Emulsion Polymerization of Styrene SOP

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MSE 4776
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This laboratory experiment will create polystyrene spheres via emulsion polymerization.

The goal of this laboratory experiment…

1. Use a new method (emulsion polymerization) to **create polystyrene spheres**
2. Understand how **process variables affect the final polymer product**
3. Use your **own spheres for further characterization** in later laboratory experiments
4. Provide an opportunity to **image your spheres using optical/electron microscopy** (See OPALL and the MILL!)

Reference literature to enhance this integrated laboratory experiment:

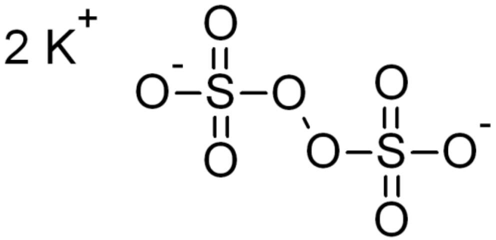
1) The original procedure
Application Note: Preparation of Monodisperse Polymer Spheres. Melissa A. Fierke, Material Matters. 2008, 3.1, 13.
2) W. B. Reynolds, *J. Chem. Ed.* **1947**, *26*, 135.
3) W. D. Harkins, *J. Am. Chem. Soc.* **1947**, *69*, 1428.
4) W. V. Smith, R. H. Ewart, J. Chem. Phys. **1948**, *16*, 592.

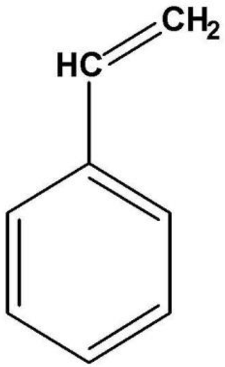
Georgia Tech

Polystyrene spheres can mostly be made with equipment already in the lab, plus a few new additions.

Materials:

- Styrene
- Potassium persulfate (KPS)
- Deionized water
- N_2 gas

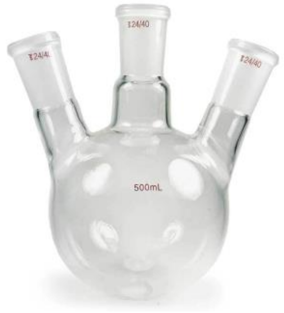




Left: Potassium persulfate initiator structure
Right: Styrene monomer structure

Equipment:

- Inhibitor removal column
- Three-necked round-bottom flask
- Hot plate
- Overhead mechanical stirrer (or stir bar)
- Dri-Block heater, thermometer, armor beads
- Glass vials
- Nitrogen source



Left: Dri-block heater used to keep reactants at elevated temperature
Above: three-necked round bottom flask where reaction takes place

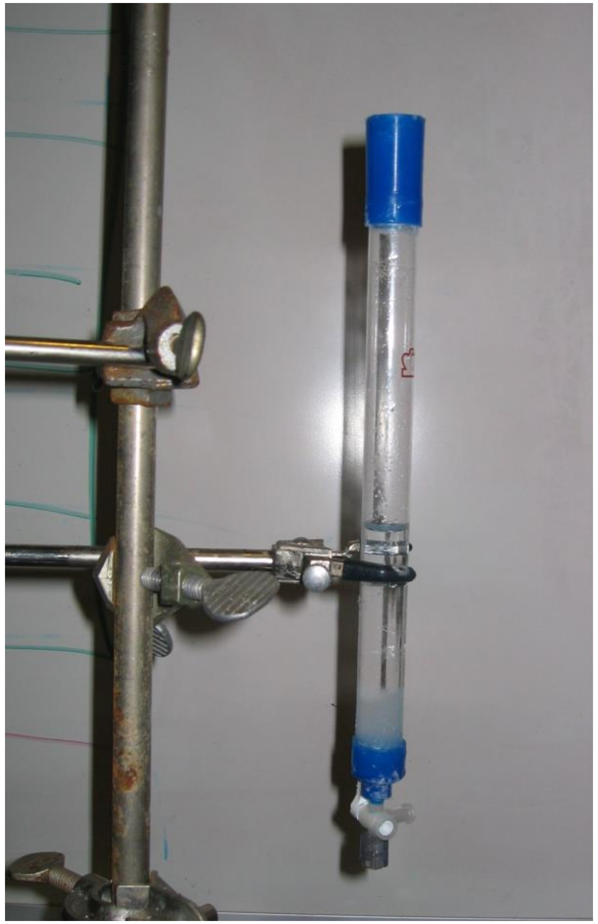
Tert-butylcatechol must be removed from the styrene stock to allow for accurate molecular weight predictions.

