Natural and Synthetic Polymers: The Preparation of Nylon

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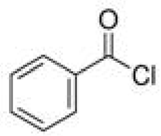
OBJECTIVES

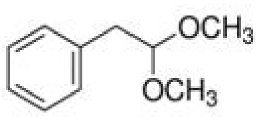
1. To learn some distinctions between natural and synthetic polymers.
2. To examine the monomers of two common fibers.
3. To become familiar with some of the physical and chemical properties of two common polymers.
4. To prepare the important polymer nylon.

PRELABORATORY QUESTIONS

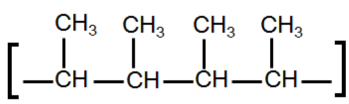
1. Explain why the nylons are called polyamides.
2. Draw the structures of adipic acid and its acid chloride.
3. Write equations for the reactions of benzoic acid and of benzoyl chloride, the acid chloride of benzoic acid, with n-propylamine to give an amide. Name the amide. In today's experiment, why will you synthesize nylon from an acid chloride rather than from a carboxylic acid?



4. Draw the structure of cellulose. Identify the acetal bonds, and circle monomer units.
5. On what basis is cellulose classified as a condensation polymer?
6. Write an equation for the hydrolysis of the following acetal in acidic solution.



7. A segment of a polymer molecule is shown below. Draw the structure of the monomer from which the polymer was synthesized. Is this an addition or a condensation polymer?



DISCUSSION

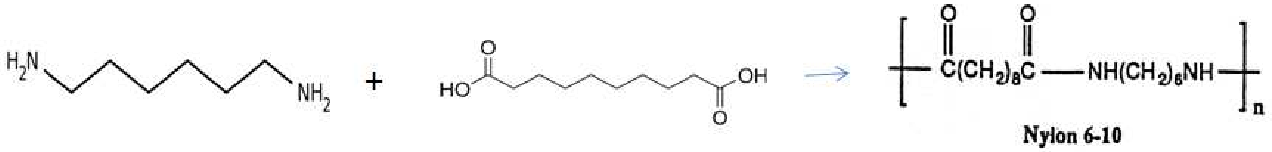
Nylon and cellulose are common polymers which make numerous contributions to our everyday lives. Nylon is a synthetic polymer. Cellulose occurs abundantly in nature as the main structural material of most plant tissues. Cotton is nearly pure cellulose. Both nylon and cotton are used in fabrics for clothing. Solid items such as gears, combs, and knobs are molded from nylon. Cellulose is converted into cellulose acetates, rayon, and other important fibers and films. Guncotton, the chief propellant in smokeless powder, is manufactured by treating fibers of cotton with a mixture of nitric and sulfuric acids under appropriate conditions. In today's experiment you will synthesize nylon and study the hydrolysis of cellulose.

What Are Polymers?

Polymers are high-molecular-weight molecules which are composed of simple, repeating units. Small molecules which are joined together by covalent bonds to become the repeating units of polymers are called monomers; hence, the repeating units are called monomeric units. When you scan the molecular structure of a polymer, you can usually recognize the monomeric units. From the structure of the recurring unit, you can deduce the structure of the monomer. Many polymers are derived from only one kind of monomer and, hence, contain only a single recurring unit. Others contain two or more kinds of monomeric units.

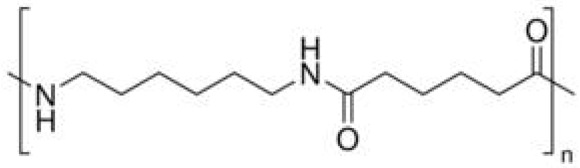
The Synthesis of Nylon

Both nylon and cellulose are examples of condensation polymers. A condensation polymer is one in which the repeating units have been formed from the monomers by elimination of a small molecule such as water or an alcohol. For example, the E. I. du Pont de Nemours Company, which pioneered nylon research, synthesizes Nylon 6-10 by condensing sebacic acid and hexamethylenediamine to give a polyamide (nylon), with the elimination of water.

