Syntheses of Nylon & Polystyrene

PreLab Question:

1. Name two (2) items (not mentioned below) that are made out of Nylon 6.10.
2. Name two (2) items (not mentioned below) that are made out of polystyrene.

Introduction:

Polymer is a term taken from the Greeks meaning “many parts”. In chemical terms, the word polymer describes a molecule that consists of repeating units of smaller molecules that are connected by covalent bonds. Synthetic organic polymers, also known as plastics, are by far the most common structural materials in the world. It is so common, that in the United States, we use plastic more than we do copper, steel, and even aluminum! Plastics are cheap and very sturdy materials. There are many types of plastics, but in this experiment, we will be looking at the syntheses of polystyrene and nylon 6.10.

Polystyrene

CD covers and plastic drinking cups are made out of the polymer polystyrene. This polymer is known to be a clear brittle plastic that is synthesized by a free radical polymerization. An initiator, such as benzoyl peroxide, is used to initiate the free radical polymerization of styrene. Once the radical initiator initiates the polymerization of styrene, propagation occurs which “builds up” the polymer chain. Once the polymer chain has “grown” and at a desirable length or molecular weight, the polymerization is terminated. The polymer is then isolated, possibly purified, characterized, and used for material use. The mechanism of the free radical polymerization of styrene is shown below.

Formation of the radical initiator:

\[
\text{Benzoyl peroxide} \quad \xrightarrow{\Delta} \quad \text{2 Benzoyloxy radical}
\]

Benzoyl peroxide
MW 242.23
dec 106°C
Polymerization of styrene:

*Initiation:*

\[
R^* + \text{CH}_2=\text{CH} \quad \xrightarrow{} \quad \text{RCH}_2\text{C}_6\text{H}_5
\]

*Propagation:*

\[
\begin{align*}
\text{RCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 + \text{CH}_2=\text{CH} & \quad \xrightarrow{} \quad \text{RCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \\
\text{RCH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 + \text{CH}_2=\text{CH} & \quad \xrightarrow{} \quad \text{RCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5
\end{align*}
\]

*Termination:*

\[
2 \text{R}^* \quad \xrightarrow{} \quad \text{R}-\text{R} , \quad \text{RCH}_2\text{CH}_2\text{C}_6\text{H}_5 + \text{R}^* \xrightarrow{} \quad \text{RCH}_2\text{CH}_2\text{C}_6\text{H}_5 , \quad 2 \text{RCH}_2\text{CH}_2\text{C}_6\text{H}_5 \quad \xrightarrow{} \quad \text{RCH}_2\text{CH}_2\text{C}_6\text{H}_5 \text{C}_6\text{H}_5
\]

**Styrene**

MW 104.15
bp 145-146°C

**Polystyrene**

MW 300,000-25,000,000

The final polymer has about 3000 monomer units in a single chain. The lifetime of the radical is about 1 second.

To prevent the styrene from polymerizing during storage, the chemical 4-t-butylcatechol is added since it is a radical inhibitor (also known as a good chain terminator). Passing the styrene through a column of alumina will remove the inhibitor and allow for styrene to be used for the polymerization reaction. You will need to do this before using styrene for the polymerization experiment.

*Nylon 6.10*

Nylon 6.10 is a polymeric material that is used in the clothing and textile industry. The synthesis of nylon 6.10 is produced by interfacial polymerization, in which monomers react with one another to form a very large molecule at the contact or interface
of two immiscible liquid layers. In this reaction, the primary amine and the acid chloride react to form an amide with a byproduct of HCl (see below).

$$2\text{SOCl}_2 + \text{HOOC(C}_2\text{H}_8\text{COOH} \rightarrow \text{C}_8\text{H}_8\text{CCl} + 2\text{HCl} + 2\text{SO}_2$$

<table>
<thead>
<tr>
<th>Thionyl chloride</th>
<th>Sebacic acid</th>
<th>Sebacoyl chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW 118.97</td>
<td>MW 202.25</td>
<td>MW 239.14</td>
</tr>
<tr>
<td>bp 79°C</td>
<td>mp 137°C</td>
<td>bp 168°C/12mm</td>
</tr>
</tbody>
</table>

$$n\text{ClC(C}_2\text{H}_8\text{CCl} + n\text{H}_2\text{N(C}_2\text{H}_8\text{NH}_2 \rightarrow \}n\text{(C}_2\text{H}_8\text{C}}\text{NH(C}_2\text{H}_8\text{NH} \}n + 2n\text{HCl}$$

