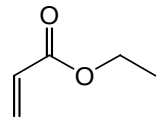
Chemistry/MatSci 5223W Thursday, February 2-
Thursday, February 9

Lab 3
Emulsion Polymerization of Ethyl Acrylate

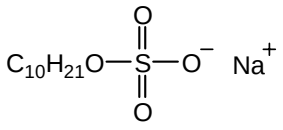
Introduction

Emulsion polymerizations are widely employed in commercial processes for the polymerization of water-insoluble monomers. The monomer is suspended as small drops in an aqueous medium by vigorous agitation. Both stirring and the addition of surfactants prevent coalescence of the drops. Polymerization actually takes place outside these droplets, in monomer-swollen micelles. A water soluble free radical initiator (such as the redox-based system used in this experiment) is commonly used in emulsion polymerization. The product of emulsion polymerization, a suspension of surfactant-coated polymer particles in water, is usually called a "latex". This suspension can actually be used directly (e.g., latex paint), or the polymer can be removed from the suspension and processed normally (e.g., latex rubber gloves). Emulsion polymerization has many advantages over bulk free-radical polymerization, including low solution viscosity, easy heat removal, and high product molecular weight.

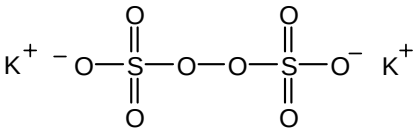
In this experiment you will perform the emulsion polymerization of ethyl acrylate. Like many of the monomers you have used so far, ethyl acrylate is commonly stored with a free radical inhibitor such as hydroquinone; this will have been removed for you. The structures of ethyl acrylate, the sodium dodecyl (lauryl) sulfate surfactant, and some of the components of the initiating system are shown below.



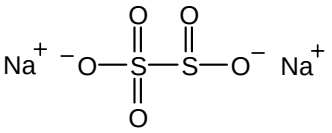
ethyl acrylate



sodium lauryl (dodecyl) sulfate



potassium persulfate



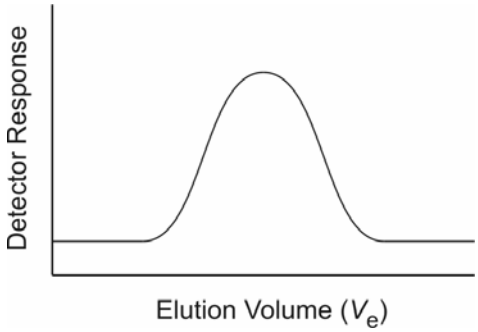
sodium metabisulfite

The initiating system is complex and predominantly involves "activation" of the persulfate decomposition by the ferrous sulfate ($FeSO_4 \cdot 7H_2O$). The species that actually act as initiators for this polymerization are sulfate radicals ($SO_4^{-\bullet}$) formed in the aqueous phase. In addition to preparing polyethylacrylate, you will investigate the effect of the chain transfer agent dodecanethiol on the molecular weight of the resulting polymer.

You will be analyzing the molecular weight of your polymer product by gel permeation chromatography (GPC). (Gel permeation chromatography is also known as size exclusion chromatography, SEC.) GPC is one of the most widely used techniques for analyzing polymer molecular weights and weight distributions. A GPC instrument consists of an injector (where

sample is introduced), an isocratic pump, a detector, and one or more columns. One key feature of GPC is the controlled pore size of the column packing (or gel). Polymers are fractionated in the GPC column based on their hydrodynamic volume, where larger molecules are excluded from a greater proportion of the internal pore volumes than the smaller molecules. As a result, larger polymer molecules in a chromatographic sample experience less of the total internal column solvent volume than the smaller molecules and elute earlier. The relative mobility of different polymers varies from solvent to solvent, from column to column, and even to some extent over time on the same column. As a result, GPC analyses are relative and must be calibrated using standards of known molecular weight. A mixture of polystyrenes with narrow molecular weight distributions is usually used. Strictly, this set of standards is only valid for calibrating GPC runs on other polystyrenes, but they are practically accurate for a wide variety of polymers. This will be done once, at the beginning of the lab, by the TA's.

In this lab, the elution of polymer from the column will be monitored by a refractive index (RI) detector. The signal from the RI detector is directly proportional to the *mass* concentration of the solute in the mobile phase. The amount of polymer at any particular elution volume V_e (calibrated to a specific molecular weight) is proportional to the signal intensity (i.e., the height of the curve h_i) at that particular V_e. This can be expressed by equation 3.1:



A typical GPC trace for a polydisperse polymer. You will deconvolute this data to determine $\overline{M_n}$ and $\overline{M_w}$ for your polymers.

