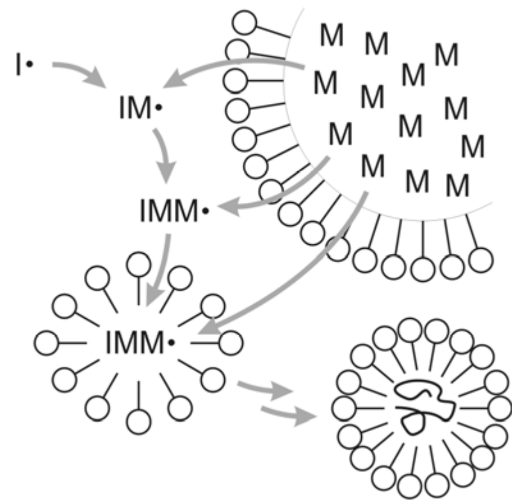
Chem/MatS/ChEn 4223W Tuesday, February 12/Thursday, February 14-
Tuesday, February 19/Thursday, February 21

Lab 3
Microemulsion Polymerization

Introduction

Emulsion polymerizations are widely employed in commercial processes for the polymerization of water-insoluble monomers. In emulsion polymerization, the monomer is suspended as small droplets in an aqueous medium, and surfactant (soap) molecules prevent coalescence of the drops. A water-soluble initiator is commonly used to initiate emulsion polymerization. Because the initiator is in a different phase from the monomer, the rates of initiation and termination are reduced in emulsion polymerization relative to bulk polymerization. As a result, emulsion polymerizations yield polymer products with higher molecular weights than bulk polymerization, and make it possible to polymerize some monomers that cannot be polymerized in the bulk. One important limitation to emulsion polymerization is that there are a number of polymerization mechanisms that are incompatible with the water used—including cationic, anionic, and many ring-opening and condensation polymerizations. As a result, emulsions have been used most extensively with free-radical polymerization.

In free-radical emulsion polymerization, polymer propagation begins when an initating radical combines with a transiently dissolved monomer molecule in the aqueous phase. As the propagating radical adds additional monomer units, the propagating chain becomes more and more hydrophobic. At this point, one of two things can happen to the propagating chain, depending on polymerization conditions. If the amount of surfactant is very low compared to monomer—conditions used in traditional emulsion polymerization—the monomer droplets are relatively large (many microns in size), with little total surface area. In this case, the chance of a propagating chain encountering the surface of a droplet is low, and instead the polymer is eventually surrounded by its own layer of surfactant, and occupies its own micelle. This micelle will exchange monomer with the larger droplets, and each monomer acquired in this way is immediately integrated into the propagating polymer chain, until the polymer terminates. The resulting product is a suspension of surfactant-coated polymer particles in water, commonly called a “colloid” or “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). Under the conditions of traditional emulsion

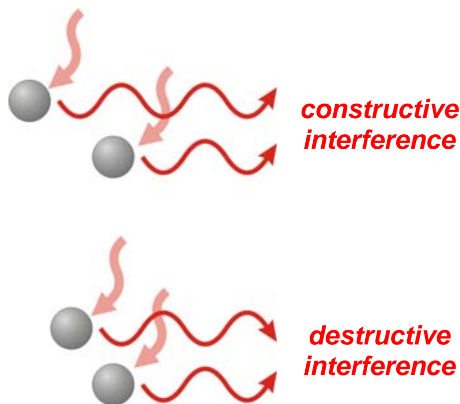


Mechanism for emulsion polymerization of a monomer M, initiated by radical I•. At all times, the monomer that is incorporated travels from emulsified monomer droplets; monomer can be added initially in the aqueous phase, but later is incorporated inside separate micelles.

polymerization, the eventual size of the polymer particles is determined by rates of polymerization and termination, and to some degree by coalescence of the product particles, because the surfactant concentration is so low. There is no size relationship between the product particles and the original monomer droplets, and the particles are relatively polydisperse.

