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#13 Addition Polymerization: Preparation of Polystyrene Using Two Types of Initiators

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I. INTRODUCTION

Description

This is an excellent lab to introduce students to addition polymerization and to the concept of initiators. Addition polymerization usually must be catalyzed (initiated) by a base, an acid, or free radical. There are three steps that are involved in addition polymerization no matter what initiator is used. These three steps are initiation, propagation, and termination.

The students will polymerize styrene using two types of initiators, benzoyl peroxide (free radical) and anhydrous aluminum chloride (cationic). They will then compare the properties of the products.

Student Audience

The experiment is recommended for chemical technology students who have had organic chemistry. Students who have not taken organic chemistry will be able to perform the lab but will not get as clear an understanding of the chemical reactions.

Goals for the Experiment

By doing this lab the student will:

- demonstrate the synthesis of polystyrene using two types of initiators,
- identify the basic properties of polystyrene made with two different initiators,
- identify polystyrene as thermoplastic or thermoset,
- write the equation for the reaction including the polymers repeat unit,
- determine the melting point and density of the two polystyrenes, and
- describe the end product uses of the two types of polystyrene.

Recommended Placement in the Curriculum

This experiment is recommended for use in the discussion of any of the following topics:

- polystyrene,
- initiators,
- chain-growth addition polymerization, and
- physical and chemical properties of polymers.

II. STUDENT HANDOUT

Addition Polymerization: Preparation of Polystyrene Using Two Types of Initiators

Scenario

Your company, Tiny Tot Toys, has been purchasing polystyrene from a local producer, PolyS. PolyS has been purchased by Overseas Conglomerate Company which is shutting down the nearby plant. This will increase the price of the polystyrene your company molds for its toys because shipping costs will be much greater. The management of T^3 wants to consider all its options including making the polystyrene on site or purchasing the old PolyS plant. OC^2 will not, however, disclose what type of initiator PolyS had been using to produce polystyrene for T^3. As a research technician for the toy company, it is your job to produce samples of polystyrene using two different initiators so that property comparisons can be made.

Safety, Handling, and Disposal

- This experiment must be done in a well ventilated hood. Students will wear safety goggles, gloves, and proper clothing.
- Acetone is highly flammable and must be kept away from open flames. Prolonged or repeated topical use may cause erythema and dryness. Inhalation may produce headache, fatigue, excitement, bronchial irritation, and, in large amounts, narcosis.
- Anhydrous aluminum chloride must be kept in a tightly closed container and protected from moisture. It combines with moisture with explosive violence and liberation of HCl and a great deal of heat.
- Benzoyl peroxide is highly toxic by inhalation and may explode spontaneously when dry (<1% of water). It should not be stored in screw-capped bottles, because the friction produced by opening the bottle could cause an explosion.
- External exposure to concentrated hydrochloric acid can cause severe burns and permanent visual damage. Inhalation of HCl vapor may cause coughing, choking, or, in severe cases, inflammation and ulceration of the respiratory tract.
- Ethanol will cause a variety of symptoms depending on the amount ingested: nausea, vomiting, flushing, mental excitement or depression, drowsiness, impaired perception, incoordination, stupor, coma, and death.
- Hexane is irritating to the respiratory tract. It is flammable and must be kept away from open flames.
- Methanol is flammable making it a dangerous fire risk. It is toxic by ingestion.
- Nitric acid is a strong acid and an oxidizing agent. It reacts violently with alcohol, turpentine, charcoal, and organic refuse. The choking fumes may cause chronic bronchitis upon continued exposure.
- Styrene is toxic by ingestion and inhalation. Styrene is flammable. Keep away from open flame.
- Toluene is toxic by ingestion, inhalation, and skin absorption. Toluene is flammable. Keep away from open flame.
- Should skin contact occur with any of these reagents, wash contaminated area immediately.
- Use appropriate caution with the Bunsen Burner.
- Read the Materials Safety Data Sheets for all the chemicals used in this investigation.
- Any unused polymerization mixture should not be poured into the sink but should be stirred until no further polymer is formed.
- Any remaining solvent/material will be disposed into the laboratory organic waste container.

