21. Synthesis of a Polymer: Nylon-6,6

A. Introduction

Nylon-6,6, a synthetic polymer was synthesized and discovered to have commercial properties in the 1930's by Wallace Caruthers and co-workers at a DuPont research laboratory. DuPont began the mass production of nylon and their first commercial nylon product, nylon stockings, hit the market in 1940. Since that time, various other forms of nylon, such as nylon-6,10 have been developed. Nylon is presently found in numerous commercial products including: clothing, parachutes, ropes, toothbrush and toothbrush bristles. Additionally, many machined parts, such as the frame of a Glock handgun is made of nylon composite.

Polymers are large (high molecular weight) molecules made by repetitive bonding together of many smaller units called monomers as shown in figure 1a. To represent the *many* units that are present, a single monomer unit is placed in parenthesis with a subscript *n* to represent some unknown number of units. One of the most commonly encountered polymers is polystyrene (Styrofoam), which is made up of many repeating styrene units as shown in figure1b. In the case of styrene, the monomer units are each joined by new single bonds (in red). Because the styrene double bond took part in the polymerization reaction process, the styrene subunits within the polymer no longer possess the alkene functionality.

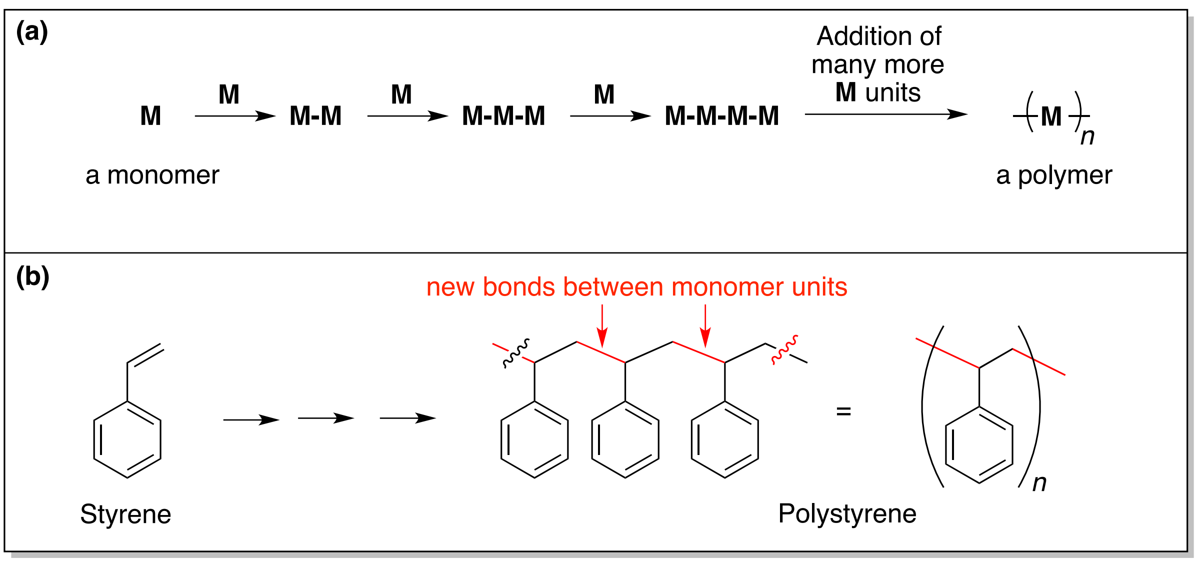


Figure 1. Polymerization: (a) Generic Example; (b) Polystyrene

Polystyrene is considered a **chain-growth polymer** because it is formed by a chain reaction where some initiator adds to the first molecule of monomer to yield a reactive species which in turn reacts with a second molecule of monomer and so on (figure 2). Additionally, polystyrene is classified as a **homopolymer** because it is made up of identical repeating units.

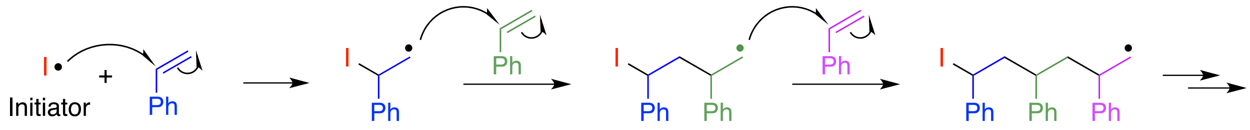


Figure 2. Radical Chain Growth Polymerization of Styrene

Different from the homopolymers are **copolymers**. Copolymers are polymers that contain two or more different monomer units embedded in their structure. Copolymers can be either random or alternating as shown in figure 3.

