

Preparing Precise Polymer Solutions

Solution concentrations are key to accurate molecular weights

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Abstract

Polymer solutions must be prepared with care. Special effort should be expended to ensure complete, homogeneous dissolution. The best method of obtaining correct concentrations is weighing the polymer and using volumetric flasks for solution volume. The second choice is weighing the polymer, then weighing the solution and using the density of solvent as an approximation for the density of the solution.

Introduction

Determination of polymer and protein molecular weights requires preparation of solutions with accurately known concentrations. The accuracy of the obtained molecular weights depends directly on concentration. Correct concentration values are also needed for viscometry, calibrating UV and RI detectors, and measuring dn/dc values. Therefore, preparation of solutions with well-known concentrations is necessary for maximizing the performance of Brookhaven equipment.

In order to aid the experimentalist, this note covers three topics useful for sample preparation. The first is a practical discussion of the mechanics of preparing solutions with volumetric flasks. The second concerns preparing solutions by a purely gravimetric method. Finally, instructions for preparing dilutions of a stock solution are included.

The light scattering relationships (e.g., the Zimm equation) are written in terms of concentration as mass of solute per volume of solution. Therefore, the best method to prepare solutions is to weigh a mass of polymer, then add solvent until the desired volume is reached. Alternatively, concentration can be obtained by weighing. In both cases, complete dissolution and mixing is critical to obtaining good results. In practice, this is implemented in a multi-step process that takes hours,

and can take longer for some macromolecules, particularly high molecular weight polymers. We recommend preparing solutions the day before making measurements.

An important prerequisite is that the operation and calibration of the scale and glassware be well understood. The manual for your analytical balance is an excellent resource, as is a text on analytical chemistry such as Quantitative Chemical Analysis by Daniel Harris, W. H. Freeman, New York, 1999. It should be emphasized that while accurate weighing and volume determination will become routine, waiting and mixing for complete dissolution will continue to be a challenge for each new polymer sample.

There are two methods of preparing a sequence of solutions. The first is to make a stock solution, then dilute the stock solution to make a series of solutions. This method is convenient and fast. However, errors in preparing the stock solution will propagate to each of the diluted solutions. The other option is to prepare each solution independently, which is far more time consuming. But, the errors in calculated concentrations will be independent, which is useful for critical work. Good results can be obtained with either method and the choice will depend on the goals and resources of the laboratory making the measurements.

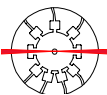
Preparing polymer solutions with volumetric flasks

Volumetric flasks allow one to measure solution volume precisely and therefore obtain accurate concentrations. However, flasks are expensive, time consuming to clean, and large volumes are required for high precision work.