(3.1) $h_i \propto N_i M_{x,i}$

where N_i is the number of polymer molecules (in moles) with exact molecular weight $M_{x,i}$ (in g/mol). Note that 10^{-6} mol of polymer with a molecular weight of 10,000 g/mol gives the same instrument response (height) as 10^{-5} mol of a polymer with a molecular weight of 1,000 g/mol. In this lab, you will interpolate $M_{x,i}$ for each data point experimentally for the instrument by injecting the set of standards with known M_x's, determining V_e for each M_x, graphing $\ln(M_x)$ vs. V_e, and then fitting these points to any function. This function can then be used to determine M_x for any V_e. There are now methods available for "universally" calibrating a column for all possible polymers; we will not use these calibrations in this class, but commercial GPC software packages sometimes do.

Since the elution volume can be converted into a molecular weight using a calibration curve, the number of molecules with exact molecular weight M_x can be calculated using eq. 3.1. The number average molecular weight of a polymer is given by equation 3.2:

(3.2) $$\overline{M_n} = \frac{\sum_{i=1}^{\infty} N_i M_{x,i}}{\sum_{i=1}^{\infty} N_i}$$

However, your GPC data contains refractive index detector responses, not N values. Combining equations 3.1 and 3.2 provides M_n with respect to h_i (the RI detector response):

(3.3) $$\overline{M_n} = \frac{\sum_{i=1}^{\infty} h_i}{\sum_{i=1}^{\infty} \frac{h_i}{M_{x,i}}}$$

This relationship will allow you to relate your data point heights to $\overline{M_n}$. Using a similar approach, you can derive (on your own) an expression for $\overline{M_w}$. You will use this calculation, as well as your calibration of the GPC instrument response, repeatedly in this course. As a result, as a part of this lab you will develop your own spreadsheet/program that will do these calculations automatically and that you can use again later.

Experimental

Emulsion polymerization of ethyl acrylate (Feb 2/3)

The goal of this experiment is to examine the dependence of the molecular weight in an emulsion polymerization on the concentration of a chain transfer agent.

Please read the instructions below carefully before you start this experiment.

- Get a green polymerization reactor from the TAs, and rinse it with deionized water. Also get a large stirplate from the TAs. Check out a deep immersion thermometer and a large stirbar from the stockroom.
- Add 200 mL deionized water to the reactor.
- Familiarize yourself with the nitrogen bubbling (sparging) apparatus, and make sure it is clean. Place your reactor and a stirplate in the hood and bubble N_2 through the water for 5 minutes. Start stirring.
- Add 8 mL of 10% (by weight) sodium lauryl sulfate *slowly* to avoid excess foaming.
- Add 70 mL of ethyl acrylate **immediately** after the addition of the sodium lauryl sulfate.
- Using the 1 mL syringe, add 0.3, 0.6, 0.9, or 1.2 mL of dodecanethiol to the mixture according to the pre-lab instructions. Allow the system to bubble with N_2 for an additional 5 minutes.
- Check to make sure N_2 is bubbling through the surfactant-monomer-chain transfer agent solution at a reasonable rate. (The TA's will demonstrate what this rate is.) Do not let the sparging tube hit the bottom of the reactor and become blocked. From this stage on, do not change the bubbling rate.
- Collect 3 disposable pipettes, a pipette bulb, and a beaker for waste. Use these to dispense the reagents below. In addition, one of you should be ready to collect timed temperature readings.
- Rinse out a clean 10 mL graduated cylinder with 5% (by weight) potassium persulfate. Measure 10 mL of persulfate with the graduated cylinder and add it to the reactor. **Record the time.**
- Thirty seconds after adding the persulfate to the reactor, add, using the same method as above, 5 mL of 5% (by weight) sodium metabisulfite. **Record the time.**

- Thirty seconds from adding the metabisulfite to the reactor, add, using the same method, 1 mL of 1% (by weight) ferrous sulfate.
- Using the deep immersion thermometer record the temperature every one minute from the time you added the ferrous sulfate. The polymerization should be run for a total of 30 minutes (so you should collect at least 30 temperature readings).

Polymer recovery (Feb 2/3)

The polymer formed is a white emulsion called a latex. The latex will be coagulated to recover the polymer by adding salt solutions (the coagulator). Three different salt solutions will be used to compare the effectiveness of these coagulators: (a) 5% $CaCl_2 \cdot 2H_2O$; (b) 5% $Al_2(SO_4)_3$; (c) 10% NaCl (all concentrations in weight percent).

