

POLYMERIZATION OF STYRENE

I. Object

The free radical initiation of vinyl reactants is a common way to prepare polymeric materials. This experiment investigates the effect of free radical initiator concentration to highlight the compromise between product properties which depend on molecular weight and polymerization rates.

II. References

1. C. H. Bamford, et al, "The Kinetics of Vinyl Polymerization by Radical Mechanisms", Academic Press, New York, 1958.
2. F. W. Billmeyer, "Textbook of Polymer Science", Interscience, New York, 1962. Chapt. 9.
3. P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York, 1953. Chapt. 4.
4. E. A. Collins, et al, "Experiments in Polymer Science", Wiley, New York, 1973. 5. W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry", Interscience, New York, 1968.

III. Equipment and Supplies

1. Styrene monomer (inhibited with p-tert-butyl catechol)
2. Benzoyl peroxide
3. Toluene and methanol
4. one 250 ml separatory funnel
5. one 600 ml beaker, one 200 ml beaker
6. Vacuum filtration equipment (Buchner funnel)
7. Non-magnetic stirrer and stirring motor
8. Constant temperature bath

9. five, 25 ml screw cap vials
10. Aluminum foil
11. Nitrogen Sparging system
12. Analytical balance
13. Vacuum oven
14. one 1 ml, one 2 ml, two 5 ml, and two 10 ml pipettes
15. 1 N NaOH solution

IV. Procedure

A. Purification of styrene.

1. Place 100 ml of styrene monomer in the separatory funnel. Add 100 ml of 1 N NaOH solution. Shake and decant. Repeat washing with NaOH two more times.
2. Pass nitrogen gas through the styrene in the separatory funnel for 10 minutes to remove dissolved air. Cool the purified styrene by keeping it on ice.

B. Preparation of reaction samples.

1. Weigh out approximately half of the styrene with an analytical balance. Add to this 0.1 g benzoyl peroxide per 1.0 g styrene to form a stock solution. Place the stock solution on ice immediately after preparing.
2. Using the pipettes, prepare the following mixtures directly in the 25 ml screw cap vials. When filled, place the covered vials on ice:

Sample	Stock Solution, ml	Purified Styrene, ml	Toluene, ml
A	2	13	5
B	4	11	5
C	8	7	5
D	15	0	5

3. Purge the vial contents with nitrogen gas for five minutes, then place a piece of aluminum foil over the vial opening and tightly screw down the cap. Label the top of the screw cap.
4. Place the vials in a constant temperature bath set to 90 °C. React for 4 hours, minimum. Note the reaction time used.

C. Purification of polymer samples

1. Immediately after completing the reaction, remove the vials and cool in ice water.

2. Place 300 ml of methanol in a 600 ml beaker and position the mechanical stirrer. Rapidly stir the alcohol while slowly pouring the reaction mixture from the vial. Polystyrene should immediately precipitate. If the vial contents are too viscous to pour, dilute the reaction mixture with additional toluene prior to pouring it in the alcohol. Filter the precipitate with a vacuum filter, then wash with additional aliquots of methanol and refilter until the alcohol is clear.
3. Dry the polymer for several hours (overnight is preferable) in a vacuum oven at room temperature. After drying, the product should have no odor and should be light and fluffy.

D. Polymer Characterization (period 2)

1. Weigh the dried polymer to determine the polymerization yield. Place the samples in appropriately labeled containers for subsequent experiments.
2. Determine the glass transition temperatures of your samples with the Differential Scanning Calorimeter. Commercial polystyrene has a T_g of about 100 °C.
3. Retain your samples for characterization of molecular weight by intrinsic viscosity.

V. Report

1. Derive the rate equation for the free radical polymerization of styrene.
2. What is the purpose of the monomer purification step? What chemistry is involved?
3. What is the purpose of the nitrogen purge? Why is this necessary?
4. Describe the yields of polymer obtained. Are they in qualitative agreement with those expected for the initiator concentrations used? Discuss possible sources of error in the procedures employed.