Polymer Synthesis

• Final Lab
• Polymer chemistry (Rayon Synthesis)
• *Pages 317 - 330*
• Pre-lab: Page 328 Post-Lab: Page 330
• Part of this experiment is NOT in your manual see additional handouts.
What is a polymer?

• Molecules substances of high molecular mass formed by joining together individual molecules called monomers
• Polymers are either natural or synthetic. **Natural polymers** such as proteins, DNA, starch, and cellulose occur in nature. **Synthetic polymers** are chemically prepared.
• The physical properties of polymers can vary tremendously.

• For example, some polymers are extremely flexible and fluid, whereas others are very hard and stress-resistant.

• One way to classify polymers is based on differences in elasticity.

• Elasticity refers to the ability of a polymer to stretch and return to its original shape.

• Elastomers are highly flexible and very elastic. One factor that affects the elasticity is the type of monomer group. Rubber, for example, is very elastic and is made from isoprene monomers.
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\[
2n \quad \text{CH}_2=\text{C} - \text{CH} = \text{CH}_2 \quad \rightarrow \quad \text{CH}_3 \quad \text{C} = \text{C} \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{CH}_2 \quad \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \quad \text{C} = \text{C} \quad \text{C} = \text{C} \quad \text{CH}_3 \quad \text{CH}_2 \quad n \\
\text{isoprene} \quad \text{poly-cis-isoprene (rubber)}
\]

• In contrast, polymeric fibers have a much lower degree of elasticity.

• The chains of a fiber are in a highly ordered arrangement, making it more difficult to stretch. Nylon, Dacron, and acrylics (Orlon) are all fibers.

• In between elastomers and fibers are plastics, which demonstrate intermediate characteristics.
Polyethylene is a flexible polymer made from ethylene. Polystyrene is a brittle polymer made from styrene.
Cross Linking

• Cross linking may increase the strength of a polymer.
• Cross linking is a type of bonding that occurs between two chains of polymer.
• As the amount of cross linking increases, the polymer become less flexible.
• Often, an agent is needed to promote cross linking.
• When you make slime you will use a cross linking agent.

• The diagram below depicts cross linking.

• The wavy lines between polymer 3 and 4 represent cross linking bonds.

- = monomer

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No Cross Linking</td>
</tr>
<tr>
<td>2</td>
<td>No Cross Linking</td>
</tr>
<tr>
<td>3</td>
<td>Cross Linked</td>
</tr>
<tr>
<td>4</td>
<td>Cross Linked</td>
</tr>
</tbody>
</table>

polymer 1
polymer 2
polymer 3
polymer 4
• Polymers can also be formed by elimination of a small molecule, often water
• This process is called condensation
• The product is called a copolymer if two different molecules are involved in the polymerization
• Nylon 6,6 is an example of a copolymer
- Each end of the chain can undergo additional condensation reactions.
- The result is the silk substitute commonly called nylon.
• The characteristics of a polymer can be changed dramatically by connecting different polymer chains.

• These connections or bridges are called cross-links.

• Perhaps the best known example of this is vulcanized rubber.

• Vulcanization is the process of adding sulfur to natural rubber latex and then heating.
Natural rubber latex is made much more useful by adding cross-links. (a) Two strands of polyisoprene (rubber). (b) Sulfur reacts by opening the double bonds in the polymer and forming bridges between adjacent strands. The product is called vulcanized rubber.
Cross Linking Poly(vinyl alcohol) to form Slime

• In this lab experiment, you will synthesize Slime from poly(vinyl alcohol).

• Poly(vinyl alcohol) or PVA is a polymer with a chemical formula \((\text{CH(OH)CH}_2\text{CH(OH)CH}_2)_n\).  

• PVA is used in many applications such as coating grease-proof paper, artificial sponges, and thickening food.

• However, PVA is not Slime! Slime is produced by cross-linking PVA polymers with borate anions, \([\text{B(OH)}^4^-]\). When borax is added to water, borate anions form.
• The reaction that forms Slime is shown below. The oxygen atoms on the borate anion can interact with the alcohol group (OH group) of PVA.

