Emulsion Polymerization of Styrene

Contributors:
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The goal of this lab is to synthesize polystyrene via emulsion polymerization of styrene with potassium persulfate, KPS, a commonly used free radical initiator for polymerization. It is recommended for each student to vary one or multiple of the following parameters to see the impact on sphere size, molecular weight, and solution opacity: stirring rate, stirring duration, monomer concentration, reaction temperature, and amount of initiator. This Standard Operating Procedure is created based on the following article and procedure:

Application Note: Preparation of Monodisperse Polymer Spheres.
Melissa A. Fierke, Material Matters. **2008**, 3.1, 13.

The following literature should also be consulted for additional emulsion polymerization theory:

W. B. Reynolds, *J. Chem. Ed.* **1947**, *26*, 135.
W. D. Harkins, *J. Am. Chem. Soc.* **1947**, *69*, 1428.
W. V. Smith, R. H. Ewart, J. Chem. Phys. **1948**, *16*, 592.

Materials:
Styrene, potassium persulfate, deionized water, nitrogen gas

Supplies:
Inhibitor removal column for the extraction of tert-butylcatechol, three-necked round-bottom flask, hot plate (with magnetic stirring if stir bar to be used), overhead mechanical stirrer or stir bar, Dri-Block heater, thermometer, armor beads, glass vials, pipet connected to source of nitrogen gas, glass wool (for filtering, optional)

Procedure:

Purification of styrene: Under fume hood, add about as much styrene monomer as you will need (10-20 mL) for this experiment into funnel to pass through inhibitor removal column to remove the tert-butylcatechol. Collect in clean beaker and cover with parafilm when not in use.

Under a fume hood, affix a three-necked round-bottom flask to a stand above a hot plate with armor beads to cover the lower half exterior of the flask. Insert a mechanical stirrer, condenser, and nitrogen inlet into each of the flask necks. Turn on the cold water attached to the condenser and ensure that the water is flowing through the condenser tubes.

Add 85 mL of deionized water to the flask and heat to 70^{o}C while stirring about 350 rpm. When temperature stabilizes around 70^{o}C, add 10 mL of the washed styrene. Allow temperature to once again equilibrate at 70^{o}C.

In a glass vial, 33.1 mg of potassium persulfate initiator is dissolved in 5 mL of deionized water and heated to 70^{o}C in Dri-Block heater. When the initiator solution has reached equilibrium, add to flash (a syringe or pipet is recommended). While solution is stirring, begin nitrogen flow and monitor temperature to bring solution to 70°C. The mixture can be stirred for a minimum of 5 minutes to a maximum of 24+ hours. Once polymerization reactions are complete, you can transfer solution to clean glass vials. If you wish to image particles with electron microscope, you may also filter through glass wool to remove large aggregates. Flask can be cleaned for re-use by cycling through deionized water, toluene, and acetone.

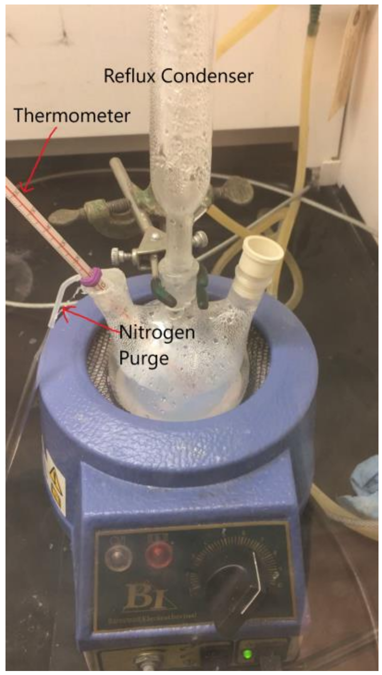

Figure 1: A view of the reactor during polymerization depicting the reflux condenser, thermometer, and nitrogen purge inlet. The magnetic stir bar is at the bottom of the flask unable to be seen through the already discolored product.

Questions to think about:

1. Draw chemical equations that describe the initiation, propagation, and termination steps in the emulsion polymerization of styrene performed in the lab.
2. What would happen if we did *not* wash the styrene monomers?
3. What is the purpose for bubbling nitrogen gas as the reaction proceeds?
4. Briefly explain how longer stirring times affect solution opacity and color.
5. Can you predict the shape of the latex particles? Which characterization methods from this course can help answer this question empirically?
6. What are the advantages and disadvantages of emulsion polymerizations compared to other polymerization methods for vinyl monomers? List other industrially important polymers that are prepared from the emulsion polymerization.

7. Draw a cartoon description of the three stages of emulsion polymerization including all the particles and indicating their relative sizes.

8. How does the solvent of the solution affect the chains? Draw a picture showing the polymer chains inside the latex particles in a good and bad solvent.

9. What would be the consequence of mixing too slowly?

10. What would be the consequence of bubbling too much nitrogen into solution?

11. What would happen if the condenser was utilizing room temperature water?

Ingredients List

Styrene monomer (inhibited)
Inhibitor removal column ($$$) or Powdered Alumina and syringe/cottonballs
3-neck flask
Overhead stirrer ($$$) or magnetic flea/stirplate
Argon gas ($$$) or N2 gas
Tygon tubing
Graduated cylinders
Plastic disposable pipets