Materials

- acetone
- aluminum chloride (anhydrous)
- benzoyl peroxide
- (optional) calcium chloride
- conc. HCl
- conc. HNO_3
- ethanol
- hexane
- methanol
- (optional) 10% aqueous sodium hydroxide
- styrene (inhibitor free or follow optional steps to remove inhibitor)
- tetrahydrofuran
- toluene
- analytical balance
- (optional) 250-mL separatory funnel
- (optional) 100-mL
- 20- x 150-mm test tube
- 25-mL graduated cylinder
- 10-mL graduated cylinder
- 2 400-mL beakers
- hot plate
- thermometer (-20 to 120 °C)
- Büchner funnel
- filtering flask
- tygon tubing and aspirator
- # 5 filter paper
- 100-mL graduated cylinder
- 6 10- x 100-mm test tubes
- metal spatula
- glass stirring rod
- Bunsen burner
- (optional) melting point apparatus
- 150-mL beaker

Procedure

1. <u>Polymerization of styrene with benzoyl peroxide as initiator</u>

a. (optional) If the styrene contains an inhibitor, the inhibitor must first be removed. To do this, measure 60 mL of inhibited styrene into a 250-mL separatory funnel and add 60 mL of 10% NaOH. Shake the contents several times while properly venting for 1 minute.

b. (optional) Separate the styrene from the separatory funnel and place into 100-mL beaker. Add approximately 2 grams of calcium carbonate into the styrene and stir. This will dry your styrene.

c. Add 20 mL of toluene and 5 mL of inhibitor free styrene to a 20- x 150-mm test tube.

d. Add 0.3 g of benzoyl peroxide.

Caution: Review the safety information on benzoyl peroxide. Handle with extreme caution.

e. Place the test tube in a 400-mL beaker half full of water on a hot plate. Maintain the temperature of the bath between 90-95 °C.

f. After 60 minutes remove the test tube, allow the contents to cool for 5 minutes, and note the viscosity of the solution. Pour the solution into 200 mL of methanol contained in a 400-mL beaker. A white precipitate of polystyrene will form.

g. Collect the polystyrene by filtration using a Büchner funnel, and wash the precipitate on the funnel with 50 mL of methanol. Remove the precipitate from the funnel and spread it out to dry on a large, clean sheet of filter paper.

h. Place 3 mL of acetone in a clean test tube and add 0.2 g of dried polymer. Stir the mixture for several minutes to see if it is soluble. Is polystyrene soluble in acetone?

i. Repeat step (f) for the following solvents: ethanol, conc. HNO_3, conc. HCl, tetrahydrofuran, and hexane.

j. Place about 0.1 g of the polymer on a metal spatula and warm it gently over a flame until the polymer melts. Touch a glass stirring rod to the molten polymer and pull away gently to draw out a fiber.

k. (optional) Determine the melting point of this polymer.

2. <u>Polymerization of styrene with aluminum chloride as initiator</u>

a Measure 5 mL of inhibitor free styrene into a 150-mL beaker.

Caution: Review the safety information on anhydrous aluminum chloride. Handle with extreme caution.

b. Carefully add, in small portions, 0.3 g of anhydrous aluminum chloride. You will notice that the reaction is highly exothermic. The temperature rises rapidly and the styrene becomes a brownish black color.

c. Allow the mixture to stand for 15 minutes. Describe the properties of the product.

d. Add 50 mL of the methanol, stir the mixture, and heat it to boiling over several minutes on a hot plate while stirring. Cool the mixture to room temperature, decant the alcohol, and compare the properties of the polymer with those of part 1.

e. Dissolve the remainder of the polymer in 25 mL of toluene, add the solution to 100 mL of methanol, and allow the precipitate to form and settle. Decant the alcohol and air dry the polymer. Again, compare properties to the polymer prepared in part 1.

f. Perform the solubility tests as described in part 1, steps (h) and (i).

g. (optional) Determine the melting point of this polymer.