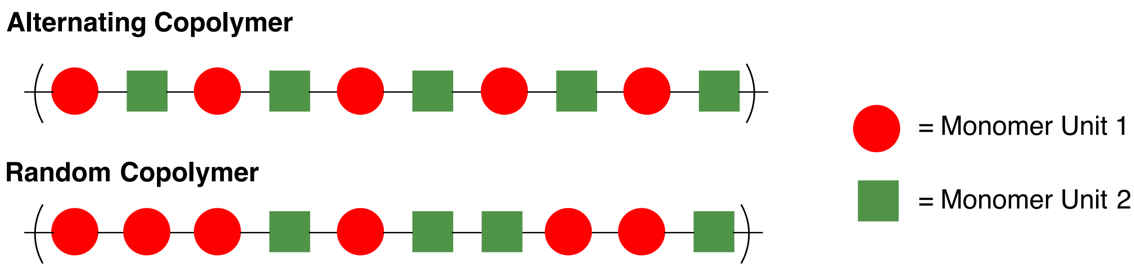
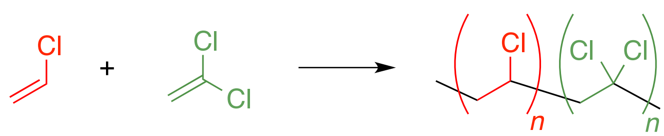


Figure 3. Alternating Versus Random Copolymers

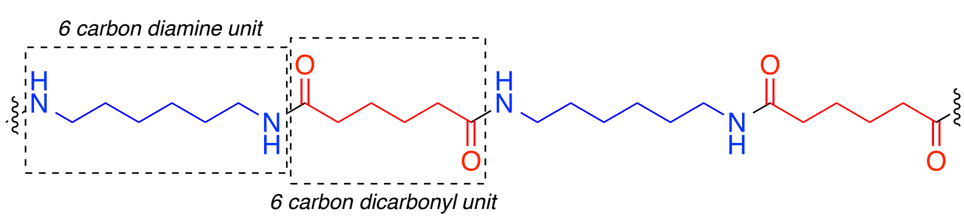
One of the best-known copolymers is Saran which is commonly used plastic wrap. Saran is prepared by the polymerization of chloroethene and 1,1-dichloroethene. In the Saran polymer, there are four times as many 1,1-dichloroethene units as there are chloroethene units. Modulating the ratios of the monomers used to form a copolymer gives products with differing properties such as different flexibilities and different tensile strengths.



Saran

Figure 4. Polymerization of Two Different Monomers to Form the Copolymer Saran

Nylon 6,6, which you will prepare in the lab experiment is an example of an alternating copolymer because it contains alternating diamine and dicarbonyl units. The 6,6 numbering refers to the number of carbon atoms in the diamine and dicarbonyl units, respectively. Another frequently encountered synthetic nylon polymer is Nylon 6,10. This polymer also has the six carbon diamine unit, but the dicarbonyl unit contains ten carbon atoms.



Nylon 6,6

Nylon is characterized differently than the chain growth type polymers discussed above. First, nylon is considered a **step growth polymer**. In a step-growth polymer, each bond of the polymer is formed stepwise, independent of the other bonds. In other words, in a chain growth polymerization, each reaction is dependent on the reactive intermediate formed in the previous step, while in a step growth polymer each bond is formed without regard to the other bond forming processes occurring in the mixture.

Nylon is also classified as a **condensation polymer**. Condensation is a reaction where two molecules are joined along with the loss of a small molecule such as water. In the lab experiment, you will be adding adipoyl chloride to 1,6-hexanediamine. The acid chloride (RCOCl) and amide react in a condensation process with loss of the small molecule HCl. The product contains a new amide bond (figure 5). The resulting product has both an acid chloride and amine functional group that can react with another molecule of 1,6-hexanediamien and adipoyl chloride, respectively. This process continues until all of the reagents have reacted to form Nylon 6,6 polymer.

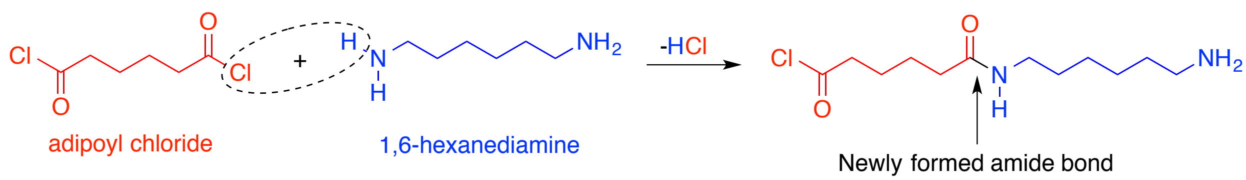


Figure 5. Formation of the Amide Bond in Nylon

In the laboratory experiment you will be layering a solution of adipoyl chloride in cyclohexane onto an aqueous basic solution of 1,6-hexanediamine (hexamethylenediamine). Because hexane and water are immiscible, a two-layer system will result. The polymerization will take place at the cyclohexane-water interface. Sodium hydroxide is added to the reaction mixture to aid in the amide formation.

