

# Chapter 6

## Viscosity

### 6.1 Introduction

Viscosity of a polymer solution depends on concentration and size (*i.e.*, molecular weight) of the dissolved polymer. By measuring the solution viscosity we should be able to get an idea about molecular weight. Viscosity techniques are very popular because they are experimentally simple. They are, however less accurate and the determined molecular weight, the viscosity average molecular weight, is less precise. For example,  $\overline{M}_v$  depends on a parameter which depends on the solvent used to measure the viscosity. Therefore the measured molecular weight depends on the solvent used. Despite these drawbacks, viscosity techniques are very valuable. This chapter discusses the theory and methods for determining polymer molecular weight by measuring solution viscosity

### 6.2 Viscosity and Viscosity Nomenclature

Figure 6.1 shows a piece of a liquid moving at a strain rate  $\dot{\gamma}$  under an applied shear stress of  $\tau$ . The viscosity of the liquid is the ratio of the applied shear stress to the resulting strain rate (or equivalently, the ratio of the shear stress required to move the solution at a fixed strain rate to that strain rate). The shear strain in Fig. 6.1 is

$$\gamma = \frac{du}{dy} \quad (6.1)$$

where  $u$  is displacement in the  $x$  direction. The strain rate is therefore

$$\dot{\gamma} = \frac{d}{dt} \frac{du}{dy} = \frac{d}{dy} \frac{du}{dt} = \frac{dv_x}{dy} \quad (6.2)$$

where  $v_x$  is velocity in the  $x$  direction. The relations between viscosity ( $\eta$ ), shear stress ( $\tau$ ), and shear rate ( $\dot{\gamma}$ ) are

$$\tau = \eta \dot{\gamma} \quad \text{or} \quad \dot{\gamma} = \frac{\tau}{\eta} \quad \text{or} \quad \eta = \frac{\tau}{\dot{\gamma}} \quad (6.3)$$

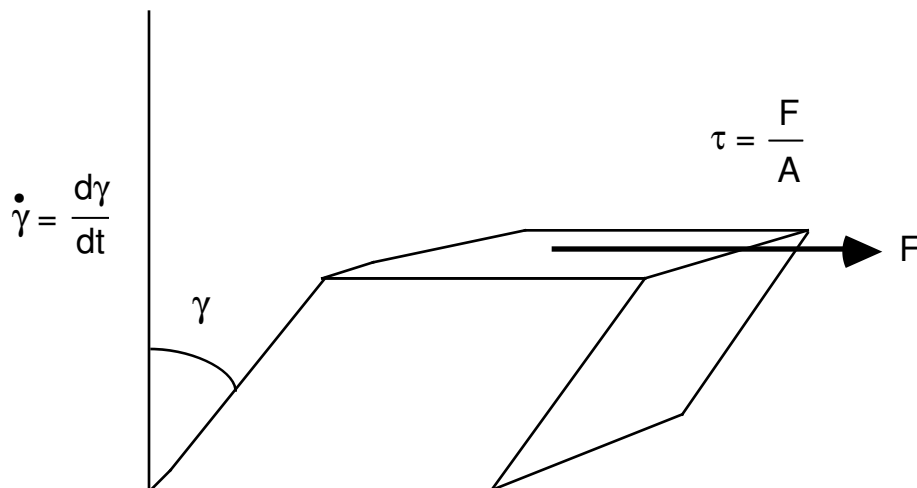


Figure 6.1: A piece of a liquid moving at shear rate  $\dot{\gamma}$  under an applied shear stress of  $\tau$ .

A Newtonian fluid is one in which the viscosity is independent of the shear rate. In other words a plot of shear stress versus shear strain rate is linear with slope  $\eta$ . In Newtonian fluids all the energy goes into sliding molecules by each other. In non-Newtonian fluids, the shear stress/strain rate relation is not linear. Typically the viscosity drops at high shear rates — a phenomenon known as shear thinning. Although the following development will not discuss shear rate effects in detail, the possibility of experimental results being affected by the shear rate of the measurement should be kept in mind. Plots of shear force *vs.* shear rate for Newtonian and non-Newtonian fluids are given in Fig. 6.2.

