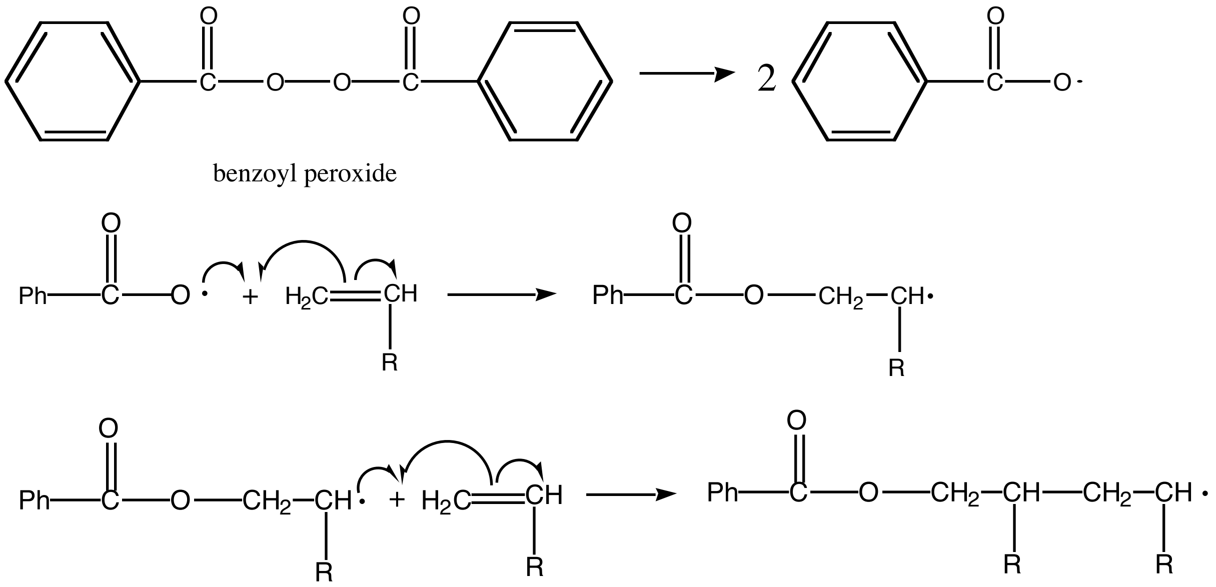
Experiment 16: Polymers

Products that are commonly referred to as “plastics” by the general public are known to chemists as *polymers*. A polymer is a *macro*molecule which consists of small molecular units that are repeated over and over again to form a long chain. The small molecular unit is called a *monomer*. In addition to synthetic polymers, such as, polyvinyl chloride, polystyrene, nylon and Teflon, we also find natural polymers all around us in the form of proteins and DNA.

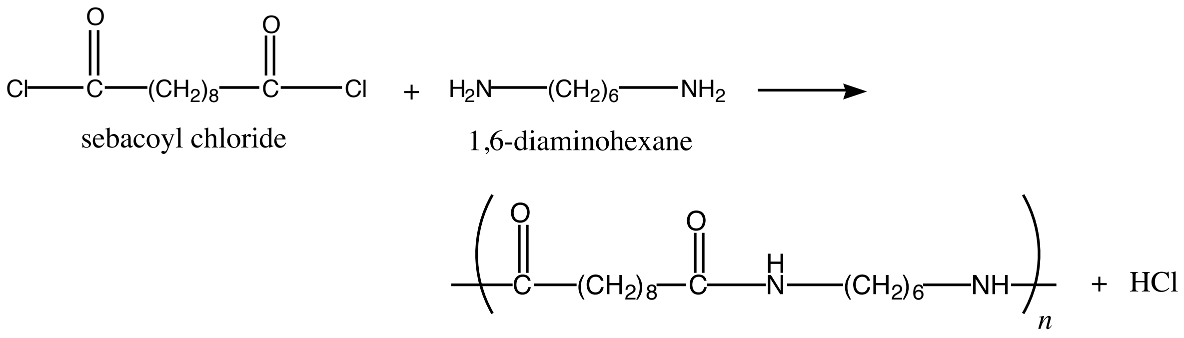
Polymers are synthesized in one of two ways. First, there are the *addition* polymers, which are formed by addition reactions that link together monomers containing multiple bonds. These polymers usually form via a free-radical mechanism in which the multiple bond is homolytically cleaved by light, heat or with the assistance of a radical initiator, such as benzoyl peroxide.



