Expt 2A and 2B: Synthesis of Polymers

INTRODUCTION

Polymers are large molecules (macromolecules) whose structure consists of repeating subunits. They occur widely in nature, for example cellulose, proteins or polypeptides and DNA, and can be prepared synthetically. It is no exaggeration to state that synthetic polymers have revolutionized modern life as plastics, synthetic fibers and resins are all examples of these types of materials. Synthetic polymers are valuable because their physical and mechanical properties are generally quite different from those of other substances, for example - strength, elasticity and the ability to be cast, stretched or molded into shapes and films. Car parts, furniture, packaging and construction materials, clothing and a myriad of toys, household objects and devices all contain plastics or polymers.

The repeating subunit from which a polymer is derived is called a "monomer" – polymers may be built up from a single monomer or from two or more monomers, in which case they are called copolymers. Polymerization is the chemical process by which monomers are covalently bound together to give the polymer chain. Polymerization reactions may be divided into two categories: (1) addition polymerizations, in which a π bond is broken in order to link two monomer units together (often alkenes) - this occurs without loss of any other molecule, so all atoms of the monomer are retained in the polymer; (2) condensation polymerizations, in which two monomers covalently bind with loss of a small molecule such as water or HCl - this is particularly common for co-polymerizations of two different monomers. In these lab experiments you will perform an example of each of these types of polymerization reactions: the addition polymerization of styrene to form polystyrene, the material used in styrofoam packaging; and the condensation polymerization of bisphenol A with epichlorohydrin to form an epoxy resin materials of this type have a wide variety of applications due to their high stability and chemical resistance.

In both of these polymers (and generally for all polymers) the physical properties are highly dependent on both the chain length of the polymer (how many monomers are linked together) and the microstructure of the chain (how exactly the individual monomers are covalently bound together). By controlling the polymerization conditions it is possible to produce polymers with variation in properties even from the same monomer, and for copolymerizations the exact ratio of the two monomers is critical for controlling the chain length and subsequent properties. These aspects will be explored briefly in this lab. One important difference between polymers and "normal" molecules is
that a particular polymer type (e.g. polystyrene) does not have a fixed molecular weight, as the length and therefore mass of each polymer chain will depend on the conditions under which it was made. Therefore for polymers we talk about the molecular weight range, whereas for small molecules with exactly known and fixed compositions we, of course, can calculate a precise molecular weight.

In the first half of this experiment, you will polymerize bisphenol A with epichlorohydrin, in a step-growth polymerization, to form an epoxy resin. Materials of this type have a wide variety of applications due to their high stability and chemical resistance. Epoxy resins are commonly used in repairs or bonding materials together.

**Part A: Condensation (step-growth) polymerization to form an epoxy resin**

**Week 1: Reaction of Bisphenol A with Epichlorohydrin to form an epoxy resin (BADGE)**

![Chemical structure of BADGE reaction](image)

In this polymerization reaction, a nucleophilic phenoxide anion derived from bisphenol A attacks epichlorohydrin to form an ether linkage. If both phenoxide ions of one bisphenol A molecule react then the resultant product is known as **bisphenol A diglycidyl ether** (or BADGE). This product also contains two reactive epoxide units at each end that can then react with further phenoxide anions and thus continue the growth of the polymer chain on both ends.

![Chemical structure of BADGE with reactive epoxide units](image)

The mechanism of the process begins with the formation of a dianion from the BPA:

![Formation of dianion](image)
This dianion is then able to act as a nucleophile and attack the epichlorohydrin, \( S_N2 \) style:

A second substitution reaction on the other anion results in the formation of BADGE:

Once BADGE has formed, other anions of BPA can continue to react on either end of the BADGE molecule, allowing the growth of the polymer to occur.

The resulting polymer is an example of a polyether (the main polymer chain contains ether linkages) and has epoxide end groups. In addition, the polymer chain has alcohol groups. For this polymer, the value of \( n \) depends on the molar ratio of the two monomers. For example, if the ratio of epichlorohydrin and bisphenol A is 2:1, then BADGE would be expected as the only product (i.e. \( n = 0 \)). The properties of the polymer depend on \( n \). The greater the value of \( n \), the harder the material that is formed. Different polymer chains can join together through cross-linking, for example by the alcohol group on one chain-reacting with the epoxide end group of another chain.