However, if the amount of surfactant used is higher than ~0.1 wt% relative to monomer, as it will be in this lab, the emulsified monomer droplets are much smaller (nanometers in size), and the suspension is commonly called a "microemulsion". In microemulsion polymerization, the propagating, hydrophobic radical has a much greater chance of encountering the surface of an existing monomer droplet. When it does, the radical will enter the droplet, and polymerize the monomer inside. Once the entire droplet has been polymerized, the propagating radical is still active, and monomer that is exchanged with other droplets can still be incorporated. In this way, the size of the particles in the final latex is determined by the thermodynamically most-stable droplet/polymer size (controlled by the initial surfactant-to-monomer ratio) rather than by polymerization kinetics. Microemulsion polymerization isn't commonly used to manufacture large quantities of bulk polymer, because a relatively large amount of surfactant needs to be used and subsequently disposed of. But if a goal of the polymerization is control over latex particle size, microemulsion polymerization performs much better than traditional emulsion polymerization.

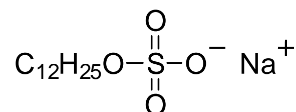
In this lab, you will analyze the size of the particles in your product latex using dynamic light scattering (DLS). DLS measures the mean hydrodynamic diameter (Z_{ave}) of a population of suspended particles by watching the time-dependent scattering of laser light off of proximal pairs of particles. The light scattered off of each particle in a pair experiences constructive and destructive interference with the light scattered from the other particle. This interference varies as the particles exhibit Brownian motion towards and away from each other, giving rise to a time-dependent scattering signal. So, DLS analyzes "correlations" in the scattering profile, in essence comparing scattering at one moment with scattering in the next. Pairs of large particles will diffuse towards and away from each other slowly, and so scattering over time will be highly correlated and will change only slowly; pairs of small particles, by contrast, will show very rapid decay of correlation in scattering signal. The Malvern NanoZS DLS instrument you'll be using collects data on many particle pairs at once, by looking at time-dependent changes in "speckle" patterns on a 2-dimensional detector grid. Analysis of how quickly features in this pattern decay yields information about the size (Z_{ave}) and size distribution (polydispersity index, PDI) in the particle sample. The conventional definition of PDI in particle analysis is not the same as the one you've learned for polymer characterization; the DLS instrument will probably report PDI values between 0 and 1, with values < 0.2 representing fairly monodisperse particle suspensions.



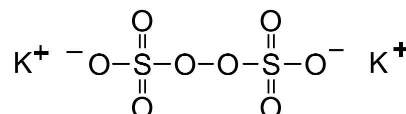
The total intensity of coherent laser light scattered off of a pair of particles varies with the distance between the particles, as a result of constructive and destructive intereference of the laser waveform.

In this experiment you will perform microemulsion polymerizations of styrene and methyl methacrylate, two

monomers that you have previously polymerized in the bulk. Sodium dodecyl (lauryl) sulfate will serve as the surfactant, and potassium persulfate ($K_2S_2O_8$) will be used as the aqueous-phase initiator. The central O-O bond in $K_2S_2O_8$ is similar to that of benzoyl peroxide, in that it is thermally labile and yields two radicals when heated. So, the species that actually act as initiators for this polymerization are sulfate radicals ($SO_4^{-\bullet}$) formed in the aqueous phase.



sodium dodecyl sulfate (SDS)



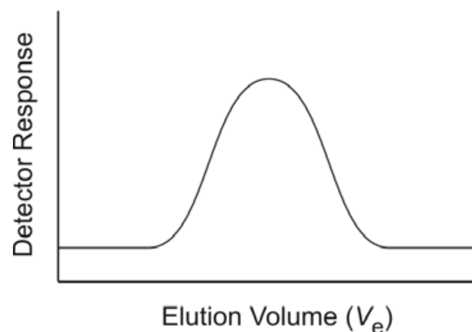
potassium persulfate (KPS)

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:

(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). That means 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



An idealized GPC trace for a polydisperse polymer. You will deconvolute this data to determine $\overline{M}_n$ and $\overline{M}_w$ for your polymers.

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.