Steps for preparing solutions volumetrically

1. Clean and dry glassware, taking care to ensure that no residues remain. Ideally, glassware is cleaned





- immediately after use, before polymer dries on the surface and makes cleaning more difficult. For example, if the flasks were used for polymer solutions, they should be rinsed with a good solvent for these polymers at least twice. Next, the flasks should be rinsed with DI water and completely dried. Note that if the flask is rinsed with a solvent such as toluene that is immiscible with water, a rinse with an intermediate solvent such as THF is desirable before rinsing with DI water. If a high vapor pressure solvent is desired for fast drying, a rinse with methanol is recommended. Acetone (particularly the grades chosen for washing glassware) tends to leave a residue. Since light scattering is a highly sensitive analytical technique, any residue in the glassware will be measured along with the sample. Needless to say, the glassware should be inspected for cleanliness before use.
- The clean, dry flask is weighed and the weight recorded. Use gloves; the weight of fingerprints adds up.
 - Dry polymer is added to the desired weight. The final weight of the flask and polymer is recorded. Subtracting the weight of the flask gives the mass of polymer.
 - Solvent is added to fill the flask about three quarters full. The flask is capped and stirred or shaken (for volumetric flasks, do not invert the flask, all material should remain below the mark indicating the volume of the flask). A vortexer or orbital shaker is useful for this purpose. After shaking, wait one hour and vortex or shake again. Continue until the polymer is completely dissolved. This may take a long time. You will know the polymer is dissolved when there is no polymer stuck to the walls of the flask AND when the solution is shaken, there are no visible concentration gradients. Swirl the flask and look through the solution at a bright object. Concentration gradients will appear as distortions in the bright object when the solution is swirled. Dissolution times vary with molecular weight. For example, a low molecular weight (10 kDa) polymer will dissolve quite quickly, while a very high molecular weight polymer (over 1 MDa) will take several days. As an initial guess, assume that it will take at least overnight to fully dissolve the polymer.
 - Once the polymer is completely dissolved, add solvent until the meniscus of the solution reaches the line on the volumetric flask. Note that you are not yet done.
 - Now, one should invert the (capped) flask multiple times to ensure good mixing. Again, inspection of the swirling solution should show no concentration gradients. Skipping this step will give erroneous results, as the concentrated polymer solution can remain at the bottom of the flask; diffusion is insufficient to drive mixing over a short time scale. Note that adding solvent and waiting overnight for a homogeneous solution to form due to diffusion can fail; mechanical mixing is required for good homogeneous solutions. Mechanical mixing will give a good homogeneous solution faster than waiting for diffusion to do the job.

Concentration Calculation

Solution concentration is given by the relation

$$c = \frac{m_{f+p} - m_f}{V_T} \quad (1)$$

where c is concentration (e.g., mg/mL), m_{f+p} is the combined mass of the polymer and flask, m_f is the mass of the empty flask, and V_T is the total volume of the solution.

Preparing polymer solutions by the gravimetric method

The gravimetric method allows one to use any available glassware, including disposable jars and caps or smaller volume samples. However, for all but the most well studied polymer/solvent systems, one must make a generally reasonable approximation to obtain the volume of solution from the measured mass of solution.

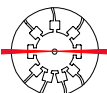
One note of warning is appropriate for those wishing to prepare small volumes of solution. The accuracy and precision of the balance is critical. For example, if one is preparing 3 mL of 5 mg/mL solution, one must accurately weigh 15 mg of sample. Therefore, the scale must weigh to within 0.15 mg to achieve even 1% accuracy.

Steps for preparing solutions gravimetrically

Many of the steps for polymer dissolution in the gravimetric method are the same as when volumetric flasks are used. For clarity the steps here are summarized and the reader may refer to the corresponding description under the volumetric flask method.

- Clean and dry glassware, taking care to ensure that no residues remain. See step 1 of the volumetric method for details on washing glassware.





- The clean, dry flask is weighed and the weight recorded.
- Dry polymer is added to the desired weight. The final weight of the flask and polymer is recorded. Subtracting the weight of the flask gives the mass of polymer.
- Solvent is added to fill the flask. See step 4 of the volumetric method for details on insuring good dissolution.
- The solution and the flask should be weighed again and solution mass obtained by subtracting the weight of the empty flask. Divide the total mass of solution by the density of the solvent to obtain solution volume. Finally, divide mass of polymer by solution volume to obtain solution concentration.

Concentration calculation

In the gravimetric method, concentration is calculated by obtaining the volume of solution based on the mass of solution and the specific gravity of the solvent. The relevant relationship is

$$c = \frac{m_{f+p} - m_f}{\left(\frac{m_{f+p+s} - m_f}{\rho_{s,0}} \right)} \quad (2)$$

where m_{f+p+s} is the mass of flask, polymer, and solvent and $\rho_{s,0}$ is the density of the solvent. The discussion below describes why the density of the solvent is recommended along with a more exact calculation.

Justification for recommended calculation

Equation (2) is somewhat inexact since it treats solution density as equal to solvent density. Here, we justify the approximation, which is necessary for all but the most well studied polymer/solvent systems.

