The Structure of Polymeric Substances

- To learn about Polymers.
- To learn about Synthetic Polymers.
- To learn about Addition and Condensation Polymerization.
- To learn about Polymer Degradation.

In this laboratory we will synthesize five synthetic polymers; PolyMethylmethacrylate, commercially known as Plexiglas, PolyStyrene, Nylon, Glyptal Resin, which is related to the commercial polymer Dacron, and PolyUrethane foam. The first two are Addition Polymers. The next two are Condensation Polymers; one being linear and the other highly cross-linked. The last is a highly cross-linked Addition Polymer. Finally, we will degrade the polymer Starch into its Glucose subunits.

Polymers are compounds of considerable importance, comprising many modern synthetic materials and a large percentage of biological components. They are molecules made up of a large number of small molecular units referred to as monomers. A typical polymer molecule may contain several thousand monomer units. These monomers may be the same or they may be varied; Polystyrene is entirely composed of the monomer Styrene, whereas naturally occurring proteins contain ~20 different amino acid monomers. Polymer molecules can be either a single long chain, like a strand of spaghetti, or a highly branched structure more akin to a tree. The length of the polymer chain, or its branches, depends heavily upon the conditions under which the polymer is synthesized. And, the length of individual polymer molecules in a given sample will usually vary somewhat about a mean value, although certain polymers, such as many proteins, will have well defined sizes.

(A polymer molecule built as a single linear chain.)

(A polymer molecule with branching.)
The three dimensional structure of these polymer molecules also varies considerably. At one extreme, the polymer chains can be intertwined in a spaghetti like mass. At the other, the polymer will be tightly coiled as a single molecule dissolved in an appropriate solvent. The exact three dimensional structure of the polymer molecule is determined by the chemical makeup of the polymer's monomer units and the chemical environment, typically the solvent, in which the polymer finds itself.

(A tightly coiled, unbranched polymer molecule.)

As noted, polymers are important both commercially and biologically. Important natural polymers are polymeric carbohydrates (starch, cellulose, etc.), proteins and nucleic acids. Nylon, Polyethylene, Orlon, Plexiglas, and Teflon are examples of synthetic polymers of commercial importance. The class of materials known as plastics is, in large measure, comprised of synthetic polymers.

Polymers are typically classified according to some scheme involving their synthesis, structure, or function. One such scheme is based upon the nature of the polymerization reaction used to form the polymer: addition, condensation, etc. Addition Polymerization occurs because two monomers are added to each other, with elimination of a double bond in the monomer. Condensation Polymerization involves condensing two monomer units together, with concomitant elimination of a small molecule once the monomers are linked.

A classic example of Addition Polymerization, is the polymerization of Ethylene to form Polyethylene:

\[ n \text{CH}_2=\text{CH}_2 \rightarrow \text{-CH}_2\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-} \]

which is usually written as:

\[ -(\text{CH}_2\text{CH}_2)_n- \]

to indicate the polymer chain contains \( n \) monomer units bound together linearly. A couple of things to note. First, the electron pair involved in the double bond of the monomer is used to bind the units of the polymer together; each unit adding to the next by sharing an electron derived from the double bond.
Second, details about what happens are at the ends of the chain are not disclosed in this formula. Somehow the ends must be capped, but because these “caps” comprise an extremely small fraction of the polymer molecule, they are usually considered to be insignificant.

The actual mechanism of monomer addition is slightly more complex than the above schematic suggests. There are three basic steps in the mechanism for the synthesis of an addition polymer. These are: chain initiation, chain propagation, and chain termination. For instance, in the Free Radical addition polymerization of Ethylene to form Polyethylene we initiate the polymerization by attacking the double bond of a monomer unit with a Free Radical “initiator” molecule, a molecule that possesses an unstable unpaired electron. This results in the binding of the initiator to the monomer and subsequent generation of another unpaired electron on the monomer. This unpaired electron can then attack another monomer unit in like fashion, again resulting in the generation of yet another unpaired electron. This cycle of attack and Free Radical generation can repeat itself many thousands of times. Occasionally, the growing ends of two chains will find each other, combine and thus terminate this cycle.