<u>Procedure:</u>

1.) Add about 20 mL of inhibited styrene to an inhibitor removal column. *It is important to add about twice as much you will need later in the synthesis since a portion of the styrene will remain in the column.*

2.) Place a 20 mL beaker directly underneath the column

3.) Wait about 20-30 minutes for the styrene to pass through the column and cover the washed styrene with parafilm.



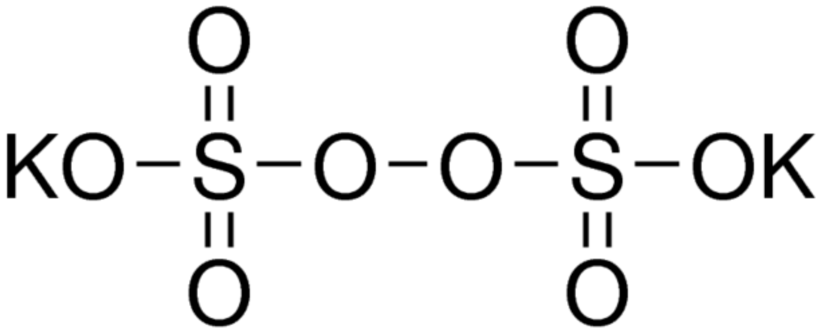
The radical initiator (potassium persulfate) must be dissolved in water and heated to 70 °C.

<u>Procedure:</u>

1.) Into a 10 mL glass vial, add 33.1 mg of potassium persulfate powder and 5 mL of water.

2.) Lightly swirl the vial in a circular motion until all the powder is dissolved.

3.) Place the vial into a Dri-Block heater set to 70°C.



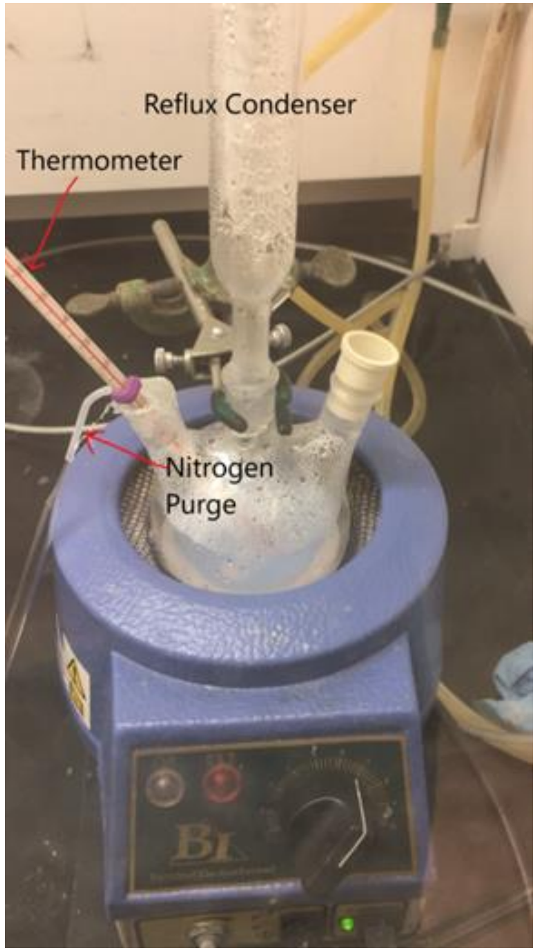
Set up the reaction equipment to ensure proper installation of the condenser, thermometer, nitrogen purge, and mixer.

Procedure:

1.) Place 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.

2.) Install a reflux condenser to prevent solvent losses, a thermometer (pierced through parafilm) to ensure the temperature remains constant, and a nitrogen purge (also pierced through parafilm with light flow to expel oxygen from the flask.

3.) Insert mechanical stirring arm into the flask or drop a magnetic stir bar into the flask. Stirring should be about 350 rpm. Turn on the cold water attachment for the reflux condenser. Ensure water is flowing through the condenser and that the water is cold by lightly placing a your fingers on the condenser feed tubes.



Let the polymerization begin by adding the appropriate reagents in the correct order.

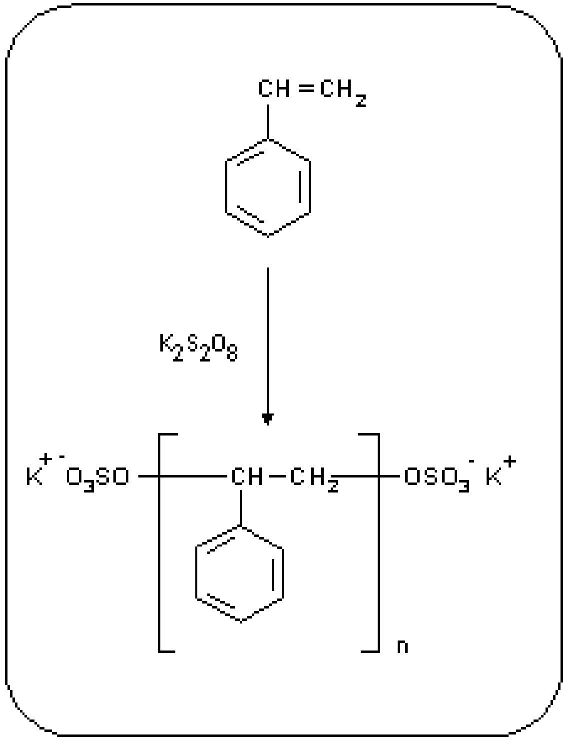
<u>Procedure:</u>

1.) Add 85 mL of deionized water to the flask while stirring at about 350 rpm.

