To close the yellow note, click once to select it and then click the box in the upper left corner.
To open the note, double click (Mac OS) or right click (Windows) on the note icon.

#20 The Influence of Initiator Concentration on the Molecular Weight of Polystyrene

Submitted by: Arturo Contreras, Visiting Scholar, Center for Chemical Education, Miami University, Middletown, OH;1996-1997.

I. INTRODUCTION

Description

Polystyrene (PS) is a hard, rigid, transparent plastic with good dimensional stability. The material has good chemical resistance to many aqueous solutions but it is soluble in many aromatic and halogenated solvents. It cannot be used at elevated temperatures (maximum 60 °C continuous, 70 °C for short periods) and it may break when subject to mechanical stress.

Polystyrene polymerizes with a chain reaction. Chain reactions require initiator molecules, like the free radical formed when benzoyl peroxide breaks up. Free radicals have single electrons, which makes them very reactive. Monomers for chain reactions often have carbon-carbon double bonds, which then are attacked by the initiator molecule to form a reactive molecule. This reactive molecule then attacks another monomer, so the chain gets longer and longer. The total number of polymer molecules formed depends on the number of initiator fragments. The more initiator you use, the more polymer molecules. That is, for the same amount of monomer, you get smaller polymer molecules by using more initiator, because there are more reactive sites competing for monomers.

Students will synthesize polystyrene and explore the influence that initiator concentration has on the molecular weight of the product.

Student Audience

This 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 may not have as clear an understanding of the reaction.

Goals for the Experiment

By doing this lab the student will:

- synthesize polystyrene,
- change the molecular weight of polystyrene by changing the initiator concentration, and
- identify the molecular weight of polystyrene samples by their viscosity.

Recommended Placement in the Curriculum

This experiment is recommended to be used in the discussion of

- polymer synthesis,
- initiators, and
- viscosity.

II. STUDENT HANDOUT

The Influence of Initiator Concentration on the Molecular Weight of Polystyrene

Scenario

In processing polystyrene (PS), one of the factors that effects end-use applications is molecular weight. By controlling the molecular weight of polystyrene and producing it with different molecular weights, a company becomes more viable because of the spectrum of uses of these materials.

Your job as lab analyst is to make low, medium, and high molecular weight products of PS. You will control the initiator concentration in processing PS and will identify the molecular weight of these products by viscosity.

Safety, Handling, and Disposal

- This experiment must be done in a well-ventilated hood.
- You must wear safety goggles, gloves, and proper clothing.
- Should skin contact occur, wash contaminated area immediately.
- Benzoyl peroxide is highly toxic by inhalation and may explode spontaneously when dry (<1% of water).
- Methanol is flammable making it a dangerous fire risk.
- Sodium hydroxide (NaOH) is corrosive and a strong irritant to tissue which include eyes, skin, and mucous membranes.
- 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.
- Do not pour any unused mixture down the sink. Any remaining solvent/material will be disposed into the organic waste container provided by your instructor.

Materials

- inhibited styrene monomer
- 10% NaOH
- 100-mL graduated cylinder
- 250-mL separatory funnel
- 100-mL beaker
- calcium carbonate
- analytical balance
- 3 large test tubes
- toluene
- benzoyl peroxide
- 4 400-mL beakers
- hot plate
- methanol
- Büchner funnel
- # 5 filter paper
- 500-mL filter flask
- aspirator
- 16 100-mL volumetric flasks

- known molecular weight polystyrene sample
- 10-gal aquarium with aquarium heater
- thermometer (-10 °C to 110 °C)
- 2 utility clamps
- laboratory stirrer
- Cannon-Fenske viscometer, #50
- 10-mL pipette
- acetone
- clean air or nitrogen under pressure

Procedure

1. Synthesis of Polystyrene

a. To remove the inhibiting agent, 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. The styrene will be the upper layer and the aqueous NaOH the bottom layer. Separate the styrene and place into a 100-mL beaker. Add approximately 2 grams of calcium carbonate into the styrene and stir. This will dry your styrene.

c. Label the three large test tubes with 0.150 g benzoyl peroxide, 0.300 g benzoyl peroxide, and 0.500 g benzoyl peroxide.

