INTRODUCTION

Polymers are large molecules made of many (poly-) small units. The starting material, which is a single unit, is called a monomer. Many of the most important biological compounds are polymers. Cellulose and starch are polymers of glucose units, proteins are made up of amino acids, and nucleic acids are made up of nucleotides. Since the 1930s a large number of synthetic polymers have been manufactured. Synthetic fibers such as nylon and polyesters, polyethylene and polystyrene used in packaging materials, and polyvinyl chloride have become common in our everyday lives.

This experiment will focus on man-made polymers and the basic mechanism by which some of them are produced. Two of the most important types of reaction used in polymer formation are the addition and the condensation polymerization reactions. The polymerization of styrene is formed by the addition reaction. Nylon is synthesized by the condensation polymerization reaction.

Addition Polymers

One of the basic types of polymers is that formed by the addition of units originally having double bonds. For example, styrene is an organic monomeric unit that contains a double bond and can undergo addition polymerization.

\[
\text{H}_2\text{C} = \text{CH} (\text{C}_6\text{H}_5) + \text{H}_2\text{C} = \text{CH} (\text{C}_6\text{H}_5) \rightarrow \text{H}_3\text{C} - \text{CH} (\text{C}_6\text{H}_5) - \text{CH} = \text{CH} (\text{C}_6\text{H}_5)
\]  

[29.1]

Since two monomer units are added to each other with the elimination of the double bond it is referred to as an addition reaction. The reaction does not begin to take place without the help of a catalyst called an initiator, which starts the reaction. The initiators commonly used in these reactions are peroxides, such as benzoyl peroxide. In the presence of heat or UV light, the benzoyl peroxide splits into two halves producing two free radicals. The double bond of the benzoyl peroxide splits yielding two species each of which has one of the electrons from the shared double bond. The resulting species that has one unpaired electron is called a free radical. The boldfaced dot represents the unpaired electron. The free radical reacts with the styrene and initiates the reaction.

\[
\text{C}_6\text{H}_5\text{COO}^* + \text{H}_2\text{C} = \text{CH} (\text{C}_6\text{H}_5) \rightarrow \text{C}_6\text{H}_5\text{COOCHCH}_2\text{CH}(\text{C}_6\text{H}_5)^*
\]  

[29.2]

We now have one molecule; twice as large as the first. The reaction will continue adding a styrene monomer to the growing chain until a giant molecule is formed containing many thousands of styrene-repeating units.

\[
\text{CH}_3\text{CH}_2\text{C}_6\text{H}_5 [\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5]_n\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5
\]

The polymer Lucite, commonly known as Plexiglas, is another example of a polymer formed by the addition reaction. The monomeric units of the polymer are methyl methacrylate. The reaction is catalyzed by benzoyl peroxide.

\[
n\text{H}_2\text{C} = \text{C(CH}_3\text{COOCH}_3 \rightarrow (\text{CH}_3\text{C(CH}_3\text{COOCH}_3)_n}
\]  

[29.3]
Condensation Polymers

In condensation reactions, the monomer contains a reactive group other than the double bond. These monomers react by splitting out a small molecule such as water from between the two reactive functional groups. Two common reactions of this type are the reactions of organic acids with alcohols and amines to give either esters or amides. In order for this reaction to continue, each monomeric unit must have two reactive functional groups. The dimer (product of the first condensation) is capable reacting further because it still has a functional group free to react. For example, the condensation of adipoyl chloride and hexamethylenediamine will produce the polyamide polymer known as Nylon 6-6.

\[
\text{CICOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COCl} + \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{adipoyl chloride} \quad \text{hexamethylenediamine}
\]

\[
\text{CICO(CH}_2\text{)}_4\text{CO[NH(CH}_2\text{)}_6\text{NHCO}((\text{CH}_2\text{)}_4\text{CO})\text{NH(CH}_2\text{)}_6\text{NH}_2 + \text{HCl}} \quad [29.4]
\]

An amide link is formed between the adipoyl chloride and the amine and HCl is eliminated. The polymer is called nylon 6-6 because there are six carbon atoms in the adipoyl chloride and six carbon atoms in the hexamethylenediamine. There are several forms of nylon, differing in the length of the carbon chains in each of the components. In this and other chemical reactions involving acids, a derivative of the acid—not the acid itself—is used. These acid derivatives are much more reactive than the acids themselves. In this reaction, NaOH is added to the polymerization reaction to neutralize the HCl formed during the condensation reaction that forms the amide link. Polymers are formed when the acid group reacts with an alcohol (hydroxyl) group to produce an ester. Again there must be at least two reactive groups.

