap water or a small amount of hot water (10-15 ml) from your water bath to a small beaker and then pour the reaction mixture from the test tube into the small beaker of hot water.

Part 2. Preparation of Polyesters

Add 5.0 g of phthalic anhydride in each of 2 large disposable test tubes (it is nearly impossible to get the test tubes clean after making these polymers). Now add 0.2 g sodium acetate to each of the test tubes and shake the 2 solids gently to mix them. To one test tube add 2.0 mL of ethylene glycol and to the second test tube add 2.0 mL of glycerol. The glycerol is very viscous, so make sure you get most of the 2.0 mL of this reagent mixed with the solid in the tube. Mount each test tube in a clamp on a stand or rack, tilting the tube at an angle so it is not pointing toward anyone. Gently heat each tube with a Bunsen burner. As the mixture begins to bubble, continue heating carefully until all the solids are dissolved or melted.

WARNING!!! Do not hold the burner directly under the end of the tube or the material may shoot out of the top of the tube. Heat the sides of the tube as well as the bottom.

Pour the liquid contents of each test tube into separate wells or aluminum cups and allow them to cool. You may want to put the aluminum cups on ice to cool them more quickly. When the samples have cooled, notice the difference in properties of these 2 polymers, even though they were made from similar materials.

Write down your observations in your notebook, indicating the physical properties of the polymers you have made and describe these properties of the polymers in the context of the starting materials that were used to make them.

Note: This last part of the experiment may be demonstrated by the instructor.

Part 3. Preparation of Nylon-66.

Nylon is a synthetic polyamide, meaning it is prepared from the combination of an organic acid and an amine. The numbering system for nylons indicates the number of carbon atoms in the chain of the acid and the amine, *i.e.*, nylon-66 contains 6 carbons in the acid and 6 carbons in the amine monomers that make the polymer.

CAUTION!! Avoid getting these solution on your skin. Wash your hands thoroughly after handling these materials.

Place about 15 mL of 1,6-diaminohexane solution in a 50 mL beaker. Put about 15 mL of adipoyl chloride solution in another beaker and carefully pour this solution down the inside of the beaker containing the diaminohexane, but avoid mixing the two solutions. There will be 2 layers of liquid in the beaker. A film should form at the interface of the two layers. This is the nylon polymer. Take a copper wire hook and gently free the polymer from the walls of the beaker. Hook the polymer near the center of the beaker and slowly raise the wire, twisting it as you raise it to form a continuous rope or thread of nylon. Fresh polymer will form at the interface of the two liquids as you remove some in making the thread. Make the fiber as long as possilbe. Rinse the rope well with water and let it dry on a paper towel. Examine the rope and write down in your notebook your observations regarding its ability to stretch, etc. Does this product resemble nylon rope you might buy in a store? Why do you suppose it is different?

Dispose of the reagents properly. Mix the remaining solution in the beaker to get all of the reagents to form polymer. Rinse this polymer with plenty of water and wrap it in a paper towel to dispose of it in the trash can. Pour the remaining solvents in the container for waste solvents in the hood.

Questions to Answer in Your Notebook:

1.* Aspirin is used to relieve pain and inflammation. Would you expect oil of wintergreen to have any of these properties? You should find information on the properties of oil of wintergreen (or methyl salicylate) and salicylic acid.

2.* Why is one polyester soft and the other hard when they cool? Explain in terms of the chemical structures of the two polyester molecules you made in the lab. (See the diagrams in the introduction).

3.* Why is there only a small amount of nylon in the solution at any given time, yet it seems you can continue removing it and more appears? What is going on in the solution to make new nylon as you pull out that which has already formed?