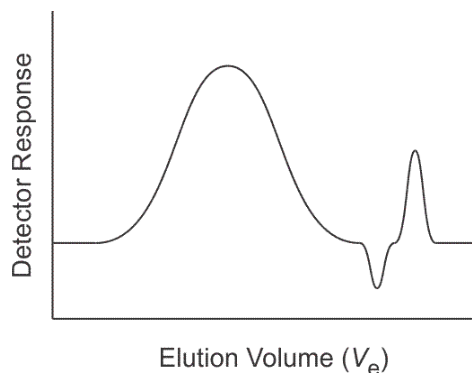
Since the elution volume can be converted into a molecular weight using a calibration curve, the number of molecules with exact molecular weight M_x can be calculated using eq. 3.1. The number average molecular weight of a polymer is given by equation 3.2:

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

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):

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

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 $\overline{M_w}$. Most commercial GPC instruments—like the Agilent 1260s we have in the Polymer Lab—are sold with software that converts GPC data into M_n and M_w automatically. However, this software is not always very good at dealing with multiple, independent features that appear in the GPC spectrum. As a result, as a part of this lab, you will do your own M_n and M_w calculation. You will use this calculation—done within a re-usable Excel spreadsheet—as well as your calibration of the GPC instrument response, repeatedly in this course.



A typical GPC trace, with small peaks corresponding to low-molecular-weight contaminants (such as unreacted monomer). These peaks can be excluded from the M_w analysis.

Experimental

<u>Microemulsion polymerization of styrene and methyl methacrylate (Feb 12/14)</u>

The goal of this experiment is to polymerize styrene and methyl methacrylate via emulsion polymerization.

- Get four 20-mL scintillation vials and a stirplate from the TAs.

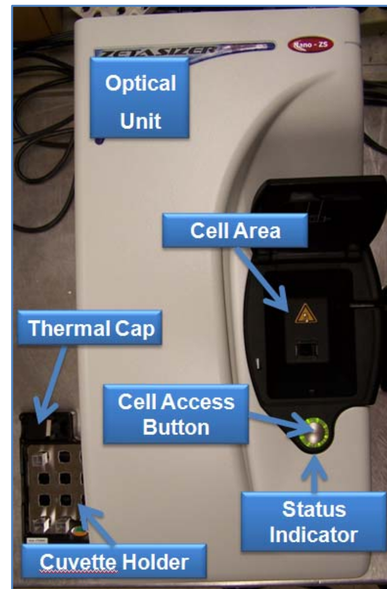
- To two of the vials, add 5 mL of 15 wt% SDS, 1 mM KPS solution (in H_2O) and a small stirbar. Then, using a syringe, add the amount of monomer you were asked to add in Assignment 5. Cover the top of each vial with aluminum foil.
- Although free-radical emulsion polymerization reduces termination by chain combination and disproportionation, it is more susceptible to termination by oxygen, because of the high solubility of O_2 in water. As a result, we'll be removing dissolving O_2 by "sparging"—by bubbling N_2 through the solution so that the dissolved O_2 is replaced by N_2. The TAs will show you how to make a sparging balloon out of a plastic syringe body and a party balloon. Make four of these balloons, and add a disposable needle to each one, but do not discard the plastic needle shield.
- Fill each balloon with N_2 gas at the cylinder by the hoods. Clamp your vials above your stirplates. Remove the needle shield from one balloon, and insert the needle through the foil and below the surface of the solution in the vial. The N_2 gas in the balloon should bubble through the solution. There may be some foaming and loss of material from the vial—do not worry about this, as long as most of the solution remains in the vial. While the first vial is sparging, feel free to sparge the other vial at the same time. When the first balloon has emptied, replace it with a second balloon and sparge again. After each vial has been sparged for ~15 min, cover each vial with a second layer of aluminum foil.
- Mark each of your two polymerization vials, and place each one in the heating block in the hood, set to 70 °C. Allow the emulsion to polymerize for 45 min, and then remove the vial from the block to cool. If you observe a color change in the solution, make sure to record it in your notebook.
- Charge each of your two remaining empty vials with 5 mL H_2O that has been filtered through a 0.45 μm-pore filter. (This is done to remove any particles from the H_2O that might interfere with your particle sizing experiment.) For each polymerization mixture, pipette 5 drops of the mixture into one of these vials, and swirl. These diluted solutions will be used in the dynamic light scattering (DLS) experiment described below.
- Pour the remainder of one of the two polymerization mixtures—the one you were instructed to purify in Assignment 5—into 75 mL of 95% ethanol in a beaker, with gentle swirling. (We find this works better without stirring.) This will "break" the polymerized emulsion, as the ethanol dissolves both the heads and tails of the surfactant.
- Divide the resulting mixture into six 15-mL centrifuge tubes, and centrifuge all six tubes in the IEC centrifuge for 1 min at 5000 rpm to separate the polymer from solution. Make sure that the centrifuge is balanced—that every tube is across from another tube containing roughly the same weight of liquid.
- After centrifuging, carefully decant away the supernatant into waste, leaving behind the solid centrifugate in each tube.
- Add ~1 mL 95% ethanol to five of the six tubes. Using a hand vortexer, swirl the centrifuged solid back into the ethanol, and pour the tube contents into the sixth centrifuge tube. Repeat this with another 1 mL ethanol in each empty tube to wash all of your material into one tube.
- Centrifuge your tube in the IEC centrifuge for 3 min at 5000 rpm. Again, make sure you balance your tube with another one (another group's, or a tube filled with water).