Often these cross-linking reactions are slow and occur on prolonged heating, a process known as “thermosetting”. Other compounds can also be added as cross-linkers to join
the chains together. In this way, a large variety of materials with widely varying properties can be easily synthesized.

The usefulness of bisphenol A (or BPA) in synthesizing plastics has led to its widespread use in many different applications but has also led to concerns about its safety, especially in containers or bottles for food and drink. Very small amounts of BPA may leach from a plastic container into the solid or liquid contents and the health effects, especially on infants and children, have come into question. For this reason, many manufacturers of baby bottles and toys have discontinued its use. Special care should be taken when using this compound in the lab, as it is known to be acutely toxic to aquatic life and is suspected of damaging fertility, although there is still uncertainty about its exact effects on humans.

EXPERIMENTAL PROCEDURE 2A- Condensation Polymer -
Linear epoxy resin formed from bisphenol A and epichlorohydrin

REAGENT/PRODUCT TABLE: Part A - Linear Epoxy Resin

<table>
<thead>
<tr>
<th>Reagents - Part A</th>
<th>MW (g/mol)</th>
<th>MP (°C)</th>
<th>BP (°C)</th>
<th>Density (g/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol A</td>
<td>228.29</td>
<td>158-159</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>92.52</td>
<td>-57</td>
<td>115-117</td>
<td>1.183</td>
</tr>
<tr>
<td>NaOH (aq)</td>
<td>40.00*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BADGE</td>
<td>340.42</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*mass of solute in solution

FOR YOUR SAFETY - Part A
1. Bisphenol A is toxic to aquatic life with a long lasting effects; suspected of damaging human fertility and the fetus. Avoid breathing dust.
2. Epichlorohydrin is hazardous and corrosive in case of skin and eye contact and inhalation.
3. Sodium hydroxide solution is corrosive.
4. Gloves and goggles must be worn for this experiment.

1. Set up a boiling water bath by placing ~150 mL deionized (DI) water in a 250 mL beaker with a couple of boiling stones on a hot plate set to about 6.

2. Obtain a large test tube (18 x 150 mm) and ensure that it is both clean and dry. Weigh out 1.14 g bisphenol A (BPA) on a weighing paper and carefully transfer the solid into your test tube. Record the mass of BPA in your notebook, along with observations of the BPA.
3. Add 5 mL of 2 M NaOH (aq) to the test tube, gently place a cork stopper in the top of the tube and agitate the tube to mix the contents.

4. Clamp the test tube in the boiling water bath from Step 1 so its suspended in the hot water bath (the BPA is slow to dissolve without heating). After 2-3 minutes heating, shake the tube (while holding the cork stopper firmly in place) to help the solid dissolve then return the test tube to the hot water bath. All of the solid should be dissolved after ~5 minutes of heating. Make a note of any color changes observed.

5. Once the solid BPA is dissolved and you have a clear solution, remove the test tube from the hot water bath and take it to the hood containing the epichlorohydrin. Remove the cork stopper and add 0.6 mL of epichlorohydrin to the solution of BPA using the syringe provided and then replace the cork stopper. Swirl the test tube gently to mix the contents. Record volume used and observation on epichlorohydrin.

6. Return the test tube to the boiling water bath, clamping it as before, and heat the solution for 1 hour. Make a careful note of any changes observed, especially in the first five minutes of heating. Swirl the tube occasionally during the heating period to ensure mixing. You may need to add extra DI water to your beaker to maintain the volume of water during the heating period.

7. After 1 hour, remove the test tube from the bath (it is easiest to use the clamp to hold the hot test tube and just remove it from the clamp holder). Quickly pour off the solution from the solid in the test tube into a beaker, marked as "aqueous waste".