• This weak interaction is called **hydrogen bonding** and is also responsible for the 3-dimensional structures of proteins.

• These weak interactions can break and reform continuously, if the correct amount of water is present.

\[
\begin{align*}
\text{poly(vinylalcohol)} & \quad + \quad \text{borate} \\
& \quad \rightarrow \\
\text{Slime lattice}
\end{align*}
\]
• Slime is very flexible when it contains enough water.
• When it is at rest, the Slime becomes rigid. Though each hydrogen bond alone is very weak, all together the hydrogen bonds form a rigid structure.
• This network of hydrogen bonding is easily disrupted by deformation through handling, squeezing, stirring, and pouring.
• As Slime dries out, the amount of water decreases and the slime becomes hard.
• If too much water is added, the weak hydrogen bonding linkages between -OH and borate become separated so that the Slime no longer gels.
• This situation is not easily reversed until enough water has evaporated from the Slime.
Synthesizing a Silicate Chain to Form rubber balls

- In the second part of the lab experiment, you will synthesize an inorganic polymer based on silicon.
- Inorganic polymers are polymers with a non-carbon backbone.
- Silicon is an element directly below carbon, yet the chemistry of carbon and silicon are very different.
- Silicones form very stable polymers and are used in many products.
• Heating dimethyldichlorosilane (Me$_2$SiCl$_2$) with water produces polymethylsilicone (Me$_2$SiO)$_n$, a polymer of high thermal stability.

• Adding methyltrichlorosilane (MeSiCl$_3$) as a cross linking agent to polymethylsilicone (Me$_2$SiO)$_n$, forms a rubber "silly putty" or a hard resin, depending on the degree of cross linking.

• Resins are commonly used to form plastic objects like cups and bottles.
• When sodium silicate solution (Na$_2$Si$_3$O$_7$ in H$_2$O) is added to ethyl alcohol, a polymer is formed.
• Sodium silicate solution contains sodium hydroxide (NaOH) and silicon dioxide (SiO$_2$).
• Sodium hydroxide is a strong base. Under these basic conditions, silicate chains form.
• When ethyl alcohol (CH$_3$CH$_2$OH) is added to sodium silicate solution, two oxygen atoms of silicate are replaced by ethyl (CH$_2$CH$_2$) with loss of water.
Overall reaction:

Silicate chains $\rightarrow$ Cross-linked silicate chains $+ \text{H}_2\text{O} + \text{O}_2$
Cellulose

- Cellulose is a naturally occurring organic polymer, found in plants and algae.
- Cellulose is the major constituent of paper and cardboard and of textiles made from cotton, linen, and other plant fibers.
- It is derived from repeating units of glucose.
Cellulose

Cellulose is a straight chain polymer: unlike starch, no coiling occurs, and the molecule adopts an extended and rather stiff rod-like conformation.
• Cellulose is not very soluble in organic solvents. This is because it has a very high molecular weight.

• Tetraamminecopper(II) hydroxide dissolves cellulose giving smaller molecules that react with water (hydrolyse) and form a more soluble species.
Rayon Synthesis

- Tetraammine copper(II) hydroxide will be prepared in a 2 step synthesis from copper(II) sulfate and ammonia, followed by removal of the sulfate ion, by addition of $\text{Ba}^{2+}$ and addition of a concentrated ammonia solution.

- Reaction of the copper complex with cellulose helps break up the polymer through electrostatic interactions.
• The rayon is precipitated through reaction of the basic solution with sulfuric acid.
• A pale blue color remains due to the copper(II) ions that are on the surface.
• The color can be removed by washing the polymer with DI water.
Note:

• Step 10, page 324, sulfuric acid will be prepared.

• Step 11, page 325 the spinning apparatus will not be prepared, alternative methods will be used.

• Wear gloves to handle your rayon, it will still have acidic residues present.