- Remove three 3 mL aliquots and one 30 mL aliquot of the white latex from your reactor. Place the 3 mL aliquots in your smallest beakers. Discard the remaining polymer latex into the Lab 3 waste container.
- Using the disposable pipettes add the three different salt solutions to the separate 3 mL aliquots, dropwise. Record the number of drops of each solution you had to add until no more polymer precipitated from the solution. Use 0.05 mL per drop as an approximation of the volume you added.
- Isolate the polymer formed from each of the beakers above, and weigh each of the three polymer samples. Use the coagulator that yielded the highest mass to precipitate the 30 mL aliquot polymer.
- Filter the polymer from the 30 mL aliquot using a Büchner funnel and house vacuum. You can get filter paper from the stockroom. Wash the polymer several times with water. The solution in the filter flask may be cloudy—don't worry about this.
- Squeeze as much water as you can out of the polymer with paper towels, and then dry the recovered polymer in the vacuum oven. The following week, weigh your polymer and record the yield.

Characterization of ethyl acrylate by GPC (Feb 9/10)

The goal of this experiment is to analyze the molecular weight of your polymer product. You will use this technique a number of times in this course.

Running the computerized GPC instrument generates a file which contains a one-column list of RI detector responses with respect to "scan number". You will need to know the flow speed and scan rate of the instrument in order to convert this data into elution volumes.

- Weigh out roughly 20 mg of your polymer sample in a small black capped vial and record the sample weight. Add approximately 1 mL of THF (solvent) for every 10 mg of polymer to the vial. Shake vigorously to disperse the polymer.
- Because the GPC column is tightly packed with tiny beads, small solid impurities (e.g., dust) can clog the instrument. As a result, everything that is loaded onto the GPC must be filtered through a 0.45 μm-pore filter. Once your polymer has dissolved in the THF, pour the solution

into a disposable syringe with an attached Teflon syringe filter and then filter the solution into a second (clean) vial.

- Take a look at the GPC instrument, and familiarize yourself with its parts. Make sure you can identify the injector, column heater, pump, and refractive index detector. Questions you may want to ask the TA: What is the sequence of components that the eluent flows through? How does the pump work? (What are those little white buttons that go in and out of the pump housing?) How much volume does the metal tubing take up? What is the operating pressure, and what consequence does this pressure have on what the GPC parts are made of? What temperature is the column oven set to? Why this temperature?
- Make sure you've recorded the flow rate of the pump.
- On the instrument, turn the injector valve to [**LOAD**].
- Flush pure THF into the injector with the injection syringe. Do this two times.
- Flush polymer solution into the injector two times with the same syringe you used in step 3. Try not to get air bubbles in the injection loop; they will interfere with the isocratic pump's ability to maintain constant pressure.
- On the computer, make sure the GPC instrument software is running. (If not, open the "Polymer Lab GPC" program from the Desktop.) In the upper left hand corner, there will be a button with an outline arrow (⇨) on it. Press this button, or hit Ctrl-R to start the software acquisition. The software will prompt you for a filename; tell it to save your data to your floppy disk. (Do not overwrite old data. You never know what you will have to keep.) **Simultaneously** hit SAVE to complete the filename and turn the injector to [**INJECT**].
- Look at the computer screen to verify that data is being collected. Record the number of scans (data points) that the computer collects per second. Running the computerized GPC instrument generates a file which contains a one-column list of RI detector responses with respect to "scan number". You will need to know the scan rate to determine the time scale for your data.
- Wait approximately 15 minutes for the run to be completed. When you are sure your run is complete, hit the red [**STOP**] button on the software. Look at the curve that was recorded; is the baseline noise variation more than about 5% of you maximum signal intensity? If not, you should double (or more) the amount of material you have dissolved in your vial, refilter, and inject again. If in doubt, ask a TA for advice, and do not dispose of your sample until you get good data.
- Once your run is complete, check to make sure your data file has been saved to your floppy disk. In addition, make sure you also save a copy of the instrument calibration run (which will be on the desktop). Make sure you find out the molecular weights of the five polystyrene standards used to generate the calibration run.

There is no Lab Report due for this Lab. Instead, you will analyze your results in Assignments 10 (due *In Lecture*, Wednesday, February 22) **and 13** (due *In Lecture*, Wednesday, March 1).