8. Take 10 mL of hot water from your water bath (measure it into a graduated cylinder) and add the hot water to the test tube. Use a glass stirring rod to work the solid (smush it around) in the hot water so that it is properly washed, keeping the test tube suspended in the water bath during this process. Then pour off the water into your aqueous waste beaker.

9. Repeat Step 8 with a second 10 mL portion of hot water from your water bath.

10. Obtain a piece of weighing paper and while the solid in the tube is still hot, remove it from the tube using the hooked end of a microspatula and place it on the paper to cool and dry. You should (hopefully) find that the solid comes out in a single piece. Make a note of the consistency of the solid while it is hot.
11. Once the solid has cooled to room temperature, test the consistency of the solid again by prodding it with your spatula. Transfer the solid to a pre-weighed vial, reweigh and obtain the mass of polymer produced.

12. If your instructor requires it, chip a small amount of solid off your large piece and obtain an IR spectrum of it.

**WASTE DISPOSAL:** Aqueous washings should be placed in the designated aqueous waste container.

**Part B: Free radical (chain growth) polymerization of styrene to form polystyrene**

In the second half of this lab experiment, you will perform an example of an addition polymerization (chain-growth) in the polymerization of styrene to form polystyrene.

\[
\text{H}_2\text{C} = \text{CH} \quad \xrightarrow{\text{initiator}} \quad \text{CH}_2\text{CH}_n
\]

Simple alkenes are one of the most common types of monomer for polymerization reactions. Although they can be polymerized by ionic mechanisms, free radical polymerization is the most common method. In this part of the lab we will polymerize styrene to form polystyrene, which is made on a huge scale industrially (millions of tons) every year. Its primary uses are in packaging materials and in containers. One major issue associated with polystyrene is environmental. The material is very stable due to the strong, nonpolar covalent bonds that comprise the alkane polymer chain and so is very slow to break down in the environment (not biodegradable). This leads to build up of plastics in the ocean and other areas if it is not disposed of properly.

Free radical polymerization requires an *initiator*, a compound that breaks apart easily to form free radicals that then begin the chain growth process. These are usually compounds that contain a weak covalent bond that can be readily homolytically cleaved with either heat or light to form radicals. We will be using tert-butyl peroxybenzoate, which contains a weak peroxy, or -O-O- bond.
Many alkenes are so reactive towards this type of polymerization that the reaction may be initiated just by the presence of $O_2$ (easily converted to a free radical). To prevent this, the monomer must be stored long term at low temperatures and in the presence of an inhibitor, a compound that preferentially reacts with $O_2$ thus protecting the monomer. The amount of inhibitor is quite small, in the range 10-15 ppm. In this experiment, we will first remove the inhibitor from the styrene monomer before attempting the polymerization reaction. This is easily done, as the inhibitor is 4—tert-butyl catechol, which contains weakly acidic phenol groups. Reaction of 4-tert-butyl catechol with a strong base, and liquid-liquid extraction, allows removal of the deprotonated form of the catechol into the aqueous layer, allows removal of the deprotonated salt form in the aqueous layer.

Polymerization of alkenes can be done in the absence or presence of a solvent. In this lab, we will do the polymerization of styrene in the solvent xylenes (dimethyl benzene, in a mixture of ortho, meta and para isomers), at reflux so the initiator thermally decomposes, followed by precipitation of the polymer produced. This allows isolation of the polymer in the form of a powdery solid, which could then be processed further (heating and casting into a specific shape using a mold). The solvent-less method lends its more to the product of thin films or fibers.

**Initiator Breakdown:**

![Initiator Breakdown Diagram]

**Free radical polymerization mechanism:**

![Free radical polymerization mechanism Diagram]

In$\bullet$ = phenyl radical

**Inhibitor reactivity:**

![Inhibitor reactivity Diagram]
EXPERIMENTAL PROCEDURE 2B - Addition Polymerization of Styrene