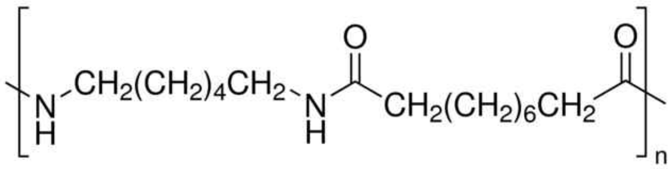


Hexamethylenediamine ***Sebacic Acid***

Nylon 6-10 is only one member of the nylon family. Another of these polyamides, Nylon 6-6, is prepared by condensing adipic acid and hexamethylenediamine. Segments of these polymers are

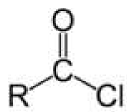


Nylon 6,6

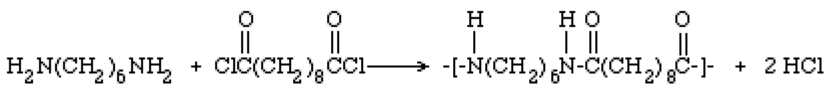


Nylon 6,10

The conditions for condensation of a dicarboxylic acid and a diamine are difficult to attain in the beginning chemistry laboratory, so you will synthesize Nylon 6-10 by a slight variation of the above procedure. Amides can be made easily, but more expensively, by heating an acid chloride, with an amine.



The first step in your synthesis of Nylon 6-10 from the acid chloride of sebacic acid (sebacoyl chloride) and hexamethylenediamine is

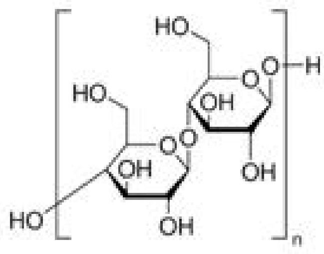


Sebacoyl chloride

The raw nylon which you will make is unsuitable for weaving into cloth without further refinement. Commercial nylon monofilament (thread) is made by forcing molten nylon through tiny orifices (openings). The thin streams of nylon harden into threads which are carefully stretched and twisted together to form a strong fiber.

Hydrolysis of Cellulose

The glucose units (monomers) in a cellulose molecule are joined together by acetal bonds. Hydrolysis of these acetal bonds forms β-glucose, which is rapidly converted to a mixture of all three forms of glucose-β-glucose, α-glucose, and the open-chain form. In today's experiment you will attempt to detect these monomers.



Segment of a Cellulose molecule

EXPERIMENT

1. Hydrolysis of a polymer, Cellulose: Formation of a Monomer

Make a compact wad of cotton (must be natural cotton) by compressing a cotton ball (about 4 cm in diameter), and place it in a large mortar. Pour 3 mL of concentrated sulfuric acid, H_2SO_4, over the cotton and grind it to a fine pulp with the pestle. **<u>Caution</u>**: C*oncentrated H_2SO_4 is dangerous! If you come in contact with acid, wash it off immediately.* Cautiously add 50 mL of water to the pulp, stir, and transfer all of the material to a 250-mL beaker. Boil the cellulose solution very gently for 30 minutes. Replace any water that evaporates during the boiling process.

When the hydrolysis solution has cooled, neutralize it by stirring in 20% sodium hydroxide, NaOH, solution until the solution is just basic to litmus. Confirm the presence of the monomer in the aqueous solution by means of Fehling's test as follows. Mix 1 mL of the hydrolysis solution with 2 mL of Fehling's reagent (equal amount of solutions A and B) and heat in a water bath for 10 to 15 minutes. Formation of a reddish brown precipitate of cuprous oxide, Cu_2O, constitutes a positive test for the monomer.

2. Synthesis of a Polymer, Nylon

Do this part of the experiment in teams of two. ***<u>Caution</u>**: Do this experiment with adequate ventilation or in a fume hood. Do not get any of the reagents on your skin, since they are highly irritating.*

Clean and dry a 50-mL beaker. To the beaker add 10 mL of a 2% solution of sebacoyl chloride in n-hexane. Obtain 10 mL of a solution which contains 3.5% hexamethylenediamine and 3% sodium hydroxide.