- Carefully decant the supernatant into waste, leaving behind the solid centrifugate. Tare and mark an aluminum foil pan, and transfer your solid from the centrifuge tube to the pan. Then put the material into the vacuum oven to dry.

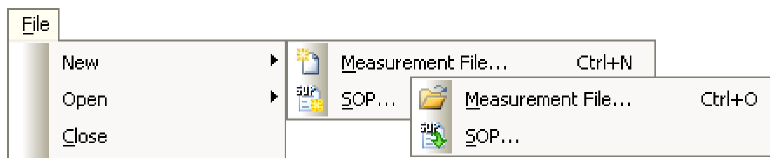
Dynamic light scattering (DLS) analysis of polymer latex (Feb 12/14 and Feb 19/21)

The goal of this experiment is to analyze the size of the particles formed in your latex.

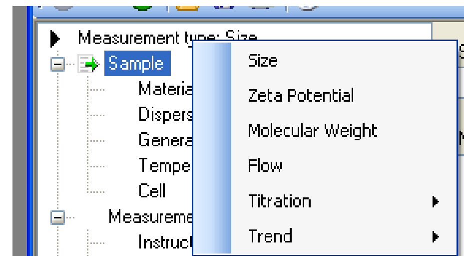
- Get a 1-cm pathlength cuvette from the TA, and rinse it 2-3 times with filtered H_2O. Try not to touch the cuvette on its sides; smudges from your fingers will interfere with the measurement.
- Fill the cuvette with one of your samples using a disposable glass pipette. Keep the remainder of the solution for measuring next week. It is important to load the cuvette with the minimum possible sample volume, which fills the cuvette up to just 1 cm from the bottom. When filling the cuvette, tilt the cuvette, pipette onto the inside wall, and allow it to fill slowly to avoid bubbles forming.
- Familiarize yourself with the DLS instrument (see picture at right).



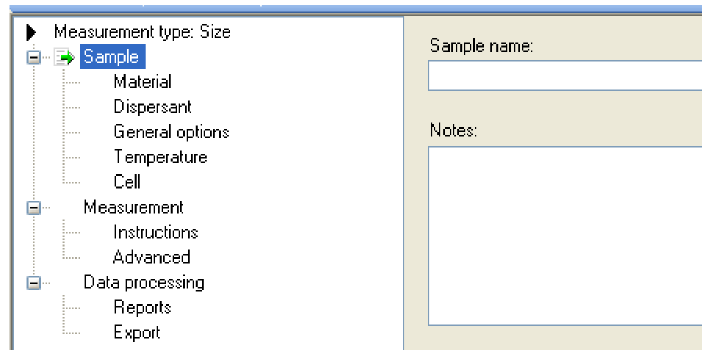
- In the DLS software, click *File* → *New* → *Measurement File* to create a new measurement file, or use an existing one with *File* → *Open* → *Measurement File*.



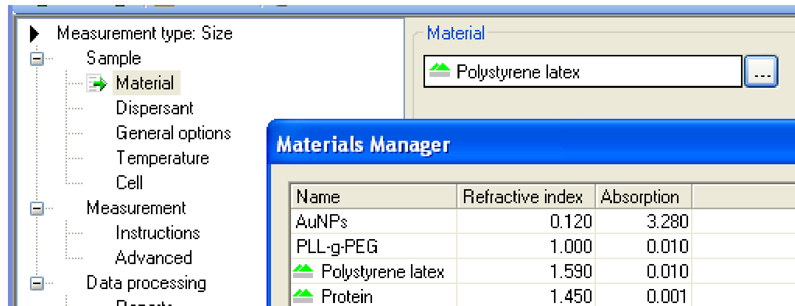
- Set the measurement method by choosing *Measure* → *Manual*. This opens the measurement edit display. In this display, click *Measurement type*, and select *Size*.