The second type of polymerization reaction produces *condensation* polymers, which are formed when monomers are linked together with the release of a smaller molecule, such as water or hydrogen chloride. The monomers in these cases must contain two or more functional groups. In all cases, when polymers are synthesized, the result is a mixture of long chain molecules of varying lengths.

Once the molecular chains are formed, it is possible for them to be joined to each other by covalent bonds through a process known as *crosslinking*. The properties of a crosslinked polymer differ markedly from those of the non-crosslinked variety, as you experienced when you made Slime® in the first lab period. The molecular chains in non-crosslinked polymers will usually slide across each other, especially when heated, so that the polymer softens and flows and can be molded to form a variety of shapes. Such polymers are called *thermoplastic* polymers. Crosslinked polymers are more rigid, hard and sometimes brittle and are referred to as *thermosetting* polymers.

You will carry out three different polymer syntheses for this experiment. Nylon 6.10 is formed by a condensation reaction between sebacoyl chloride (decanedioyl chloride) and 1,6-diaminohexane:

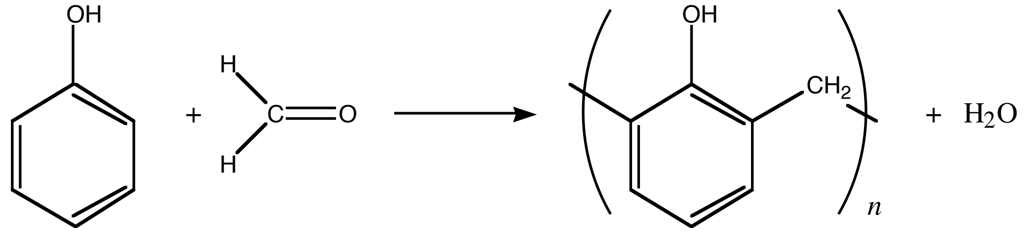


$$\mathrm{Cl{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}Cl} + \mathrm{H_2N{-}(CH_2)_6{-}NH_2} \longrightarrow \left(\mathrm{\overset{O}{\overset{\|}{C}}{-}(CH_2)_8{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}(CH_2)_6{-}NH}\right)_n + \mathrm{HCl}$$

Nylon 6.10

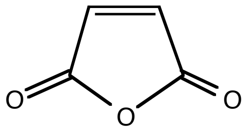
The amide bond which connects the monomers in the nylon molecule is the same kind of bond that is found in proteins where it is referred to as a peptide bond. In the preparation that you will perform, the polymer forms at the interface between two immiscible solutions and is drawn out as a long rope. Nylon is used in textiles, bristles and high impact sporting equipment.

The second condensation polymerization you will carry out is a reaction between phenol and formaldehyde to produce a polymer known as Bakelite (see mechanism at the top of the next page).

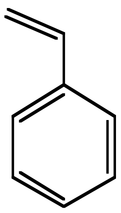


Bakelund performed this synthesis at the beginning of the twentieth century, producing the first synthetic polymer. Crosslinking occurs when the polymer is heated. Many years ago, Bakelite could be found in electrical plugs, switches and the handles of pots and pans.

Polystyrene, a polymer which foams readily and serves as a good insulator, is synthesized from styrene via a free radical polymerization. Instead of synthesizing polystyrene, you will prepare a *co-polymer*, an addition polymer which contains two different monomer units that are present in either a random or alternating arrangement, using styrene and maleic anhydride.



Maleic anhydride
M.W. 98.06
mp 54-56°C



Styrene
M.W. 104.15
bp 145-146°C

You will carry out this co-polymerization under free radical conditions with the help of the radical initiator benzoyl peroxide. Note that the styrene radical that is generated is stabilized by resonance delocalization, which is why styrene is such a good polymerization substrate (see bottom of next page). The properties of the resulting co-polymer will be different from those of

