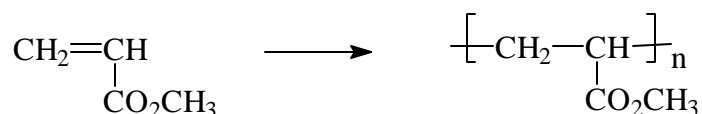


MICROSCALE EMULSION POLYMERIZATION

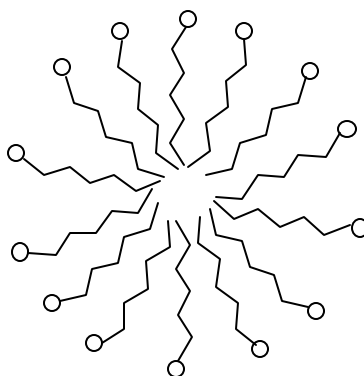
Lisa M. Swanson and John P. Droske
University of Wisconsin-Stevens Point
Department of Chemistry
Stevens Point, WI 54481

INTRODUCTION



Emulsion polymerizations are among the limited number of organic reactions that utilize an aqueous reaction media. The polymer-forming reaction takes place in water containing surfactant, monomer, and a water-soluble initiator. These polymerizations offer desirable characteristics such as ready heat dissipation, less reliance on volatile organic solvents, and low viscosities even at high molecular weights. Emulsion polymerization has been used extensively for the preparation of commercial products including water-based paints and synthetic rubber.

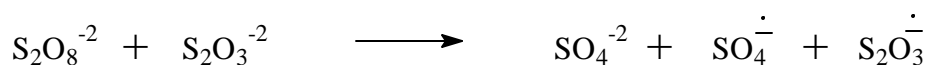
The reaction process by which this polymerization occurs is quite fascinating. Polymerization occurs in micelles, or very small soap bubbles, having diameters of 2-10 nm.¹ The micelles form upon addition of a surfactant to water. Surfactant molecules have ionic "heads" and nonpolar hydrocarbon "tails". Upon dissolution, the like regions align and an aggregate is formed where the hydrocarbon tails are directed inward and the ionic ends face outward toward the aqueous environment. A nonpolar "pocket" is created on the inside of the micelle due to the hydrocarbon ends of the molecules.



Idealized Micelle

This grouping of surfactant molecules occurs under conditions called the "critical micelle concentration". The resulting micelles are very small and contain only 50 to 100 molecules.

A water-soluble, free-radical initiator diffuses into the micelle to initiate polymerization. Redox initiators such as the ammonium persulfate/sodium thiosulfate system are commonly employed.



free-radical initiator system from
ammonium persulfate and sodium thiosulfate

The polymerization can take place in the monomer droplets, in the aqueous phase, and/or in the micelles which are filled with monomer. However, the first two are very minor contributors. This is because initiation tends not to occur in the monomer droplets because the initiator is water-soluble. Also, polymerization is not likely in the aqueous phase due to the minimal amount of monomer. Therefore, the majority of the initiation and propagation occurs in the micelles themselves.

Polymerization is initiated by diffusion of a free-radical into the micelle. Monomer also continuously diffuses from the aqueous phase into the micelles with the aqueous concentration being kept constant by suspended monomer droplets. Due to the small dimensions of the micelle, diffusion of another free-radical into the micelle leads to quick termination as a result of coupling of the free-radicals. Thus, the micelles tend to be "on" (polymerization occurring via a single growing chain) or "off" (those micelles without a growing chain). Polymer molecular weights can become very high before termination, the final stage of this chain growth polymerization.

PROCEDURE

It is important that the ammonium persulfate and sodium thiosulfate solutions are freshly prepared.

1. Calibrate 2 disposable pipettes, one calibrated to 0.5 mL and the other calibrated to 1.0 mL. **Save for step 5.** (The calibration is done by placing 0.5 or 1.0 mL of water from a burette or calibrated pipette into a 1 to 5 mL conical vial, carefully withdrawing the water from the conical vial into a pasteur pipette, and then marking under the meniscus with a permanent marker.)
2. In a 5-ml conical vial, wash 2 ml of methyl acrylate three times with 0.5 ml portions (10 drops) of 10 % sodium hydroxide, with vigorous shaking. Carefully remove the sodium hydroxide between washings using a pasteur pipette.

3. Place 0.005 g ammonium persulfate into a 100 ml volumetric flask. Mix well and dilute to the mark with distilled water and . Transfer 1 ml of this solution to a 5-ml conical vial.
4. Into another 100 ml volumetric flask, place about 0.005 g of sodium thiosulfate and mix and dilute to the mark. Transfer 1 ml of this solution to the 5-ml conical vial in step 3.
5. Weigh out about 0.01 g of sodium lauryl sulfate and add it to the 5-ml conical vial. Shake the vial vigorously for about 1 minute. Using the calibrated disposable pipette, add 0.5-ml of the washed methyl acrylate to the 5-ml conical vial containing a spinvane.
6. Fit the vial with a condenser and place it on a hot plate. Initially set the heater on high. A milky white color should appear within 10 minutes of heating. Heat the reaction mixture gently at the reflux temperature reaction for 1 hour . Work on step 8 during the heating time. **NOTE:** After the reaction has started (i.e. after it becomes turbid), there is an exotherm and the reaction may become very vigorous. Be prepared to turn down the heat to maintain a gentle reflux.
7. After 1 hour, cool the reaction mixture in an ice bath.
8. Make about 200 mL of a 5% salt solution by adding about 5 g of sodium chloride per 100 ml of distilled water. Heat ~30 ml of this 5% salt solution to near its boiling point with magnetic stirring. Pour 10 ml of this hot salt solution into another 50 ml beaker containing a magnetic stir bar. Heat ~50 ml of distilled water in a 50 ml beaker.
9. Remove the spinvane from the reaction vial. Pour the cooled reaction mixture into the magnetically stirring salt solution. A white, marshmallow-like mass will form. Stir the polymer for about 5 minutes or until the solution becomes clear.
10. When stirring is complete, decant the salt solution. Add 3 x 5 mL portions of hot salt solution to the polymer, pressing the polymer with a 20 ml beaker (plastic, if available) and decanting the solution each time. Then add 3 x 5 ml portions of warm distilled water to the polymer, again pressing with a 20 ml beaker and decanting the solution each time.
11. Collect the polymer by suction filtration. Press the polymer in the funnel with a small beaker to facilitate drying. Place in your lab drawer on a watch glass to dry (cover above the polymer with paper).
12. A film can be cast on a glass plate from a solution of the polymer in toluene. These are suitable for IR analysis. Sufficient polymer also is obtained for viscometry.