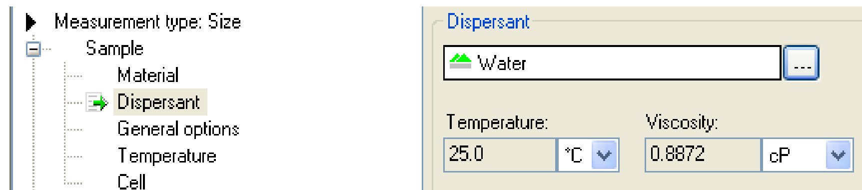
- In the same window, highlight *Sample*, and then give your sample a name in the "Sample name" text box. Make sure both your group number, polymer type, and vol% are in the sample name. ("Group2-PS-4%", for example.)



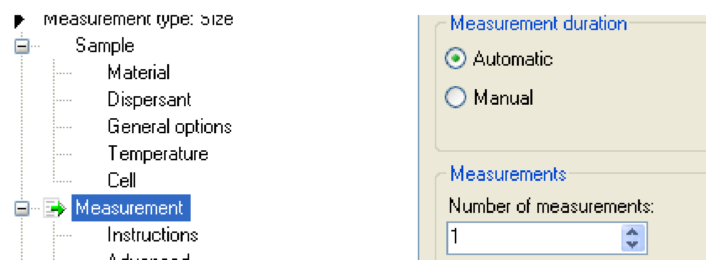
- Under *Sample*, click *Material*. In the *Materials Manager* window, select “Polystyrene latex” to indicate the expected refractive index of your material. We will use this setting for both PS and PMMA, because the refractive indices of these materials are similar.



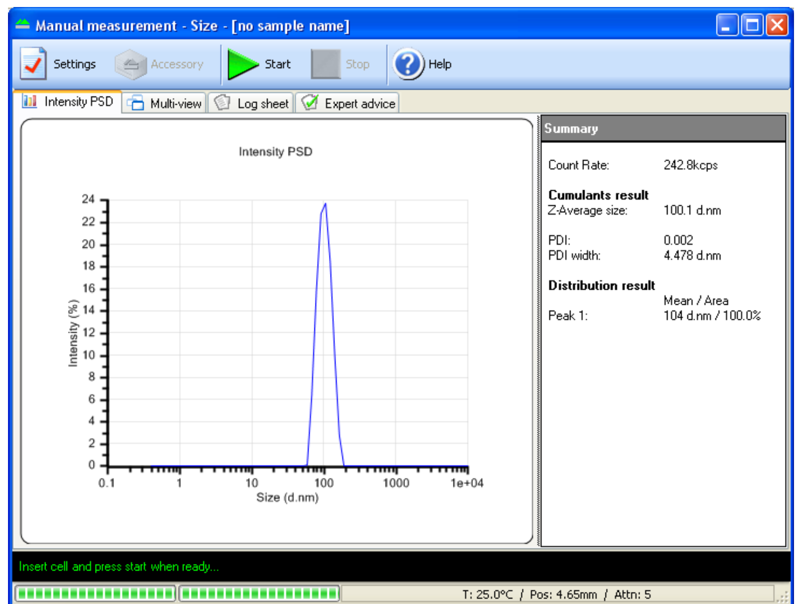
- Next, click *Dispersant*, and select “Water”. Make sure the temperature is set to “25 °C”, and the equilibration time to “0 min”.



- Still under *Sample*, click *Cell*, and choose “Disposable sizing cuvette”.
- Click *Measurement*. Choose the “Automatic” measurement radio button, and instruct the instrument to take 1 measurement.