<table>
<thead>
<tr>
<th>Hexane-1,6-diamine</th>
<th>Nylon 6.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW 116.21</td>
<td></td>
</tr>
<tr>
<td>mp 45-46°C</td>
<td></td>
</tr>
</tbody>
</table>

**Procedure 1. Synthesis of Polystyrene**

_Caution! Styrene is flammable, an irritant, and has a bad odor. You must work with this chemical in the hood._

First, obtain a Pasteur pipette and place a small piece of cotton inside the pipette. Very carefully, pack the cotton gently until it cannot be moved further down the pipette. Fill the pipette half way with alumina and then add 1.5 mL of styrene. Collect roughly 1 mL of the styrene from the pipette into a clean graduated cylinder, then place the styrene into a test tube. Add 50 mg of benzoyl peroxide and a boiling stick to the test tube and heat in a sand bath. Once it reaches a certain temperature (roughly 135°C), polymerization will occur causing the solution to thicken and the viscosity to increase. Place another boiling stick into the solution and press the two boiling sticks together. Using both boiling sticks, obtain some of the sticky solution and carefully pull apart the sticks. Fibers will start to form; carefully collect the product. Collect as much fibers as you can from the solution. Tape some fibers into your lab notebook.

**Cleaning Up:** Shake out the alumina from the pipette and place it onto a piece of paper; allow the alumina to dry in your hood. Once dry, the used alumina can be put into the trash bin. If spilling of benzoyl peroxide occurs, for each gram spilled, react with 1.4 g of sodium iodide in 28 mL of acetic acid. Neutralize with sodium carbonate after 30 minutes, dilute in water, and flush down the drain.
Analysis: Solubility Test

Obtain 9 shorty vials or small test tubes and place 1 mL of the following solvents into the vial: 12M HCl, 10% HCl, ethanol, hexanes, cyclohexanes, olive oil, dichloromethane, bromine, and 2-butanone. Place pieces of the polystyrene fibers into the solvents and record if the fiber is resistant or dissolves. In your final report, discuss the solubility test results and give reasons for the results.

Cleaning Up: Place each solution into its appropriate waste container.

Procedure 2. Synthesis of Nylon 6.10

Caution! In this experiment, you will be using the chemical thionyl chloride*. Thionyl chloride is dangerously reactive in water and is an irritant to skin, eyes, and lungs. Use precaution while using it in the hood!

You will use the following set-up for the synthesis of nylon 6.10.
*Important Note: Measure out thionyl chloride in your hood and wear gloves! Take the bottle to your hood, and, using a 1 mL disposable syringe, draw out the thionyl chloride and dispense it into the test tube. Cap up the bottle of thionyl chloride and return it to its storage location. Take the plunger out of the disposable syringe and keep it in your hood to allow the syringe to dry out. After it’s dry, wash the syringe with water, then dispose of the syringe in the trash bin.

In a test tube, place 0.25 g of sebacic acid, 0.25 mL of thionyl chloride (see above)*, and 1 drop of N,N-dimethylformamide (DMF). Heat the reaction tube in the water bath and maintain the temperature between 60°C-70°C. As it heats, obtain a 50 mL beaker and line the bottom and the sides with silicone grease. After 5-10 minutes of heating, the solution will turn into a yellow/green solution. Continue heating for an additional 10 minutes then carefully remove the gas trap connection and rubber septum from the test tube. In a graduated cylinder, add 0.25 g of hexamethylenediamine, 6 mL of distilled water, and 1 mL of 3M NaOH. Place the yellow solution into the 50 mL beaker. Rinse the test tube with a small amount of dichloromethane and add into the 50 mL beaker. Gently pour in the solution from the graduated cylinder into the beaker. Let it set for about 20 seconds and, using a copper wire hook, hook the film that lays at the interface of the solutions. Draw up and wind up as many fibers as you can. Continue drawing fibers until you are unable to do so. Wash the polymer thoroughly with water and press it as dry as possible. After the polymer has dried, determine its weight and calculate the percent yield. Save 10-15 mg of polymer for IR analysis; see the back inside cover of the lab guide for instructions on sample prep for IR analysis. Tape a piece of the polymer into your notebook.

Cleaning up: Add the cotton from the trap to the used reaction mixture. Stir vigorously to cause the nylon 6.10 to precipitate. Decant the water and dichloromethane and then squeeze the solid as dry as possible. Place the solid in the NHO container. Place the dichloromethane in the halogenated organic solvents container. Dilute the aqueous layer and flush down the drain.

Post Lab Questions:

1. Write a balanced equation for the reaction of sebacoyl chloride with water.

2. Describe another way to make nylon.