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#10 Condensation Polymerization: Preparation of Nylon 6/6

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I. INTRODUCTION

Description

Nylon 6/6 is produced here by the melt method. Students will first produce “nylon salt” from the reaction of hexamethylene diamine (HMDA) and adipic acid. In this particular case, the stoichiometric equivalence of the functional groups is achieved by isolating the 1:1 salt before allowing the condensation to take place. Then the nylon salt is converted, under pressure and heat, to nylon 6/6.

Student Audience

This experiment is recommended for chemical technology students who have had organic chemistry. Otherwise experienced students who have not taken organic chemistry will be able to perform the lab but will not get as clear an understanding of how the reaction is occurring.

Goals for the Experiment

By performing this lab, the student will:

- synthesize nylon 6/6,
- calculate the %-yield by mass,
- identify the polymer as thermoplastic or thermoset,
- write the equation for the reaction including the repeat unit of the product,
- determine the melting point of product,
- determine the density of product, and
- describe the end-product use of this polymer.

Recommended Placement in the Curriculum

This experiment is recommended to be used in the discussion of any of the following topics:

- synthesis of nylon,
- thermoplastic and thermoset polymers,
- polymerization reactions, and
- physical properties of polymers.

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II. STUDENT HANDOUT

Condensation Polymerization: Preparation of Nylon 6/6

Scenario

The investigation of a famous murder case, in which the body was wrapped in a carpet, led to a suspect whose car trunk contained a few carpet fibers. As part of the forensic evidence needed for a conviction, it is necessary to prove that the carpet fibers in the suspect's car match those found with the body. Additional detective work identified the carpet material as nylon 6/6. Samples from the two sources were submitted to a contract analytical lab, where you are employed, to determine if the fibers from the car were identical to those from the carpet.

Safety, Handling, and Disposal

- Wear safety goggles and lab coat while working in the lab. Rubber gloves should be worn while performing this experiment.
- Should skin contact occur while performing this experiment, wash contaminated area with water immediately.
- Hexamethylenediamine (1,6-diaminohexane) is irritating to the skin, eyes, and respiratory system.
- Adipic acid (hexanedioic acid) may be irritating to the skin, eyes, and mucous membranes.
- Ethanol is highly flammable. Keep away from heat, sparks, or open flame. Avoid inhalation.
- Use appropriate care with the open flame, hot silicon oil and vacuum apparatus.
- Dispose of any solvents into the laboratory organic waste container provided by your instructor.

Materials

- adipic acid (hexanedioic acid, $HOOC(CH_2)_4COOH$)
- hexamethylenediamine (HMDA; 1,6-diaminohexane, $H_2N(CH_2)_6NH_2$)
- ethanol
- nitrogen
- 250-mL beaker
- 100-mL graduated cylinder
- course filter paper
- Büchner funnel
- 600-mL beaker
- silicon oil
- ring stand, ring, and wire gauze
- thermometer, -20 °C to 350 °C
- Bunsen burner
- large ignition tube
- stopper to fit ignition tube
- heat resistant tape
- wire mesh screen
- one hole stopper (to fit ignition tube) with tubing to attach to vacuum pump
- tongs

- vacuum pump
- analytical balance
- (optional) melting point apparatus

Procedure

1. Weigh out 10.00 g of adipic acid and record the weight. Dissolve it in 100 mL of ethanol in a 250-mL beaker.
2. To this solution, add 12 mL of 70 %-v/v aqueous hexamethylenediamine.
3. Heat the mixture for 10 minutes at low heat. A white precipitate will form. This is the salt, hexamethylene diammonium adipate.
4. Collect the product on course filter paper in a Büchner funnel and wash with three 10-mL volumes of ethanol.
5. Air dry the product until no ethanol remains.
6. Weigh the dry product and calculate the %-yield by mass.
7. (optional) Determine the melting point of the product.
8. Use 300 mL of silicon oil in a 600-mL beaker to set up an oil bath. Place on the ring stand with ring and wire gauze over the Bunsen burner in the hood.
9. Preheat the oil bath to 215 °C.
10. Place 10 g of the salt in an ignition tube, purge with nitrogen, and seal with a rubber stopper. Wrap heat resistant tape around top of ignition tube and rubber stopper to seal. Place a wire mesh screen around the ignition tube.
11. Place the ignition tube set-up in the 215 °C oil bath and leave for one hour. Monitor the oil bath temperature and adjust the burner as needed to keep the temperature as close as possible to 215 °C.

Note! It is possible to use a single oil bath for several ignition tubes at the same time.

12. Carefully remove the ignition tube from the oil bath using tongs and allow it to cool to near room temperature.
13. Raise the temperature of the oil bath to 265–270 °C.
14. Once the ignition tube is cool, remove the wire screen, unwrap the tape, and remove the stopper. Add an additional 0.55 grams of adipic acid to the ignition tube.
15. Insert a one hole stopper with stem into the ignition tube and attach the stem to one of the vacuum pump inlet manifold hoses.