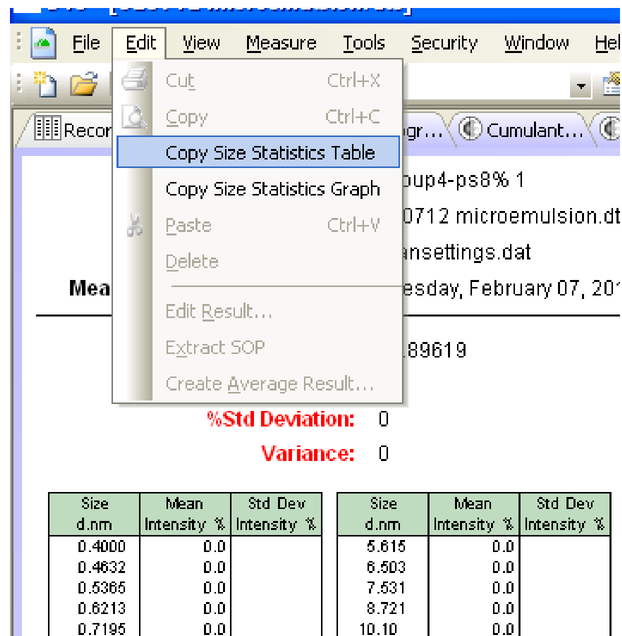
- Click OK. The measurement display window should become active.
- Insert the sample cuvette into the cell holder. When you insert it, the small triangle at the top of the cuvette (most cuvettes have it) should be pointed towards the cell access button; this will face the polished optical surface of the cuvette towards the laser.
- Close the cell area lid. In the measurement window, click the start button (▶). The



instrument will take a measurement and save the results to the open measurement file.

- In your notebook, record the value for Z_{ave} and PDI (in the cumulant fit results) and list the size and width of the peaks found by the software (in the distribution fit results).

- Copy the graphed results to an Excel spreadsheet. To do this, select the *Intensity stats table* tab. Then copy the table to the Windows Clipboard by selecting *Edit* → *Copy Size Statistics Table*. Open Microsoft Excel (if it isn't already open) and paste (*Ctrl-V*) the table into the active worksheet. Save the worksheet as its own file.



- Remove the cuvette from the instrument, discard the solution, and wash the cuvette with filtered water.

- Repeat the steps above for your other polymer sample.

- Keep your scintillation vials until next week. At that time, take another size measurement on your dispersion.

Characterization of polystyrene and poly(methyl methacrylate) by GPC (Feb 19/21)

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

Running the computerized GPC instrument generates a file which contains RI detector responses with respect to time. You will need to know the flow rate of the instrument in order to convert these times into elution volumes.

- Weigh out roughly 5 mg of your polymer sample in a small glass vial and record the sample weight. Add approximately 1 mL of tetrahydrofuran (THF, a solvent) to the vial. Shake vigorously to disperse the polymer. Because the polymer has a high molecular weight, this may take a while.

- 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

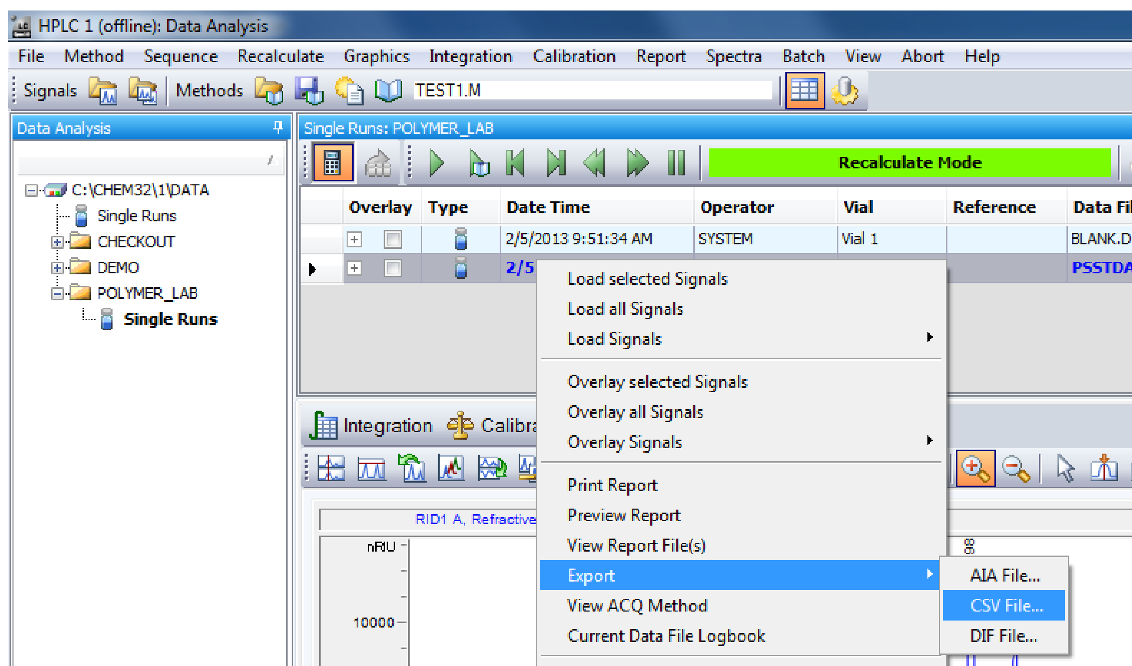
does the pump work? How much volume does the metal tubing take up? What is the operating pressure, and what consequence does this pressure have on what the GPC parts are made of? What temperature is the column oven set to? Why this temperature?