Tilt the beaker containing the hexamethylenediamine solution, and carefully pour the sebacoyl chloride-hexane solution down the side of the denser solution using a galss rod; *the layers must not mix together!* Put a piece of paper towel on the floor, and place the beaker on the towel.

Notice that the monomers have reacted at the interface between the layers to form a film of nylon. Use your spatula to loosen the film from the sides of the beaker. Now grasp the nylon film in the center with a pincette and slowly lift it, twisting as you lift. As you continue to lift and twist, a rope of nylon will form. Pull out about 1 m of rope and cut it with a pair of scissors. Put a piece of paper towel under the rope so that the chemicals do not drop on the desk or floor and carry it to the hood. ***Caution****: Don not touch the polymer with your hands until it has been washed.* Dip the rope into a 50% aqueous alcohol solution, and thoroughly rinse it to remove all of the chemical reagents. Stretch out the nylon rope on a paper towel under the hood and press it with paper towels. When the rope is dry, cut off 30 cm of it, label it with your names (use masking tape for a label), and submit it to your instructor. Cut the remaining rope into short lengths (5 to 10 cm) for tests described in the next paragraph.

Test the strength of your nylon by pulling on both ends of a piece. Using forceps, hold a piece of nylon in a flame to see if it will burn. Determine whether your nylon pieces are soluble in, or are affected by, the following solvents: acetone (under the hood), commercial liquid bleach, 25% sulfuric acid, 25% sodium hydroxide, and concentrated sulfuric acid (a small beaker of sulfuric acid will be provided under the hood—dip a piece of fiber into the solution). Now repeat all of these tests on cotton and compare the results with those for nylon.

You may wish to pull out some more nylon rope to take with you to show your friends. Be sure to wash it carefully as you did before. Destroy the remaining monomers by stirring the two layers together with your spatula or stirring rod. Put the ball of nylon in the trash basket (never down the drain), and dispose of the remaining solvents as directed by your TA.

QUESTIONS AND PROBLEMS

1. Is amylose an example of an addition or a condensation polymer? Explain.

2. Draw the structures of cellulose and amylose, side by side, and discuss the difference in their structures. Do both of these polysaccharides give the same product upon hydrolysis? Explain.

3. Write an equation for the synthesis of Nylon 6-6 from adipoyl chloride and hexamethylenediamine.

4. Draw the structure of a segment of the nylon that would be obtained by heating oxalic acid with ethylenediamine, $NH_2CH_2CH_2NH_2$. Name this nylon, using the numbering system discussed in this experiment.

5. The disaccharide cellobiose, which is an isomer of maltose, is formed during the hydrolysis of cellulose. Draw the structure of cellobiose. Compare its structure with that of maltose. Is cellobiose a reducing sugar? Is its an acetal? Is it a hemiacetal? Write an equation for the hdyrolysis of cellobiose.

6. List at least six commercial uses of nylon. For which of these uses would cotton also serve?

EXPERIMENT

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OBSERVATIONS AND RESULTS

1. Hydrolysis of a Polymer, Cellulose: Formation of a Monomer

Describe the results of Fehling's test:

What is the name of the monomer that is suggested by this test? Draw the structure of the monomer that is present in the hydrolysis solution.

Write an equation for the reaction that occurs between the monomer and Fehling's reagent.

Draw a segment of a polymer (cellulose) molecule, and show how water molecules break the acetal bonds to form a monomer molecule.

2. Synthesis of a Polymer, Nylon

Draw the structure of each monomer, and circle the functional groups which are involved in the polymerization (condensation) reaction.

Using an appropriate functional group from each monomer, show the condensation step.

Describe the results of the various tests on your nylon.

Strength:

Flammability:

Acetone:

Sulfuric acid (25%):

Sulfuric acid (concentrated):

Sodium hydroxide (25%)

Commercial liquid bleach:

If you had heated your nylon in aqueous sulfuric acid (25%) for an hour or so, it would have reacted and dissolved. Write an equation for the reaction that takes place under those conditions.