2.) Set the hot plate to 70°C and use the thermometer to ensure a constant water temperature of 70°C.

3.) Add 10 mL of your washed Styrene to the flask and again let the temperature equilibrate to 70°C.

4.) Remove the potassium persulfate solution from the Dri-Block heater and quickly pour it into the flask. Use parafilm to seal off any open valves caused by pouring the styrene and initiator solution.



Sit back, watch, and remove the product.

Procedure:

1.) Watch the reaction run for a minimum of 5 minutes to a maximum of 24 hours (vary this duration and see what happens!) maintaining 70°C. After about 5 minutes you should see the product turn a light blue color (left photo). After multiple hours, the product should be white (right photo).

2.) Once polymerization reactions are complete, transfer the product to clean glass vials.

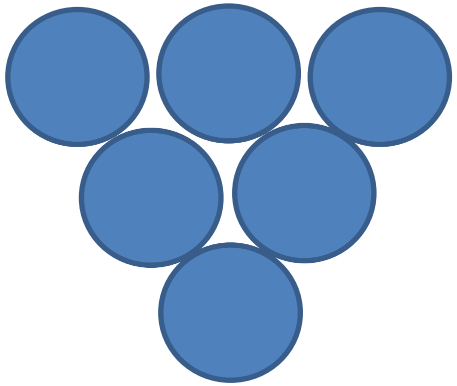
3.) Turn off the hot plate, nitrogen flow, and condenser fluid. Ensure the glassware is washed by cycling the flask with deionized water, toluene, and acetone after use.

There are several process variables students can modify to obtain different products.

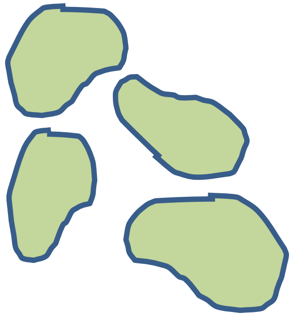
<u>Process Variables:</u>

- Stirring rate
- Stirring duration
- Monomer concentration
- Reaction temperature
- Amount of initiator

How will this impact sphere size, sphere shape, molecular weight, opacity?



OR



Think about **HOW** and **WHY** these variables will change your spheres!

Before you begin, it is helpful to think about the **questions** below for better understanding.

Draw chemical equations that describe the initiation, propagation, and termination steps in the emulsion polymerization of styrene performed in the lab.

What would happen if we did *not* wash the styrene monomers?

What is the purpose for bubbling nitrogen gas as the reaction proceeds?

Briefly explain how longer stirring times affect solution opacity and color.

Can you predict the shape of the latex particles? Which characterization methods from this course can help answer this question empirically?

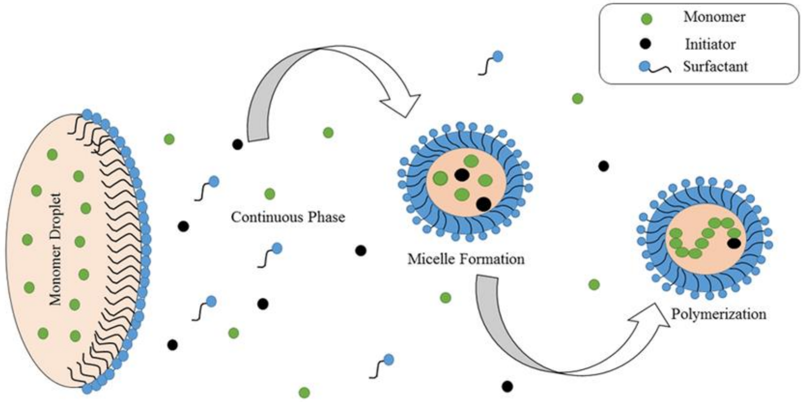
Before you begin, it is helpful to think about the **questions** below for better understanding.

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.

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

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.

What would be the consequence of mixing too slowly?



Your cartoon should look something like this.

Iqbal, Sajid & Ahmad, Sharif. (2017). Recent development in hybrid conducting polymers: Synthesis, applications and future prospects. Journal of Industrial and Engineering Chemistry. 10.1016/j.jiec.2017.09.038.