d. To each of the three large test tubes, add 10 mL of styrene and 40 mL of toluene. Add the appropriate amount of benzoyl peroxide to each of the three test tubes.

e. Agitate gently until the benzoyl peroxide has gone into solution.

f. Place the 3 test tubes into a 400-mL beaker half filled with water and place the beaker on a hot plate. Maintain the temperature of the water bath between 90 °C and 95 °C for 1 hour.

g. Prepare 3 400-mL beakers by labeling to match the test tubes and adding 200 mL methanol to each.

h. Remove the test tubes from the beaker and allow to cool for five minutes. Add the contents to the methanol in the 3 labeled 400-mL beakers. A precipitate of polystyrene will form in each beaker.

i. Vacuum filter each of the precipitates using a 500-mL filtering flask and Büchner funnel. Wash each precipitate with 50 mL portions of methanol and allow to dry for 48 hours.

2. Viscosity of Polystyrene

a. You have your three dry polystyrene samples synthesized using different initiator concentrations plus a known molecular weight polystyrene provided by the instructor. Using 16 100-mL volumetric flasks, prepare four concentrations of each of the four samples using toluene as the solvent:
0.200 g/dL, 0.400 g/dL, 0.600 g/dL and 0.800 g/dL. (dL = deciliter = 100 mL)

b. Prepare a 10-gallon aquarium by filling it nearly to the rim with tap water.

c. Place the aquarium heater into the aquarium and adjust it so the temperature is constant at 25 °C (±0.1 °C). The thermometer should be secured in the aquarium in order to monitor the temperature.

d. Place a lab stirrer in the aquarium in order to circulate the water and keep the temperature constant throughout the aquarium.

e. Secure 3 number 50 Canon-Fenske viscometers into the aquarium exposing the openings above the surface of the water. Allow the viscometers to acclimate for a few minutes once constant temperature is reached.

f. Measure the efflux time of 10 mL pure solvent (toluene). Do this 6 times and record all measurements.

g. Now place 10 mL of the 0.200 g/dL concentration of one of the polystyrene samples into the viscometer and measure its efflux time 6 times and record data.

h. Between measurements of the different concentrations of dilute polymer solution, rinse the viscometer with toluene, then with acetone, and blow dry with clean air or nitrogen.

i. Repeat step g for each of the concentrations of each of the polystyrene samples including the known provided by your instructor.

j. Calculate the average (mean), standard deviation, and relative standard deviation for each concentration of each sample.

Calculations

1. The average efflux time (t_i) is used to determine a reduced viscosity (η_{red}) and an inherent viscosity (η_{inh}) for each concentration (C). Both η_{red} and η_{inh} are plotted vs. C and the y intercept(s) determined. (See Figure 1.) This value (or the average value if the intercepts are not the same) is the intrinsic viscosity, [η]. The viscosity average molecular weight, M_v, can be calculated from the intrinsic viscosity by the Mark-Houwink-Sakurada equation:

$$[\eta] = KM_v^a$$

   where "K" and "a" are the Mark-Houwink constants which are unique for every polymer-solvent combination.

2. Prepare a table of mean ti, η_{sp}, η_{red}, η_{inh} and complete the calculations necessary to fill it in.

   a. $\eta_{red} = \eta_{sp}/C$ where η_{sp} is specific viscosity and C is the concentration.

   b. $\eta_{sp} = (t_i - t_o)/t_o$ where t_i is efflux time of polymer solutions and t_o is efflux time of the pure solvent.

   c. $\eta_{inh} = \text{Ln } \eta_r/C$ where Ln η_r is the natural log of the relative viscosity (η_r) and C is the concentration of the polymer solution.

   d. $\eta_r = t_i/t_o$ where t_i is efflux time of polymer solutions and t_o is efflux time of the pure solvent.

3. Determine the intrinsic viscosity, [η], by plotting both the reduced viscosity and inherent viscosity on the y-axis vs. concentration, C, on the x-axis. The y-intercepts (at x = 0) can be found by the linear least squares method and/or graphically. Ideally the y-intercept should be the same for both the reduced and inherent viscosities. This value (or the average value if the intercepts are not the same) is the intrinsic viscosity, [η].