Note! It is possible to use a single vacuum pump for multiple ignition tubes.

16. Turn on the vacuum pump and place the ignition tube in the 267°C oil bath for one hour.
17. After one hour, turn off the burner but keep the vacuum on. Allow the ignition tube to cool and then remove it from the oil bath. Turn off the vacuum.
18. Remove the nylon 6/6 plug carefully from the ignition tube.

19. (optional) Follow your instructor's directions regarding whether or not to determine the mass, density, and/or melting point of the nylon 6/6 .
20. Turn in the sample to your instructor along with your data and the answers to the questions.

Questions

1. Who discovered nylon? What company did this person work for?
2. Where is nylon 6/6 used as an end product?
3. Is nylon 6/6 a thermoplastic polymer or is it a thermoset polymer?
4. How would you determine the average number of repeat units in the polymer?
5. What properties might be used to characterize this polymer?
6. Is the synthesis of nylon 6/6 an addition polymerization or is it a condensation polymerization? Discuss these two types of polymerization.
7. What condensate is removed during the reaction?
8. Write the net equation for the reaction.
9. Is the synthesis of nylon 6/6 a chain-growth polymerization or is it a step-growth polymerization. Discuss these two types of polymerization.

References

Department of Polymer Science at the University of Southern Mississippi Web Site, the Macrogalleria; http://www.psrc.usm.edu/macrog/synth.html (accessed 19 March 1998).

Shakhashiri, B.Z. *Chemical Demonstrations, Volume 1*; The University of Wisconsin Press: Madison, 1983; pp. 213-215.

Smith, W.F. "Principles of Materials Science and Engineering," Third Edition, pp. 374–377.

III. INSTRUCTOR NOTES

Condensation Polymerization: Preparation of Nylon 6/6

Purpose
To produce nylon 6/6 by the melt polymerization method and to identify its properties.

Time Required
This laboratory investigation should take 5-6 hours.

Suggested Group Size
It is recommended that each student do this activity individually or in small groups of 2-3 students.

Materials
Per class
- adipic acid (hexanedioic acid, $HOOC(CH_2)_4COOH$)
- hexamethylenediamine (HMDA; 1,6-diaminohexane, $H_2N(CH_2)_6NH_2$)
- ethanol
- nitrogen
- vacuum pumps
- analytical balances
- (optional) melting point apparatus

Per several students or groups of students
- 600-mL beaker
- silicon oil
- ring stand, ring, and wire gauze
- thermometer, -20°C to 350°C
- Bunsen burner

Per student or small group
- 250-mL beaker
- 100-mL graduated cylinder
- course filter paper
- Büchner funnel
- large ignition tube
- stopper to fit ignition tube
- heat resistant tape
- wire mesh screen
- one hole stopper (to fit ignition tube) with tubing to attach to vacuum pump
- tongs

Safety, Handling, and Disposal
- Students should wear safety goggles, lab coats, and rubber gloves while performing this experiment.
- Should skin contact occur while performing this experiment, wash contaminated area with water immediately.

- Hexamethylenediamine (1,6-diaminohexane) is irritating to the skin, eyes, and respiratory system.
- Adipic acid (hexanedioic acid) may be irritating to the skin, eyes, and mucous membranes.
- Ethanol is highly flammable. Keep away from heat, sparks, or open flame. Avoid inhalation.
- Be sure that the students understand the dangers associated with the hot silicon oil, the open flame, and the vacuum apparatus.
- Provide an organic waste container for the disposal of any excess solvents.

Points to Cover in Pre-Lab

- Make sure students understand the safety, handling, and disposal procedures of this experiment.
- Explain the solution condensation polymerization used to make nylon 6/6.
- Discuss set-up of silicon oil bath. Remind students that the oil bath will be very hot and that they should not sit front of the set-up.
- Discuss the technique used in setting up sealed ignition tubes purged with nitrogen.
- Discuss the technique used in the vacuum set-up process for converting the salt to nylon 6/6.
- Students should be familiar with finding density by water displacement. Discuss as needed.
- If students will be taking melting points and are not familiar with the melting point apparatus, demonstrate how it works.

Procedural Tips and Suggestions

- You may wish to set up the oil bath(s) and have them heating instead of having the students do steps 6 and 7 of the procedure. Each oil bath can accommodate more than one ignition tube. The actual number will depend on the size of the ignition tubes. This will also make for more efficient use of the hoods.
- The vacuum pump can also be used with multiple ignition tubes. This is especially helpful if you have only one vacuum pump.
- The various ignition tubes which use the same oil bath should go into the oil bath at close to the same time in step 14. This way all the tubes will be ready when the heat is turned off after an hour.
- To minimize the potential danger of students contacting the hot oil, do not let them remain in front of the hood during the two heating periods.

Plausible Answers to Questions

1. Who discovered nylon? What company did this person work for?

A: In 1937, Wallace Carothers of the Dupont company first produced nylon.