In order to calculate exact concentration, the following relation is used

$$c = \frac{m_p}{m_s v_{s,0} + m_p v_{p,*}} \quad (3)$$

Here, m_p is the mass of polymer ($m_p = m_{f+p} - m_f$) and m_s is mass of solvent ($m_s = m_{f+p+s} - m_{f+p}$). $v_{s,0}$ is the specific volume of pure solvent and $v_{p,*}$ is the apparent partial specific volume of the polymer in that solvent. Values for $v_{p,*}$ are tabulated for some polymer solvent systems in the [Polymer Handbook](#) (Brandrup et al., eds., J. Wiley, New York). Note that the denominator can be considered as the mass of the solution times the specific vol-

ume of the solution. Since density is the reciprocal of the specific volume, equation (3) can be used to follow the effects of calculated concentration on specific volume.

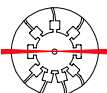
Let us examine the sensitivity of calculated concentration to the apparent partial specific volume chosen for the calculation. Consider the case of preparing 100 mL of 5 mg/mL of PS in toluene by adding 99.54 mL of toluene to 500 mg of PS. Here, we will use a density of toluene at 25 °C of 0.862 g/mL. The apparent partial specific volume of PS in toluene is 0.916 mL/g. In the table below the calculated concentration using equation (2) is shown as a function of the value chosen for the apparent partial specific volume of PS. Values well above and below the correct value of 0.916 give nearly trivial differences in calculated concentration. From this table, it is clear that a 10% overestimate of apparent partial specific volume has a tiny (0.05%) effect on calculated concentration. Even using over twice the correct value or less than half the correct value has a small (0.5%) effect on calculated concentration.

Apparent partial specific volume (mL/g)	Calculated concentration (mg/mL)	Relative difference compared to use of literature value
0.250	5.0167	0.3%
0.500	5.0104	0.2%
0.916	5.0000	0 %
1.008	4.9977	-0.05 %
2.000	4.9730	-0.5 %

In short, the values used for apparent partial specific volume are not particularly important for these dilute solutions and the best approach is to use the solvent specific volume, or, equivalently, solvent density.

A review of published data for $v_{p,*}$ shows a range of about 0.3 to 1.1 mL/g for various polymers in a variety of solvents. It is far more important to use correct values for solvent density and maximize scale performance for weighing accuracy. Therefore, we suggest using equation (2) for calculating solution concentration. Of course, if apparent partial specific volume data is available, improved accuracy will be obtained by using equation (3).





Concentration calculations for dilutions

One method of preparing a series of solutions is to prepare a stock solution. The stock solution is then used to prepare a series of dilutions for analytical measurements.

Weighing is used to calculate concentrations of the dilutions since scales are often more precise than glassware for dispensing various volumes of material.

Preparation of dilutions

1. Prepare a stock solution using either method listed above. The stock solution concentration should be the highest concentration you wish to measure.
2. Clean glassware for dilutions.
3. Calculate desired volumes of stock for each dilution. To reach a target concentration c_{target} with a solution volume v_{solution} , the volume of stock, v_{stock} required is

$$v_{\text{stock}} = v_{\text{solution}} \frac{c_{\text{target}}}{c_{\text{stock}}} \quad (4)$$

4. Weigh the empty flask.
5. Add target volume of stock solution using a clean pipette or syringe. Weigh flask and stock solution. Subtract to obtain mass of stock added, m_{stock} .
6. Add enough solvent to reach desired solution volume, that is $v_{\text{solution}} - v_{\text{stock}}$, then weigh flask and diluted solution. Subtract to obtain total mass of solution, m_{solution} .
7. Swirl the flask to ensure good mixing.

Concentration calculation

The concentration of a dilution is calculated using the relationship below

$$c_{\text{dilute}} = c_{\text{stock}} \frac{m_{\text{stock}}}{m_{\text{solution}}} \quad (5)$$

where c_{dilute} is the concentration of the diluted solution.

Conclusions

Careful preparation of polymer solutions is a vital first step for light scattering measurements. The best method for obtaining these concentrations is to use volumetric flasks and careful weighing. If volumetric flasks are impractical, careful weighing and treating the solution density as equal to the solvent density is a reasonable approximation for dilute solutions.