**Chain Initiation**

\[ R^\cdot + CH_2=CH_2 \rightarrow R\cdot CH_2=CH_2. \]

**Chain Propagation**

\[ R-CH_2CH_2^\cdot + nCH_2=CH_2 \rightarrow R-(CH_2CH_2)_n-CH_2CH_2^\cdot. \]

**Chain Termination**

\[
\begin{align*}
2R-(CH_2CH_2)_nCH_2CH_2^\cdot & \rightarrow [R-(CH_2CH_2)_nCH_2CH_2]^2_2 \\
& \rightarrow R-(CH_2CH_2)_nCH=CH_2 + R-(CH_2CH_2)_nCH_2CH_3.
\end{align*}
\]

The nature of the Initiator \( R \) (a generalized notation indicating the exact molecule involved is unspecified) depends on the particular polymer being formed and the conditions under which the polymerization reaction is being carried out. Peroxides are favorite initiators because they possess an unstable O-O single bond that readily splits upon heating:

\[ R-O-O-R \rightarrow R-O^\cdot + O-R \]

Polyesters and Polyamides are examples of Condensation Polymers. A polyester is formed from the reaction of a dihydroxy alcohol and a dicarboxylic acid, with concomitant elimination of water:
For concreteness, the material marketed as Dacron is formed from the condensation polymerization of Ethylene Glycol and Terephthalic Acid:

\[
\begin{align*}
\text{(Dihydroxy Alcohol)} & + \text{(Dicarboxylic Acid)} & \rightarrow & \text{(Polymer)} \\
\text{HO-CH}_2\text{CH}_2\text{-OH} & + \text{HO-C-C-C-OH} & \rightarrow & \text{HO-CH}_2\text{CH}_2\text{-O-C-C-OH} \\
\text{(Water is Eliminated)} & \downarrow & \downarrow & \text{H}_2\text{O}
\end{align*}
\]

The detailed mechanism of this condensation is slightly more complex than that of the corresponding addition reaction, so we will not delve into its specifics.

For this exercise, we will focus on five synthetic polymers and one naturally occurring polymer, Starch. First, we will synthesize the addition polymer Plexiglas and the condensation polymer Nylon. Then we will then generate the cross-linked condensation polymer Glyptal. After that we will generate the cross-linked polymer Polyurethane. Finally we will hydrolyze the condensation polymer Starch back into its Glucose monomers.

Poly(Methyl Methacrylate), commercially known as Plexiglas, is formed from the alkene Methyl Methacrylate:

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2=\text{C} \\
\text{C}=\text{O} \\
\text{O-CH}_3
\end{align*}
\]

When a sample of Methyl Methacrylate is treated with a small amount of the initiator Benzoyl Peroxide:
the initiator splits and initiates the polymerization of the Methyl Methacrylate units. It should be noted the polymerization of these monomer units is in a Head-to-Tail fashion:

Because the optical properties of this resin are reasonably good, it makes a suitable "glass" substitute, and as such, is marketed under the names *Plexiglas, Lucite*, and *Perspex*.

Another example of this type of addition reaction is the formation of PolyStyrene from Styrene. Benzoyl Peroxide can also be used as an initiator for this polymerization. Expanded Polystyrene, composed of 90-95% Polystyrene and 5-10% Blowing Agent (CO₂, etc.), and Extruded Polystyrene, know *Styrofoam*, are common commercial products.

One of the most important nylons, called *nylon 6,6*, can be prepared from the six-carbon dicarboxoyl chloride, Adipoyl Chloride, and the six-carbon diamine, Hexamethylenediamine:
The polyamide forms with the elimination of Hydrogen Chloride (HCl) molecules:

\[ -\left(\begin{array}{c}
\text{C} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{C} \text{NH} \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{NH} -
\end{array}\right)_n - \]

Commercially, this reaction is carried out by combining these two compounds in a 1:1 stoichiometric ratio and heating the mixture to a temperature of 270°C at a pressure of 250 pounds per square inch. The nylon produced in this way has a molecular weight of ~10,000. The fibers produced are then stretched to four times their original length, in a process called "cold drawing". This orients the polymer chains along the fiber axis and increases the fibers' strength.