REAGENT/PRODUCT TABLE: Part B - Polystyrene

<table>
<thead>
<tr>
<th>Reagents - Part B</th>
<th>MW (g/mol)</th>
<th>MP (°C)</th>
<th>BP (°C)</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>styrene</td>
<td>104.15</td>
<td>-31</td>
<td>145-146</td>
<td>0.906</td>
</tr>
<tr>
<td>xylene (mixture of isomers)</td>
<td>106.17</td>
<td></td>
<td>137-140</td>
<td>0.86</td>
</tr>
<tr>
<td>tert-butyl peroxybenzoate</td>
<td>194.23</td>
<td></td>
<td></td>
<td>1.021</td>
</tr>
<tr>
<td>methanol</td>
<td></td>
<td></td>
<td>148.5</td>
<td>0.791</td>
</tr>
</tbody>
</table>

FOR YOUR SAFETY - Part B
1. Styrene is a very hazardous compound in care of eye contact (irritant) and is hazardous in case of skin contact. Wear gloves at all times when handling styrene.
2. Xylenes are hazardous, in case of skin and eye contact (irritant).
3. Tert-butyl peroxybenzoate is an oxidizer and can cause fires on contact with flammable material. It is also hazardous in case of skin and eye contact (irritant).
4. Methanol is flammable and may cause eye and skin irritation.
5. Gloves and goggles must be worn for this lab.

Set up a sand bath in a small crystallizing dish on your stirrer/hotplate. The hotplate should be set at a heating setting of 5. Your sand bath needs to be stabilized between 120° and 130°C for the polymerization reaction. Periodically check your temperature by placing the thermometer into the sand bath, at an angle, being very careful not to touch the bottom of the crystallizing dish. If the thermometer overheats (i.e. touches the bottom of the crystallizing dish or any sand hotter than 140°), it will pop/explode! Your reaction temperature can also be controlled somewhat by movement of the sand towards your round bottom flask (increases the heat slightly) or away from the flask (decreases the heat slightly).

Important: Set up the minihood on your bench over the work area where you are handling styrene so as to minimize inhalation of styrene vapors.

Purification of styrene by removal of the inhibitor (4-tert-butyl catechol)
1. Get a large sample vial with a white cap (check that the plastic insert is in place in the cap so it seals properly) from your locker. Take it to the hood and obtain 3 mL of styrene from the hood and place in the sample vial then add 3 mL of aqueous 3M NaOH to the sample vial. Cap the vial and return to your station. Record amounts used in your lab notebook. Record starting material/reagent observations.
2. Shake the vial thoroughly **but not vigorously**. Shaking too hard will create an emulsion that will be difficult to separate. Let the layers separate and note the colors of both the organic (top) and aqueous (bottom) layers.

3. Using a Pasteur pipette, and by tipping the vial at an angle, carefully remove as much of the lower aqueous layer as you can and place it in a beaker labeled “aqueous basic waste”. Err on the side of caution—in both this step and Step 5—better to leave behind a bit of aqueous solution than remove any of the styrene top layer with the bottom aqueous layer.

4. Add 3 mL DI water to the styrene in the vial. Cap the vial tightly and shake thoroughly, but again, not vigorously.

5. Allow the layers to separate and again carefully remove the lower aqueous layer with a pipette (err again on the side of caution), placing this layer in your aqueous basic waste beaker also.

6. Begin to dry the styrene by adding 3 pellets of anhydrous CaCl₂ pellets. Cap the vial and allow it to sit for 1-2 minutes and check to see if a small new water layer has developed. If so, pipette the new water layer out before adding any more CaCl₂. After removing any possible new water layer, add another 10 pellets of CaCl₂. Allow the styrene to dry for at least 5 minutes or until the added CaCl₂ pellets are no longer clumping together and some are moving freely when shaken. Check that your styrene is clear, not cloudy. While it is drying, assemble your alumina column (Step 7).

7. Obtain a small piece of cotton and using a microspatula, push the cotton piece down into a short tipped Pasteur pipette so that it forms a plug at the point when the pipette narrows. Obtain about 1 g of alumina for your stationary phase and place it in the pipette on top of the cotton so that the pipette is at least **half-filled** with alumina. This is your column for further purifying the styrene. Clamp it to the iron lattice and place a **pre-weighed** clean, dry sample vial underneath to collect the purified styrene. The set-up is shown at right:
8. Using a clean pipette, suck up some of your dried styrene from the CaCl₂ drying agent and carefully add it to top of the alumina column, making sure the column doesn't overflow. The liquid should run down through the alumina by gravity and start to collect in the vial underneath. Repeat until all of your styrene has been loaded onto the column.