- Make sure you've recorded the flow rate of the pump.
- On the instrument, turn the injector valve to [**LOAD**].
- Inject polymer solution into the injector with a microsyringe. 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, and that the refractive index detector is collecting data. The ChemStation software window should be titled "***Instrument 1 [online]***". In the Menu Bar, select *Run Control → Sample Info*. In the Sample Info window, provide information about your sample, and give the software a file folder to save your data to. (Say, C:\chem32\1\DATA\Polymer_Lab\Group5.) Click OK.
- Turn the injector to [**INJECT**] to begin your GPC run.
- Wait approximately 15 minutes for the run to be completed. When you are sure your run is complete, 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.

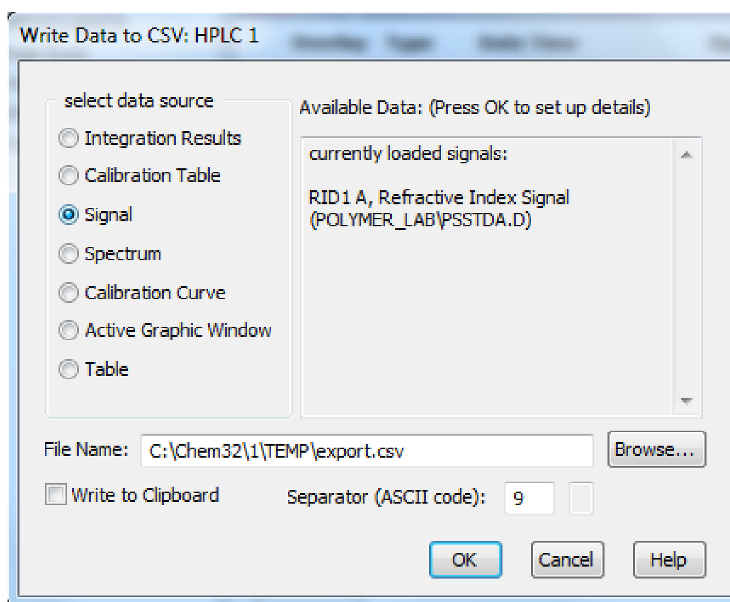
Obtaining data from the Agilent 1260 GPC (Feb 19/21)

- To export data, you will be using on *offline* instance of the GPC software. Check to see if one is already open by looking for a Window titled "***Instrument 1 [offline]***". If you don't find one, start the offline ChemStation program by double-clicking the **Instrument 1 offline** icon on the desktop.

- In the ChemStation window, in the bottom left, select **Data Analysis**. Then, in the navigation window on the left, browse to the POLYMER_LAB folder. The directory listing window in the center should list your data file.
- Right-click your data file's name to open a pop-up window, choose **Export** and click **CSV file**.



- In the window that pops up, select the **Signal** radio button. Click **Browse…** to name your .CSV file and save it either to a local directory (say, C:\chem32\1\DATA\Polymer_Lab) or your USB drive directory. Click **OK**.



- In the Signal Export dialog window, check the **Time axis** and **Y axis** boxes. Click **OK**.
- You should be able to find your data file in the c:\Chem32\1\DATA\Polymer_Lab folder. Your file contains retention time (left column) and RID signal (right column) values. If you want to convert retention times to retention volumes, you will need to note the flow rate.
- You should also save a copy of the instrument calibration run in the same way--find out from the TA's where the file is. In addition, 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 8 (due *In Lecture*, Monday, February 25) and **10** (due *In Lecture*, Monday, March 4).