Questions

1. What is polystyrene?
2. Write the net reaction for the polymerization.
3. How did the melting points of the polystyrene made with the different initiators compare? Why might they not be the same?
4. Compare the reactions of polystyrene to nylon 6/6.

5. What is polystyrene used for in restaurants, supermarkets, schools, and health care institutions? Discuss the environmental impact of these uses.

6 What percentage of the nation's petroleum and natural gas consumption is used to make polystyrene?

7. How do manufacturers and shippers use polystyrene?

III. INSTRUCTOR NOTES

Addition Polymerization: Preparation of Polystyrene Using Two Types of Initiators

Purpose

To produce polystyrene using two different types of initiators and compare the properties of the products.

Time Required

This laboratory procedure should take 2–3 hours.

Group Size

It is recommended that each student do this lab individually or with a partner.

Materials

Per class

- acetone
- aluminum chloride (anhydrous)
- benzoyl peroxide
- conc. HCl
- conc. HNO_3
- ethanol
- hexane
- methanol
- styrene (inhibitor free)
- tetrahydrofuran
- toluene
- analytical balance
- (optional) melting point apparatus

Per student or pairs of students

- 1 20- x 150-mm test tube
- 25-mL graduated cylinder
- 10-mL graduated cylinder
- 2 400-mL beakers
- hot plate
- thermometer (-20 to 120 °C)
- Büchner funnel
- filtering flask
- tygon tubing and aspirator
- # 5 filter paper
- 100-mL graduated cylinder
- 6 10- x 100-mm test tubes
- metal spatula
- glass stirring rod
- Bunsen burner
- 150-mL beaker

Safety, Handling, and Disposal

- This experiment must be done in a well ventilated hood. Students will wear safety goggles, gloves, and proper clothing.
- Acetone is highly flammable and must be kept away from open flames. Prolonged or repeated topical use may cause erythema and dryness. Inhalation may produce headache, fatigue, excitement, bronchial irritation, and, in large amounts, narcosis.
- **Anhydrous aluminum chloride** must be kept in a tightly closed container and protected from moisture. It **combines with moisture with explosive violence and liberation of HCl and a great deal of heat.**
- Benzoyl peroxide is highly toxic by inhalation and may explode spontaneously when dry (<1% of water). It should not be stored in screw-capped bottles, because the friction produced by opening the bottle could cause an explosion.
- Ethanol will cause a variety of symptoms depending on the amount ingested: nausea, vomiting, flushing, mental excitement or depression, drowsiness, impaired perception, incoordination, stupor, coma, and death.
- Hexane is irritating to the respiratory tract and, in high concentrations, narcotic.
- External exposure to concentrated hydrochloric acid can cause severe burns and permanent visual damage. Inhalation of HCl vapor may cause coughing, choking, or, in severe cases, inflammation and ulceration of the respiratory tract.
- Methanol is flammable making it a dangerous fire risk. It is toxic by ingestion and the TLV is 200 ppm in air.
- Nitric acid is a strong acid and an oxidizing agent. It reacts violently with alcohol, turpentine, charcoal, and organic refuse. The choking fumes may cause chronic bronchitis upon continued exposure.
- Styrene is toxic by ingestion and inhalation. *The Threshold Limit Value* (TLV) for styrene is 50 ppm in air. Styrene is flammable. Keep away from open flame.
- Toluene is toxic by ingestion, inhalation, and skin absorption. Its TLV is 100 ppm in air. Toluene is flammable. Keep away from open flame.
- Should skin contact occur with any of these reagents, wash contaminated area immediately.
- Use appropriate caution with the Bunsen burner.
- Read the Materials Safety Data Sheets for all the chemicals used in this investigation.
- Any unused polymerization mixture must not be poured into the sink but should be stirred until no further polymer is formed.
- Provide an organic waste container for any remaining solvent/material. Dispose of this material according to local, state, or federal regulations.