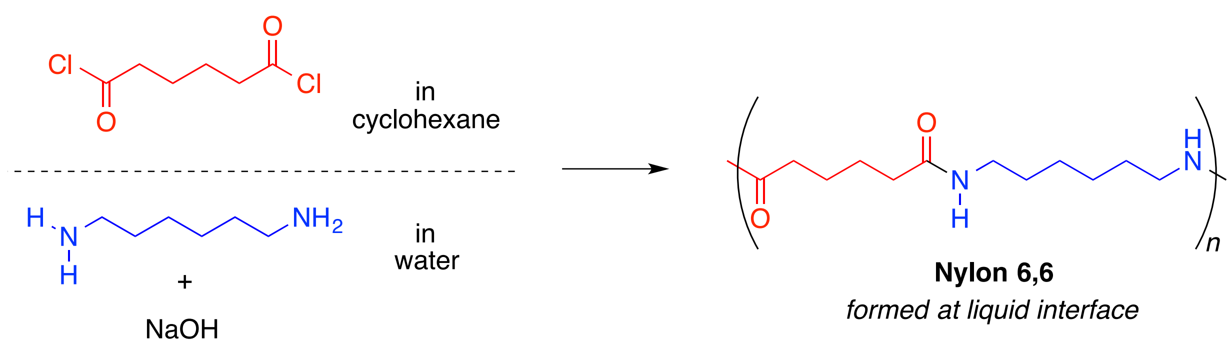


Figure 6. Formation of Nylon 6,6

B. Experimental Procedure

Place 10 mL of a 5% solution of adipoyl chloride in cyclohexane in a 50 mL beaker. Place 10 mL of a 5% aqueous solution of hexamethylenediamine in a separate 150 mL beaker. Add 7 drops of 20% sodium hydroxide solution to the hexamethylenediamine solution. Slightly tilt the beaker containing the aqueous diamine solution and carefully pour the acid chloride solution down the wall of the beaker to form two layers. If the solutions are poured together too vigorously, too much mixings of the solutions will occur and it will be impossible to form a nice film at the interface between the two solutions. A polymer film should form immediately at the liquid-liquid interface. Using your forceps gently pull a solid mass of polymer from the center of the liquid-liquid interface. At this point, you should be able to continue pulling polymer form the flask to produce a long rope of nylon. You can wind the rope around a test tube as it is being continuously pulled from the flask. Alternatively you can slowly walk along the bench as you continuously pull a long strand of rope from the flask. You can get a rope that is several feet long. Rinse the rope several times with water and lay it on a paper towel to dry.

Once you can no longer pull nylon rope from the flask, vigorously stir the remainder of the two-phase solution to see if any additional polymer forms. Decant the liquid from any polymer remaining in the flask. Wash this polymer first with 50% aqueous ethanol and then with water. Allow the polymer to dry.

Record the following observations in your notebook:

- The total mass of polymer formed. (The polymer must be thoroughly dried)
- The mass of your longest piece of nylon rope.
- The length of your longest continuous piece of nylon rope.
- Describe the color, appearance, texture, and shape of the nylon rope.
- Stretch test for tensile strength. Cut a 1-inch section of your nylon rope. Stretch it along a ruler to the point where it breaks. Record the maximum length that the nylon stretched to before breaking.

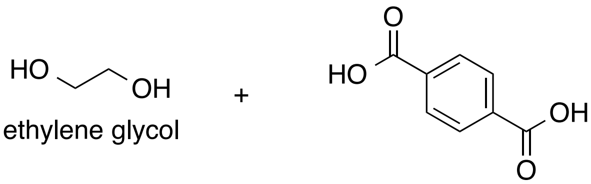
C. Pre-Lab Questions

1. In the experiment, you are instructed to use 10 mL of a 5% solution of adipoyl chloride and 10 mL of a 5% solution of hexamethylenediamine. Assuming these solutions are %volume/volume, calculate the mmol of each reagent that will be used in the experiment. Which reagents is the limiting reagent?

Reagent	Mol. Wt.	Density
Adipoyl chloride	183 g/mol	1.26 g/mL
Hexamethylenediamine	116 g/mol	0.89 g/mL

2. What is the theoretical yield (mg) of nylon that is formed in the experiment? Since you do not know the molecular weight of the polymer, you can get the theoretical yield in mg by the following procedure:
   - Determine the mass of adipoyl chloride used from the mmol of the limiting reagent.
   - Determine the mass of the hexamethylenediamine used from the mmol of the limiting reagent.
   - Determine the mass of HCl lost from the mmol of the limiting reagent.
   - Theoretical yield of polymer = mass adipoyl chloride + mass hexamethylenediamine – mass HCl.

3. Poly(ethylene terephthalate), PET, is a condensation polymer used to make plastic soda bottles. The two materials below are used to make PET. The condensation occurs with loss of HOH. Draw the structure of a PET fragment.



ethylene glycol

1,4-benzenedicarboxylic acid

D. Post-Lab Questions

1. Nylon 4,6 is a commonly used industrial nylon variant that can withstand higher temperatures than nylon 6,6. Draw the structure of nylon 4,6.

2. What is the percent yield of polymer that you obtained in the laboratory experiment?