In both types of polymerization reaction, the length of the polymer chain is dependent on the environmental conditions. Usually the chains can be made longer by heating the products further. This process is referred to as curing. It is difficult to write a specific reaction for a polymerization since we do not know how many monomeric units have condensed to form the polymer. The letter \( n \) is used to designate an indefinite number of the repeating unit. The reaction for the formation of a polyester is written as follows:

\[
n \text{HOOCCH}_2\text{COOH} + n \text{HO(CH}_2\text{)}_2\text{OH} \rightarrow n \text{HOOCCH}_2\text{COOH(CH}_2\text{)}_2\text{OH} + n \text{H}_2\text{O} \quad [29.5]
\]

A. Preparation of Condensation Polymer (Nylon)

1. All work should be done wearing gloves and in the fume hood until the nylon product is completely washed with lots of water and is safe to touch.

2. Add 2.0 ml of 20% NaOH solution and 10 ml of 5% aqueous solution of hexamethylenediamine to a 50 ml beaker and mix.
   (Optional: add a few drops of phenolphthalein indicator to the aqueous base solution to color the nylon. The more indicator that is added the deeper the pink color will be.)

3. Measure 10 ml of 0.25 M adipoyl chloride in cyclohexane solution. Carefully layer this solution above the aqueous solution in the beaker by very slowly pouring it onto the aqueous layer without disturbing the lower cyclohexane layer. There should be two distinct layers in the beaker. Nylon will form at the interface between the two layers.

4. Using a spatula, glass rod or bent wire, dip below the interface of the 2 layers and gently pull up the nylon film from the center. Pull it slowly. If you pull too quickly, the nylon thread will break.
5. Gently wind the nylon thread around the spatula or glass rod and continue to slowly pull the nylon thread. If the thread breaks, pick it up again at the interface between the two solutions. The process can be repeated until one of the solutions is consumed.

6. Thoroughly wash the nylon thread and dry it on a paper towel. Do not handle the nylon until it has been thoroughly washed. Carefully pull on the nylon. Make observations about its physical properties.

B. Preparation of Slime.

Poly vinyl alcohol (PVA) solution (already prepared):
Prepare a 4% solution of PVA and water. (40 grams of PVA in 960 ml of distilled water). Heat the water and slowly with stirring add the PVA until it completely dissolves. This will take 15 minutes or longer. Do not allow the solution to boil. Cool the solution and store in a stoppered bottle.

Borax (sodium tetraborate) solution (already prepared):
Prepare a 4% borax solution by dissolving 4 grams of borax into 100 mls of distilled water. This can be stored in a stoppered bottle.

1. Into a zip-lock baggie pour 10 mls of the PVA solution. (One-two drops of food coloring can be added if desired.)

2. Add 2 mls of the borax solution. Seal the zip-lock baggie and squeeze the baggie to completely mix the two solutions.

3. The liquid PVA solution should have become gel-like. You have prepared Slime! The slime can be removed from the zip-lock baggie. Take care if food coloring was used, as the food coloring may stain fabric or your hands.

4. Slowly pour the slime back and forth. Allow it to slowly flow back into the baggie. Observe its behavior.

5. Grasp the slime with both hands and quickly pull it apart. Observe the difference in behavior between pulling it apart quickly and slowly.
Enzymes

EXPERIMENT 71 FACTORS AFFECTING ENZYMATIC ACTIVITY

Work in pairs for this experiment. Read and study each part before you begin. Certain operations must be carried out quickly, and you must have your equipment and chemicals ready, and know what to do.

The digestion of starch is catalyzed by the enzyme amylase, which is found in saliva. Chloride ions are known to be activators and as with all enzymes, amylase will have highest activity at a particular pH and temperature (or ranges of these). Amylase is a protein and is therefore susceptible to denaturation by a variety of agents and conditions, some of which will be studied in this experiment. In part A you will study how temperature affects the activity of amylase. In part B the influence of pH on the salivary digestion of starch will be examined, and in part C you will study what a heavy metal can do to enzymic activity. Part D investigates the effect of the concentration of the enzyme on the rate of digestion.