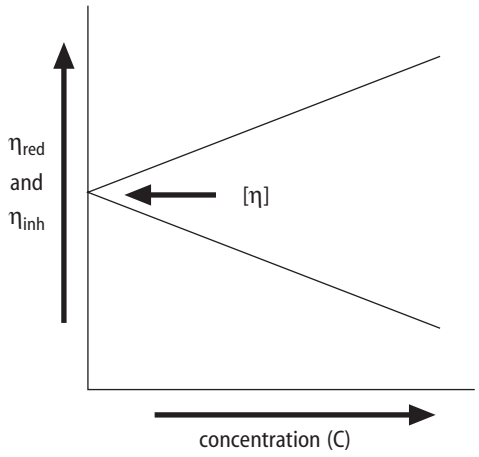

Figure 1 Plot of η_{red} and η_{inh} vs. concentration, C.

4. Calculate the viscosity molecular weight, M_v, by using the Mark-Houwink-Sakurada Equation: $[\eta] = KM_v^a$

A representative "K" value for polystyrene in toluene has been reported to be 1.7×10^{-4} dL/g at the temperature of the water bath, 25 °C, (and 1.2×10^{-4} dL/g at 30 °C). A corresponding "a" value for PS is 0.69 at 25 °C (and 0.70 at 30 °C). The reported values, especially for K, show considerable variation even at a single temperature.

Questions

1. What are the three steps affecting molecular weight in free radical polymerization?
2. What happens to the molecular weight of polystyrene as you increase the concentration of the initiator? Why?
3. Why is the water bath maintained at a constant temperature?
4. In general, how does viscosity measure molecular weight?
5. Does the standard deviation or the relative standard deviation vary with concentration? Why might this occur?
6. Discuss potential sources of error in your measurements and how they would affect your results.
7. Why is molecular weight an important property of polymers?

References

Brandrup, J; Immergut, E.H.; Eds. *The Polymer Handbook; 3rd Ed.*; John Wiley and Sons; New York; 1989; pp. VII/1 through VII/32.

Carraher, C. E. Jr. *Polymer Chemistry, an Introduction, 4th Ed.*; Marcel Dekker, Inc. New York, 1996.

Department of Polymer Science at the University of Southern Mississippi Web Site, the Macrogalleria; http://www.psrc.usm.edu/macrog/ (accessed 23 June 1998).

III. INSTRUCTOR NOTES

The Influence of Initiator Concentration on the Molecular Weight of Polystyrene

Purpose

To determine if initiator concentration has an effect on the molecular weight of polystyrene.

Time Required

This laboratory investigation should take 6-8 hours.

Suggested Group Size

It is recommended that students work in small groups of 3-4.

Materials

Per class

- inhibited styrene monomer
- 10% NaOH
- calcium carbonate
- analytical balance
- toluene
- benzoyl peroxide
- methanol
- known molecular weight polystyrene sample
- acetone
- clean air or nitrogen under pressure

Per group of students

- 100-mL graduated cylinder
- 250-mL separatory funnel
- 100-mL beaker
- 3 large test tubes
- 4 400-mL beaker
- hot plate
- Büchner funnel
- # 5 filter paper
- 500-mL filter flask
- aspirator
- 16 100-mL volumetric flasks
- 10 gal aquarium with aquarium heater (See comment in “Procedural Tips and Suggestions.”)
- thermometer (-10 °C to 110 °C)
- 2 utility clamps
- laboratory stirrer
- Cannon-Fenske viscometer, #50
- 10-mL pipette

Safety, Handling, and Disposal

- This experiment must be done in a well-ventilated hood.
- Students must wear safety goggles, gloves, and proper clothing.
- Should skin contact occur, wash contaminated area immediately.
- Benzoyl peroxide is highly toxic by inhalation and may explode spontaneously when dry (<1% of water).
- Methanol is flammable making it a dangerous fire risk. It is toxic by ingestion and the Threshold Limit Value (TLV) is 200 ppm in air.
- Sodium hydroxide (NaOH) is corrosive and a strong irritant to tissue which include eyes, skin, and mucous membranes.
- Styrene is toxic by ingestion and inhalation. The 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.
- Do not allow students to pour any unused mixture down the sink. 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:

- Discuss the relationshop between a polymer's structure and molecular weight and its properties.
- Make sure students understand the safety, handling, and disposal procedures of this experiment.
- Discuss molecular weight distribution (MWD), M_n, M_w, and M_v,.
- Discuss the calculations in determining viscosity molecular weight (M_v).
- Demonstrate viscosity bath set up.
- Discuss and demonstrate the use of the viscometer.