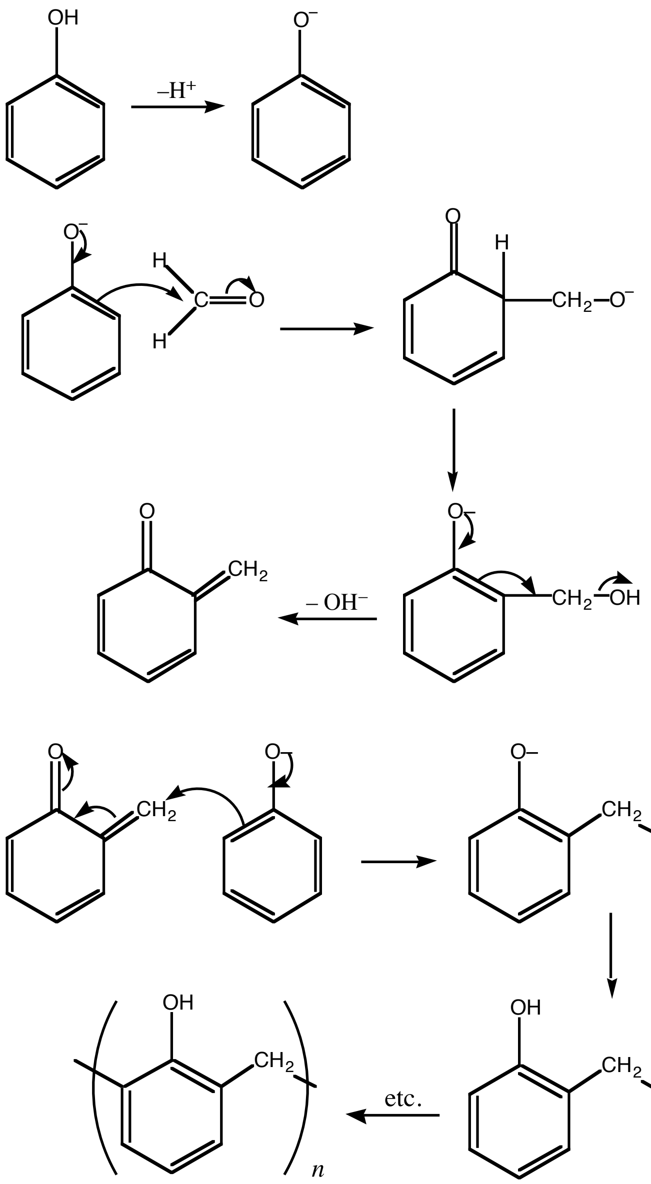


Figure 1. Mechanism for the formation of Bakelite

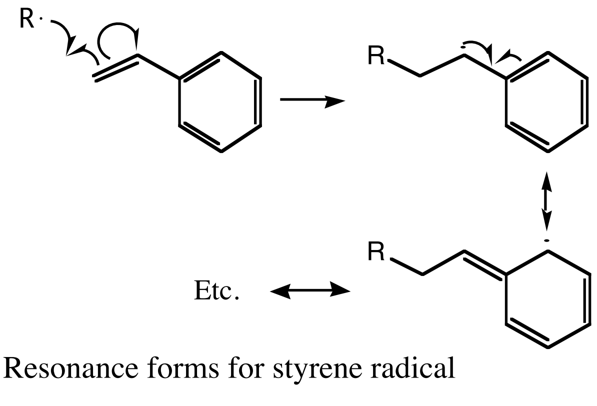


Figure 2. Resonance forms for styrene radical

polystyrene. The anhydride bonds can be hydrolyzed to form the sodium salt of the corresponding diacid, and the co-polymer is often coated onto cellulose acetate yarns in this form to reduce the buildup of static charge as well as to improve fiber adhesiveness and abrasion resistance.

Outline the steps of the following procedures.

Part 1. *Nylon by Interfacial Polymerization*

A solution has been prepared with a concentration of 0.59 M 1,6-diaminohexane **(contact hazard!)** dissolved in sodium hydroxide solution. Add 10 mL of this solution to a 50 mL beaker. Obtain 10 mL of a 0.29 M solution of sebacoyl chloride in hexane **(contact and vapor hazard! lachrymator!)**, and transfer it to the beaker by slowly pouring the solution down the interior wall. Allow the reaction mixture to stand undisturbed for about 1 minute as a white film of Nylon polymer forms at the liquid interface.

Do not pour any chemicals from this experiment down the sink since this will clog the drains!

Reach into the *center* of the beaker with forceps, and grasp the Nylon film at the interface. *Slowly*, pull up a polymer strand vertically out of the solution and wrap the top of the strand around the center of a large test tube (25 x 150 mm). Wind the Nylon thread around the test tube by rotating it, taking care to continue drawing the polymer strand from the *center* of the beaker at a steady rate. If the Nylon snaps, a fresh strand can be generated with the forceps; however, it should be possible to continue drawing an unbroken Nylon strand until the bulk of the reaction mixture has been consumed.