The amylase needed for these experiments will be contributed by the experimenters, and this introduces a problem. There are widely differing amylase activities in the salivas of different people. Consequently some of you will obtain disappointing, inconclusive results in the search for evidence that digestion of starch is occurring. Others may discover amylase activity so high that it is difficult to stop it. A group discussion following the experiment would be a good way of comparing results. Another way to "even out" this variation is to combine the salivas of two or more people and use the mixture. The pancreatin for part D is provided.

Assemble the following equipment:
- a thermometer (2, if available)
- 5 or 6 dropper pipets
- 3 large (400-800 mL) beakers
- 2 small (100-250 mL) beakers
- 10-12 large test tubes
- a porcelain spot plate

Preliminary Work

1. Prepare constant temperature baths: You will need four of these. Fill the three larger beakers half to two-thirds full of water, and heat one to 37 °C, one to 70 °C and one to boiling. Once these have come to the proper temperature, maintain that temperature as closely as possible, adding water as necessary to replace water lost by evaporation. The fourth beaker (150 or 250 mL) should contain an ice-water slush, at 0 °C.
2. Collect saliva: You and your partner will have to contribute 2 mL each of saliva, collected in a small, clean, dry beaker, or a large test tube. (Daydream a little about your favorite food while making your contributions.) When the saliva collection is complete, combine the contributions in one small beaker, mix well, and save this mixture for parts A, B, and C of the following experiments.

3. Obtain iodine solution: You will need a few milliliters of the dilute iodine test solution either in a dropper bottle or in a test tube with a dropper kept in the solution, ready for use. This should be kept at your work station. When you use this solution, four drops of the starch-saliva mixture should be placed in a depression on the clean porcelain spot plate, with 1 drop of the iodine solution. If starch is present, you will see a dark blue color. If there is no change from the amber color of the reagent, then starch has been digested and is no longer present as such.

4. Obtain the Benedict's solution: You will need 15-20 mL of Benedict's reagent. In each of 5-6 test tubes, place 3 mL of the blue reagent. Have these ready for Part A. When you use this, a test tube containing the 3 mL of Benedict's reagent plus four drops of the saliva-starch mixture you are testing must be placed in the boiling water bath for at least 5 minutes (often longer). If a reducing sugar is present (indicating that the starch has been digested), the blue color of the reagent will change to green or orange or brick-red, depending on the amount of sugar present. Again, no color change means that no digestion (or incomplete digestion) has taken place.

71 A. THE INFLUENCE OF TEMPERATURE ON ENZYME ACTIVITY

Procedure.

1. Put 5 mL of a 1% buffered starch solution in each of three test tubes. Place one tube in the 37 °C water bath, one in the 70 °C bath, and one in the ice-water bath. Leave them in their respective baths, occasionally stirring or swirling them, until they have reached the temperature of the bath.

2. From your saliva “stock”, prepare a dilute solution by mixing 1 mL of saliva with 50 mL of distilled water. Mix the solution well, then transfer 5 mL portions into three more clean test tubes. Place one in each of the temperature baths as in step one. You now have a tube of starch and a tube of diluted saliva in each bath (37 °, 70 °, and 0 °C). Allow them to come to the temperature of the bath. Save the rest of the diluted saliva mixture for part C.

3. Begin with the test tubes in the 37 °C water bath.

   (a) Remove the two test tubes, and pour the contents of one into the other, mixing quickly and thoroughly. With the starch-and-saliva mixture all in one test tube, return the tube to the bath.

   (b) Immediately withdraw 4 drops of the mixture and put it on the spot plate. Test it with a drop of iodine solution, and record the color.
(c) Immediately withdraw another 4 drops and add this to one of the test tubes containing the Benedict’s reagent. Mix, and place in the boiling water bath. (These are the “0” minute tests.)

(d) Note the time. You will be repeating the routine above (items b and c) every three minutes for the next 12 minutes, and after that, every 5 minutes, until you see a color change in the Benedict’s reagent. You may stop testing for starch when the starch test becomes negative. To increase efficiency, leave the dropper in the test tube during this time.

4. When you can turn your attention to the next step (perhaps while you are waiting for the Benedict’s reagent to react), remove the two test tubes from the 70 °C bath, pour the contents of one into the other, mixing quickly and thoroughly, and return to its bath the one tube containing the mixture. Immediately test the solution (using 4 drops, as before), for starch with the iodine solution on the spot plate. Note the color on the report sheet. (This is the “0” minute test.) Repeat every 3 minutes, as before, until the test shows no starch. Again, efficiency is improved by keeping a dropper in the test tube during this time. You also avoid contamination with another solution. You will not test this solution, or the one at 0 °C, with Benedict’s reagent.