Procedural Tips and Suggestions

- Although the Mark-Houwink parameters, "K" and "a," are temperature sensitive as is the viscosity, the constant temperature bath could be made optional since the molecular weight-initiator concentration relationship would still be evident. The uncertainty in the "K" and "a" values may represent a greater source of error than small temperature variations.
- Materials such as the aquarium and the viscometer may be shared among groups if necessary. This may extend the time needed for the class to complete the lab.

Plausible Answers to Questions

1. What are the three steps affecting molecular weight in free radical polymerization?

A: The three steps are initiation, propagation, and termination. The more initiation sites, the shorter the polymer chains and the lower their molecular weights. The longer propagation continues, the longer the polymer chains and the higher their molecular weights. The more readily termination occurs, the shorter the polymer chains and the lower their molecular weights.

2. What happens to the molecular weight of polystyrene as you increase the concentration of the initiator? Why?

A: When the initiator concentration is low, fewer free radicals are available and thus propagate fewer, longer chains. The number of free radicals generated increases as the initiator concentration increases. The monomers are attracted to these sites and because there are many active sites, short chains will form. The molecular weight of polystyrene decreases as the concentration of the initiator increases.

3. Why is the water bath maintained at a constant temperature?

A: The viscosity molecular weight, M_v, can be determined by using the Mark-Houwink-Sakurada Equation: $[\eta] = KM_v^a$ where both K and a are temperature dependent.

4. In general, how does viscosity measure molecular weight?

A: The long polymer chains tend to get tangled up, making it difficult for the solution to flow. At the same g/dL concentration, the longer the chains, the more tangling, and the greater the viscosity. In other words, if the molecular weight of the polymer is high (very long chains), then the viscosity would be high. So, the viscosity of a polymer solution is proportional to the molecular weight of the polymer.

5. Does the standard deviation or the relative standard deviation vary with concentration? Why might this occur?

A: The answer to this will depend on the data set. In some cases, measuring short times may be difficult and show more error. If the standard deviation shows little change with increasing molecular weight, the relative standard deviation will decrease with increasing molecular weight.

6. Discuss potential sources of error in your measurements and how they would affect your results.

A: The cleanliness (or lack thereof) of the viscometer could impact on the results. The temperature of the bath—both actual temperature and temperature fluxuations—could cause errors. So could how accurately the students measure the efflux time and how accurately they make up the solutions.

7. Why is molecular weight an important property of polymers?

A: Molecular weight can have a direct bearing on many polymer properties including melt viscosity (which affects processability), toughness (impact strength, melt strength, etc.), tensile properties, resistance to environmental stress cracking, etc.

Extensions and Variations

1. To check on the accuracy of this method, plot the M_v values for the synthesized PS (on the x-axis) against viscosity (on the y-axis). Measure the viscosity of the PS standard and read the M_v from the graph. Compare that with the certified value. Explain errors in this method.

2. Discuss GPC (SEC) to determine M_h, Mw, MWD. Gel Permeation Chromatography or, more correctly, Size Exclusion Chromatography is a process that determines the molecular weight parameters: number average molecular weight (M_h), weight average molecular weight (Mw), and molecular weight distribution (MWD).

References

Brandrup, J; Immergut, E.H.; Eds. *The Polymer Handbook; 3rd Ed.*; John Wiley and Sons; New York; 1989; pp. VII/1 through VII/32.

Carraher, C. E. Jr. *Polymer Chemistry, an Introduction, 4th Ed.*; Marcel Dekker, Inc. New York, 1996.

Department of Polymer Science at the University of Southern Mississippi Web Site, the Macrogalleria; http://www.psrc.usm.edu/macrog/ (accessed 23 June 1998).