Rinse the excess solvent from the surface of the Nylon spool by rotating the test tube under a stream of tap water. Slide the Nylon from the test tube as an intact loop by inserting a metal spatula between the polymer and the glass surface. Observe the physical appearance and texture of the Nylon, and test the tensile strength of the wet Nylon by stretching the loop until it snaps. Lay the polymer on a paper towel to drain (blotting it between two towels will speed up the drying process). Remove a small amount of the polymer to test its solubility in toluene, acetone and methanol. Weigh the polymer now, then store it in your drawer and weigh it again next week.

Do not pour any chemicals from this experiment down the sink! In cleaning the reaction beaker and test tube, residual deposits of Nylon fiber may be removed satisfactorily by scraping with a metal spatula.

Part 2. *Condensation Polymerization of Phenol and Formaldehyde: Bakelite*

Caution! Phenol is a toxic substance and can cause serious burns. Wear gloves when handling and avoid contact with skin!

Formaldehyde is a suspected carcinogen and should also be handled with gloves.

Place 3.0 mL of liquefied phenol and 10 mL of 37% (by weight) aqueous formaldehyde solution in a 25 mL round-bottom flask. Add 1.5 mL of concentrated aqueous ammonia to the solution, and swirl the flask to completely mix the contents. Reflux the reaction mixture using a thermowell (it is important that it actually reach the boiling point). Watch the solution as you heat it and note when it becomes cloudy. Heat for 5 minutes beyond the point where it turns cloudy (about 15-20 minutes of reflux in total).

Pour the warm reaction mixture into the *test tube provided by your TA*. **Immediately wash out your round-bottom flask with acetone!** At this point, the solution in the test tube will consist mostly of a cloudy, upper layer and a smaller, darker, lower layer. Remove the cloudy upper layer using a Pasteur pipet and dispose of it in the appropriate **Byproducts jar**.

While warming the test tube over a steam bath, add acetic acid dropwise to the thick mixture. Stir the contents of the test tube with a wooden stick during this addition. Add the acid just until the solution is clear (1-2 mL). Avoid adding too much acetic acid. Plug a temperature probe into a hot plate, and heat a beaker of water to 60-65°C. Heat the mixture for 30 minutes in this water bath. Place the wooden stick in the center of the polymer in the test tube, and label the test tube **clearly** with your name, lab period and TA's name. Give the test tube to your TA, and it will be placed in an 80-85° oven. The polymer will be removed from the oven the next morning and returned to you in lab next week. At that time, you will break up some of the polymer into small pieces and test its solubility in toluene, acetone and methanol.

Part 3: *Synthesis of a Co-polymer of Styrene and Maleic Anhydride*

Caution! Styrene has irritating vapors. Use only in the fume hood. Avoid contact and keep it away from flames.

Maleic anhydride is corrosive and toxic.

Benzoyl peroxide is a flammable solid that may explode on heating or impact. Use only a small amount. Do not leave benzoyl peroxide in contact with paper, cloth or wood and clean all spills immediately with water.

In a *dry* 100 mL round bottom flask, mix 2.5 mL (4.6 g) of styrene with 1.5 g of maleic anhydride, 30 mL of toluene and 0.1 g of benzoyl peroxide (dispense using a plastic spoon). Swirl the flask until most of the solid material has dissolved (may still be somewhat cloudy) and add a boiling chip. Reflux the reaction mixture, using a thermowell, for 15 minutes. Note when a precipitate forms.

Allow the reaction mixture to cool to room temperature, then add 10 mL of methanol and stir with a glass rod. Collect the product by vacuum filtration, wash it with methanol, remove the boiling chip, and allow it to dry. Place the filtrate in the appropriate **Byproducts** jar.

Test the solubility of the polymer in toluene, acetone and methanol. Spread the polymer on a piece of filter paper or a watchglass and leave it in your drawer. Weigh the dry polymer next week.

Name ______________________________ Date ___________________________
T. A. ______________________________ Lab period _______________________

Results and Calculations (to be handed in two days after the next lab period)

Determine the limiting reagent in the reaction between 1,6-diaminohexane and sebacoyl chloride. Calculate the percent yield of nylon using the molecular weight of one repeating monomer unit for the weight of the product.

Was the weight of nylon a week later very different from the weight of nylon at the end of the lab period? Provide a possible explanation.

Assume that the co-polymer is a 1:1 mixture of styrene and maleic anhydride and draw the structure of the repeating monomer unit. Calculate the percent yield based upon the amount of maleic anhydride used. Again, use the molecular weight of one repeating monomer unit for the weight of the product.