Finally, Glyptal resin is formed in a condensation reaction between Terephthalic Acid (see above) and Glycerol; in a manner similar to that involved in the formation of Dacron. However, by using Glycerol instead of Ethylene Glycol we introduce three polymerization points per monomer and allow for a degree of cross-linking in the final resin.

\[
\text{HO-CH}_2\text{CH-CH}_2\text{OH}
\]

(Polymerization Points)

Finally, Polyurethane foam, another example of a cross-linked polymer, forms when an isocyanate compound adds to an alcohol:

\[
\text{(an isocyanate)} \quad \text{R} - \text{N} = \text{C} = \text{O} \quad \rightarrow \quad \text{R} - \text{N} - \text{C} = \text{O} \quad \text{(a urethane)}
\]

\[
\text{H-OR} \quad \text{(an alcohol)} \quad \rightarrow \quad \text{H} - \text{OR}
\]

Note this is addition reaction results in the loss of a double bond between the N & C of the isocyanate. For concreteness, consider the addition of Toluene Diisocyanate to Glycerol:
Note, as with the Glycerol monomer of the Glyptal resin, multiple polymerization points exist which leads to cross-linking within the polymer.

Starch is a natural polymer made-up of Amylose (a linear polymer) and Amylopectin (a highly branched polymer), which themselves are formed from monomers of Glucose, that is found in plants. It is a form of Glucose storage, and thus a form of energy storage, within the plant tissues.

In the above rendition, each Glucose monomer comprising the Starch molecule is represented by a six pointed ring, with each point representing a Caron atom. In a reverse of the Condensation reaction required to synthesize this molecule, the Glucose monomers can be clipped apart by adding the Water molecules back in. This is usually done in a highly acidic environment as the Acid will act as a catalyst for the depolymerization reaction. The presence of the resulting Glucose molecules can be detected because they give a positive test when treated with Benedict’s Reagent.
Thus, we will synthesize five synthetic polymers, *Plexiglas*, Polystyrene, *nylon*, *Glyptal* and Polyurethane, and then hydrolyze the natural polymer Starch.
Pre-Lab Safety Questions

1. Do a short internet search for a Safety Data Sheet (SDS) for Methyl Methacrylate and for Styrene. What are the health effects associated with inhalation of these substances?

2. What is another major hazard we should be aware of when handling Methyl Methacrylate and Styrene?

3. How long should you flush your skin with Water if either Hexamethylenediamine or Adipoyl Chloride come into contact with your skin?

4. Can you remove your safety goggles when performing the model building exercises of this laboratory? Explain.
**Procedure**

*Preparation of Plexiglas*

1. **In a fume hood**, place 40 drops of methyl methacrylate in a disposable test tube.
2. Add 5 small pieces of benzoyl peroxide to it.
3. **In a fume hood**, place the test tube in a hot water bath. It should harden in about ten minutes.
4. Observe the product.

*Preparation of PolyStyrene*

1. **In a fume hood**, the Styrene monomer is cooked in a beaker with the Benzoyl Peroxide initiator. When polymerization is underway, your laboratory instructor will notify the class to obtain a sample of the still fluid polymer.
2. Take an aluminum weighing boat to the fume hood to obtain a sample of the Polystyrene. Your instructor will pour the liquid into your boat.
3. Allow your sample to harden and then observe its properties.

*Preparation of Nylon 6,6*

**Caution:**

These solutions are caustic. Avoid contact with the solutions. If some gets on your hands, wash immediately with water.

1. Place ~15 mL of 4% Hexamethylenediamine solution in a small beaker.
2. Over this solution, carefully pour ~15 mL of 3% Adipoyl Chloride solution. Do this thru a funnel which is placed so that its outlet is placed just above the surface of the solution. **Avoid excessive mixing of the solutions.**
3. Set-up a stirring rod on a clamp to pull the polymer over. With a wood splint, catch the polymer film that has formed at the interface between the two solutions. Pull the polymeric fiber over the stirring rod, to the length you desire.
4. Wash the polymer thoroughly with Water and then with 50% Acetone. Allow it to air dry.
5. Observe your product.
**Preparation of Glyptal Resin**

1. Place 0.3g of Phthalic Anhydride (This is used instead of Terephthalic Acid because the Anhydride is more reactive.) and 0.1g of Anhydrous Sodium Acetate (a reaction catalyst) into a 15-cm disposable test tube.

2. Add 0.1 mL of Glycerol.

3. Clamp the test tube to a Ring Stand above a Bunsen Bruner. Put the clamp near the top of the test tube and angle it at 45°. **Flame the test tube gently with a light Yellow Flame**, periodically moving the flame away so as to not overheat the reaction mixture. While heating, stir the mixture with a stirring rod until the Phthalic Anhydride dissolves and the solution appears to boil. (As Water is eliminated during the Condensation reaction, the evolved gas is steam.) **If the solution is overheated, it will char and become dark. Additionally, the solution may be ejected from the test tube.** (While carrying-out this reaction, be sure not to point the test tube in the direction of your lab mates.)