Points to cover in Pre-Lab

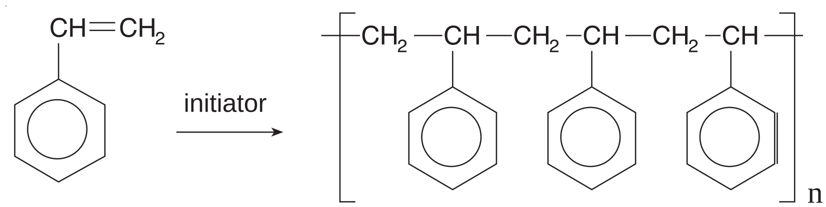
- Make sure students understand the safety, handling, and disposal procedures of this experiment.
- Discuss chain-growth polymers and compare this process with step-growth.
- Discuss initiation, propagation, and termination reactions and the relation to molecular weight.
- Discuss initiators and the role they play in a chain growth process.
- There are three types of initiators that are used in chain growth processes: cationic, anionic, and free radicals. Discuss each and indicate the types that the students will be working with.
- Discuss tacticity (stereo regularity) and its influence on properties (crystallinity, Tg, etc.)

Plausible Answers to Questions

1. What is polystyrene?

A: Polystyrene is a light weight plastic derived from petroleum by-products and natural gas. Although best known for its use in the packaging industry, most polystyrene is used to make durable goods, such as television cabinets, appliances, and furniture.

2. Write the net reaction for the polymerization.



3. How did the melting points of the polystyrene made with the different initiators compare? Why might they not be the same?

A: The melting points might differ due to different average chain lengths of the two products or the products may be different stereoisomers. Other possibilities include contamination with reactants or solvents.

4. Compare the reactions of polystyrene to nylon 6/6.

A: Polystyrene is a chain-growth polymer that requires an initiator to begin polymerization. The molecular weights of the monomer and the repeat unit are the same in an addition polymer. Nylon 6/6, on the other hand, is a condensation polymer that has active sites on its monomers that are self reactive and do not require an initiator to start polymerization. In general, step-growth polymers are condensation systems in that their monomers and repeat units have different molecular weights.

5. What is polystyrene used for in restaurants, supermarkets, schools, and health care institutions? Discuss the environmental impact of these uses.

A: Schools, health care facilities, and restaurants rely on the sanitation, insulation, and sturdiness that polystyrene food service packaging provides. These facilities use both foam and solid polystyrene. Foam include plates, cups, bowls, and food trays. The solid form of polystyrene is used in clear plastic glasses, deli containers, and beverage lids.

The environmental impacts of PS and other materials are very much dependent on the industry that produces them and on the consumer. The industry should not only inform the public of the advantages of their products but also facilitate an increase in plastics recycling in an environmentally responsible and economically sustainable manner. The public in turn must make a corresponding effort to recycle efficiently and effectively.

6. What percentage of the nation's petroleum and natural gas consumption is used to make polystyrene?

A: The manufacture of all polystyrene, to make both durable and packaging products, uses a fraction of one percent of the nation's natural gas and petroleum. All plastics, according to the American Petroleum Institute, consume only about three percent of US natural gas and petroleum.

7. How do manufacturers and shippers use polystyrene?

A: Manufactures and shippers use polystyrene in several forms as protective packaging. One is the shape molding-formed foam pieces that contour around specific products, such as television sets, stereo equipment, and appliances to protect them in transit. Foamed polystyrene is also used as loose packing in the form of small pellets or "peanuts."

Reference

Shakhashiri, B.Z. *Chemical Demonstrations, Volume 1*; The University of Wisconsin Press: Madison, 1983; pp. 241-242.