5. Repeat the routine outlined in step 4 with the two test tubes from the ice-water bath. Record the results on your Report Sheet.

71 B. THE INFLUENCE OF pH ON ENZYME ACTIVITY

NOTE: You no longer need the 70°, 0°, or boiling water bath. Only the 37° bath is needed for parts B-D.

1. Transfer 1 mL of your “stock” saliva (not the mixture prepared for Part C) to 25 mL of distilled water and mix well. Take 3 mL of this diluted saliva solution and put 1 mL in each of three test tubes. Label these tubes “5”, “7”, and “9.” To the test tube labelled “5” add 5 mL of the pH 5 buffer provided; to the tube marked “7” add 5 mL of the pH 7 buffer, and to the tube marked tubes. Place these in the 37 °C bath. Allow all 6 test tubes to reach the temperature of the bath.

3. When the contents of the tubes are at 37 °C, pour one starch solution into one saliva solution, the second starch solution into the next saliva solution, and the last starch solution into the last saliva solution. Mix the contents of each test tube (you now should have only three test tubes containing any solution), and return the three labelled test tubes with their solutions to the water bath.

4. Immediately begin testing each of the solutions for starch, using 4 drop samples as before, with the iodine solution. Take samples from each tube every three minutes as you did for part A, until any one of the solutions no longer gives a positive test. Record your results on the Report Sheet.
EXPERIMENT 71 FACTORS AFFECTING ENZYME ACTIVITY

71 A. EFFECT OF TEMPERATURE

<table>
<thead>
<tr>
<th>Time Interval (Minutes)</th>
<th>Color Produced by Iodine Reagent on Starch-Saliva Mixtures at</th>
<th>Benedict's Test</th>
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<tbody>
<tr>
<td></td>
<td>70 °C</td>
<td>37 °C</td>
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<td>&quot;0&quot; minutes</td>
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<td>27</td>
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</table>

1. At what temperature was digestion the most rapid (optimum temperature)?

2. Explain why enzymes should be sensitive to temperature changes.

3. Are enzymes denatured by low temperatures?

4. What other factors influence the rates of reactions?
Enzymes

5. Was starch still present when reducing sugar was first detected in the hydrolysate? Name the sugar:

71 B. EFFECT OF pH

<table>
<thead>
<tr>
<th>Time Interval (Minutes)</th>
<th>Color Produced by Iodine Reagent on Starch-Saliva Mixtures at 37 °C and at</th>
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<tbody>
<tr>
<td></td>
<td>pH 5</td>
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<tr>
<td>&quot;0&quot; minutes</td>
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6. At what pH was digestion the most rapid (the optimum pH)?

Describe something other than an enzyme that will catalyze the hydrolysis of starch.

7. Draw the structure of the bond present in the peptide linkage:

8. Write a short statement expressing your conclusions from the results found.
**Nylon**

1. Describe the appearance of the nylon during synthesis. Describe the appearance of the washed nylon thread.

2. Is the nylon soluble in water?

3. How strong is a nylon thread?

4. What molecules have been eliminated in the condensation reaction to polymerize nylon 6,6?

5. Name three applications in which nylon is used. What does this indicate about its elasticity?

6. Explain why this nylon is called nylon 6,6.

7. A polyester is synthesized from sebacoyl chloride, ClOC(CH$_2$)$_6$COCl, and ethylene glycol, (HO)CH$_2$CH$_2$(OH). Draw the structure of the polyester formed.
Slime

1. Describe what happens when borax is added to the PVA solution.

2. Describe what happens when the slime is allowed to flow.

3. Describe what happens when the slime is rapidly pulled apart.

4. Recall the properties of solids and liquids given in Chapter 11 (Table 11.1 – pg 408 of textbook). Does slime behave like a liquid or a solid? Give examples of when it behaves like a solid and when it behaves like a liquid.

5. Scientists call substances like slime non-Newtonian liquids. These substances have properties of both solid and liquid states. They become more like a solid when greater pressure is placed on them. They also flow like a liquid and take the shape of the container. Give an example of another substance that behaves in this way.