4. After the Water is driven off, allow the tube to cool. If the final product is not viscous, the reaction is not complete and the mixture will have to be re-heated.

5. Observe your product.

**Preparation of Polyurethane Foam**

1. Obtain a small Dixie cup.

2. Add approximately 10 mL of both the isocyanate and alcohol solutions to the cup. Quickly mix the solutions with a wood splint.

3. Allow the system to react.

4. Observe the product.

**Hydrolysis of Starch**

1. **Your laboratory instructor will prepare two solutions, one in which ~1.5g of Starch has been dissolved in 50 mL of Water. The other solution contains the same amount of starch to which 10 mL of 1.0M HCl has been added and the system boiled for 20-30 minutes.**

2. Obtain ~2-3 mL of the pure Starch solution in a test tube. Add 5 mL of Benedict’s Reagent. Heat the test tube in a boiling Water bath for 5 minutes and note any change.
3. Repeat this test using a few milliliters of 1% Glucose solution. Again, note the results.

4. Finally, do the same with a portion of the starch solution that has been boiled in acid. Note the results.

**Model Building Exercises**

After you have cleaned-up your workstation, check-out a molecular modeling kit. To better understand the structures of the polymers you have just synthesized, build the following models.

1. Build a model of a section of Poly(methyl methacrylate) containing 3 monomer units.

2. Build a model of a section of nylon 6,6 containing 4 monomer units. (Work with a neighboring group on this project, but do not mix-up the model kits.)

3. Head-to-tail polymerization of propylene produces a polymer in which every other carbon atom in the main polymer chain has two possible configurations. (Denoted by an asterisk in the following diagram.)

This leads to three possibilities for the polymer formation.

Isotactic (*iso-* for same and *taktikos* for order) Polypropylene has all the methyl groups along the same side of the polymer chain.

Syndiotactic (*syndo-* for two together) has a strict alternating of the methyl groups along the polymer chain.

Atactic (*a-* for without) has a random arrangement of methyl groups along the polymer chain. Until 1963, only atactic polypropylene could be formed. The discovery of Ziegler-Natta catalysts allowed for the synthesis of the ordered forms of Polypropylene. Atactic
Polypropylene has a low softening point, poor mechanical properties, and is of a lesser commercial interest.

Use the model kits to build models of isotactic and syndiotactic Polypropylene containing at least 4 monomer units.
Data Analysis

1. Write a complete reaction for the chain initiation step for the polymerization of Methyl Methacrylate using Benzoyl Peroxide as an initiator.

2. Use the above reaction product to write one cycle of the chain propagation step for the polymerization of Methyl Methacrylate.

3. Write the formula for a section of Poly(methyl methacrylate) containing 3 monomer units.

4. Repeat questions 1-3 for PolyStyrene.

5. Write the formula for a section of nylon 6,6 containing 4 monomer units.

6. Write the formula for a section of Glyptal resin containing at least 6 monomer units and one branch.
Questions

1. *Bakelite*, one of the earliest synthetic polymers prepared, is made by a condensation reaction between Phenol and Formaldehyde. This polymer forms a hard resin because of the many branches and cross-links which exist within the polymer.

a) What are the formulas of Phenol and Formaldehyde? (You may want to consult your book for this.)

b) Identify one Phenol monomer unit in the above sketch of the polymer.

c) Identify one of the Carbon atoms, supplied by the Formaldehyde monomer, in the above sketch of the polymer.

d) Identify at least one branch in the above sketch of the polymer.
2. Lignins are complex natural products that occur together with the polymer cellulose in the "woody" part of plants such as shrubs and trees. Because lignins are high molecular weight polymers, their exact structures are not known. They are composed of three basic monomer units:

- coniferyl alcohol
- sinapyl alcohol
- p-coumaryl alcohol

Different plants have different lignin compositions. The actual polymeric structures of lignins contain a variety of types of linkages between the above phenol based monomer units. There also seem to be glycosidic bonds (more on this later in the course) between the lignin polymer and the cellulose polymer units in the wood.

A typical Softwood Lignin is depicted on the next page. Examine this structure and answer the following questions:

a) Identify one instance of each monomer unit in the depiction of Lignin.

b) Identify one branch in the above polymer. (There are only two branches depicted in this softwood lignin, even though lignin is a fairly highly branched polymer.)
Typical Softwood Lignin