2. Where is nylon 6/6 used as an end product?

A: Nylon 6/6 has a wide range of uses. Nylon fibers are used for carpets, tire cord, rope, hosiery, apparel, and home furnishings. The high strength of nylon allows manufacture of lightweight and very sheer fabrics. High strength nylon also has a variety of automotive and industrial uses.

3. Is nylon 6/6 a thermoplastic polymer or is it a thermoset polymer?

A: Nylon 6/6 a thermoplastic polymer.

4. How would you determine the average number of repeat units in the polymer?

A: The most often used way to determine the average number of monomers in a polymer is to measure the number average molecular weight (Mn) by Size Exclusion Chromatography and divide by the molecular weight of the repeat unit. This number is an average because there are polymer chains of different length (i.e., a molecular weight distribution) in the product. If the molecular weight is not too high, it may be possible to determine Mn from the NMR spectrum of the polymer by comparing the relative peak areas for the end groups with the peak area for the backbone groups.
It may also be possible to use titration methods to quantify the end groups.
A newer, more accurate but more expensive method for obtaining absolute molecular weights of polymer chains (including proteins) is matrix assisted laser desorption ionization mass spectroscopy (MALDI mass spec).

5. What properties might be used to characterize this polymer?

A: Melting point, crystallinity, and density might be used to characterize these materials. The melting point for nylon 6/6 is approximately 260 °C and its density is 1.14 g/mL.

6. Is the synthesis of nylon 6/6 an addition polymerization or is it a condensation polymerization? Discuss these two types of polymerization.

A: The synthesis of nylon 6/6 is a condensation reaction. Condensation polymerization involves the reaction of two functional groups (such as the amine and carboxylic acid in this nylon preparation) to produce a new functional group (amide for nylon) and a small molecule such as water or HCl. With addition polymerization, the entire monomer becomes part of the polymer. Synthesis of polyethylene from ethylene monomers is an example of addition polymerization.

7. What condensate is removed during the reaction?

A: Water (-H from the amine nitrogen and -OH from the carboxylic acid) is the condensate that is removed from this reaction.

8. Write the net equation for the reaction.

A: $HOOC(CH_2)_4COOH + NH_2(CH_2)_6NH_2 \longrightarrow -[NH(CH_2)_6NH-CO(CH_2)_4CO]- + 2H_2O$

9. Is the synthesis of nylon 6/6 a chain-growth polymerization or is it a step-growth polymerization. Discuss these two types of polymerization.

A: The reactions involved in the production of nylon 6/6 are step-growth. In step-growth reactions, the growing chain may react with other growing chains, joining them together. A chain-growth polymerization involves the chain length increasing by reaction of a single monomer (and only a single monomer) at the end of a growing polymer chain.

Note that both condensation and addition polymerizations can be either step- or chain-growth.

Variation

Nylon 6/6 can also be made by interfacial polymerization. If you do this experiment make sure student wear goggles and lab coats. It is also advisable to wear rubber gloves because harsh chemicals can damage skin and clothing if spilled.

Materials

Per class

- hexamethylenediamine (HMDA; 1,6-diaminohexane, $H_2N(CH_2)_6NH_2$)
- NaOH
- distilled water
- adipoyl chloride [$ClCO(CH_2)_4COCl$]
- hexane (Ligroin can be used in place of hexane.)
- analytical balances
- (optional) melting point apparatus

Per student or small group

- 3 100-mL beakers
- 3 10-mL graduated cylinders
- funnel
- forceps
- glass rod

Procedure

a. To prepare the hexamethylenediamine (HMDA) solution, dissolve 3.0 g of hexamethylenediamine and 1.0 g of NaOH in 50 mL distilled water in a labeled 100-mL beaker.

Caution! The solution of NaOH is highly exothermic.

Note: HMDA can be dispensed by placing the reagent bottle in hot water until sufficient solid has melted and can be decanted.

b. Measure 5 mL of the HMDA solution in a 10-mL graduated cylinder.

c. To prepare adipoyl chloride solution, dissolve 1.5 to 2.0 mL of adipoyl chloride in 50 mL hexane (or ligroin) in a second labeled 100-mL beaker.

d. Measure 5 mL of the adipoyl chloride solution in a second 10-mL graduated cylinder and pour into the third 100-mL beaker.

e. Slowly pour the 5 mL of adipoyl chloride solution through a funnel onto the top of the beaker containing the HMDA. Do not mix or stir. A film will form at the interface between the two solutions.

f. With forceps, grab a hold of the film at the center, pull slowly, and wind the resultant fiber onto a glass rod. Dry the nylon fiber by sandwiching between paper towels.

g. (optional) Determine the melting point of the fiber.

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References

Department of Polymer Science at the University of Southern Mississippi Web Site, the Macrogalleria; http://www.psrc.usm.edu/macrog/synth.html (accessed 19 March 1998).

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