9. You may use a pipette bulb to help push as much styrene through the column as you can, by carefully placing it over the top of the column and squeezing out the air. Be very careful NOT to allow the deflated pipette bulb to reinflate while stuck to the column or it will pull your styrene and the column upwards towards/into the pipette bulb! You should notice that a colored impurity is retained on the top half of the alumina column (make note of the color of the column). Reweigh the vial to obtain the mass of the pure styrene you've collected. Calculate the volume that you obtained.

**Synthesis of Polystyrene**

10. Use a 3 mL syringe to draw up 2 mL of purified styrene and transfer to a 10 mL microscale round bottom flask with a magnetic stir bar inside. Place the round-bottom flask into a 50 mL beaker, and take it to the hood. Add 4 mL of xylenes as solvent.

11. While in the hood, carefully add 6 drops of tert-butyl peroxybenzoate initiator to the solution.

12. Your sand bath should be stable between 120-130°C. Attach a microscale water-cooled condenser to your flask with hoses attached (water flows in bottom, out the top). Clamp the apparatus around the center of the water-cooled condenser. Turn on the water for the tubing and lower into the sand bath. Stir the solution with the magnetic stir plate (setting 5-6).

13. After a few minutes, you should see the solution start to bubble vigorously as the reaction initiates. (What gas is being given off?) The solution should also reach reflux but this is hard to see until the bubbling of gases subsides a little.
14. Heat the mixture at reflux for 30 minutes then loosen the clamp and raise the apparatus up from the sand bath, away from the heat. Allow it to cool for a few minutes then remove the condenser.

15. Using a pipette, transfer the reaction solution into a 50 mL beaker that contains 25 mL of methanol. Swirl the mixture gently for a minute and make a note of any observations.

16. Carefully pour the top layer of liquid (the "supernatant solution") off the sticky gooey solid obtained in the beaker. This process is called decanting. You should be able to remove almost all of the solution.

17. Add 10 mL of fresh methanol to the crude polymer. Using your glass-stirring rod, stir/poke/prod/mix the polymer with the methanol. After grinding for a bit, decant or pipette out the methanol and add a fresh 10 mL and continue grinding up the polymer until the polymer appears to be a powdery solid.

18. Vacuum filter the polymer from the methanol solution using your Hirsch funnel. Pull air through it to dry the polymer for at least 5 minutes. Turn off the vacuum line, remove the Hirsch funnel from the filtering flask and place the Hirsch funnel containing your product inside a 100 mL beaker in your locker drawer and allow it to dry until next week.

19. During the next lab period, get a clean, dry large sample vial from your locker and obtain a weight on the vial and cap. Transfer the solid to a pre-weighed vial and reweigh. Determine the mass of your polymer by the difference in weights and, if instructed to do so by your instructor, run an IR on your polystyrene.

**WASTE DISPOSAL:**
1. Dispose of supernatant solution from polymerization, filtrate and any left over residual styrene in the designated organic waste container.
2. Aqueous layers from extraction should be placed in the designated aqueous basic waste container.
3. The columns should be placed in the designated beaker in the fume hood.
4. The round-bottom flask and the condenser should be rinsed with acetone to remove any remnants of styrene (any cloudy white "fog" is styrene - rinse with acetone until removed from inside AND outside). All remaining glassware can be washed with soap and water, including the vial with drying agent (which dissolves in water).
epoxy resin

Date: Tue Sep 19 10:13:30 2017 (GMT-04:00)

Scans: 8

Resolution: 4.000
polystyrene
Wed Sep 20 11:17:03 2017 (GMT-04:00)

Date: Wed Sep 20 11:17:03 2017 (GMT-04:00)
Scans: 8
Resolution: 4.000