We let  $\eta_0$  be the viscosity of the pure solvent and  $\eta$  be the viscosity of a solution using that solvent. Several methods exist for characterizing the solution viscosity, or more specifically, the capacity of the solute to increase the viscosity of the solution. That capacity is quantified by using one of several different measures of solution viscosity. The most common solution viscosity terms are:

1. Relative viscosity

$$\eta_r = \frac{\eta}{\eta_0} \quad (6.4)$$

2. Specific viscosity

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \eta_r - 1 \quad (6.5)$$

3. Inherent Viscosity

$$\eta_i = \frac{\ln \eta_r}{c} \quad (6.6)$$

4. Intrinsic Viscosity

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} \quad (6.7)$$

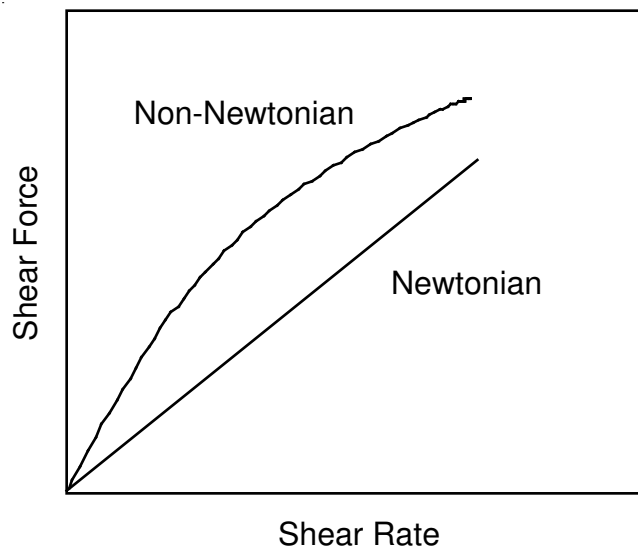


Figure 6.2: Schematic plots of shear force *vs.* shear rate for Newtonian and non-Newtonian fluids.

In these equations,  $\eta$  is solution viscosity,  $\eta_0$  is viscosity of the pure solvent, and  $c$  is concentration.

Relative viscosity is self-explanatory. Specific viscosity expresses the incremental viscosity due to the presence of the polymer in the solution. Normalizing  $\eta_{sp}$  to concentration gives  $\eta_{sp}/c$  which expresses the capacity of a polymer to cause the solution viscosity to increase; *i.e.*, the incremental viscosity per unit concentration of polymer. As with other polymer solution properties, the solutions used for viscosity measurements will be nonideal and therefore  $\eta_{sp}/c$  will depend on  $c$ . As with osmotic pressure, it will probably be useful to extrapolate to zero concentration. The extrapolated value of  $\eta_{sp}/c$  at zero concentration is known as the intrinsic viscosity —  $[\eta]$ .  $[\eta]$  will be shown to be a unique function of molecular weight (for a given polymer-solvent pair) and measurements of  $[\eta]$  can be used to measure molecular weight.

The remaining form for the viscosity is the inherent viscosity. Like  $\eta_{sp}$ ,  $\ln \eta_r$  is zero for pure solvent and increases with increasing concentration, thus  $\ln \eta_r$  also expresses the incremental viscosity due to the presence of the polymer in the solution. Normalizing  $\ln \eta_r$  to concentration or  $\ln \eta_r/c$  gives the inherent viscosity. In the limit of zero concentration,  $\eta_i$  extrapolates the same as  $\eta_{sp}/c$  and becomes equal to the intrinsic viscosity. This can be proved by:

$$\lim_{c \rightarrow 0} \frac{\ln \eta_r}{c} = \lim_{c \rightarrow 0} \frac{\ln (1 + \eta_{sp})}{c} = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = [\eta] \quad (6.8)$$

We can thus find  $[\eta]$  by extrapolating either  $\eta_{sp}/c$  or  $\eta_i$  to zero concentration. When  $c$  is not equal to zero the specific viscosity and inherent viscosities will be different, even for an ideal solution. In ideal solutions  $\eta_{sp}/c$  will be independent of concentration, but  $\eta_i$  will depend on concentration.

### 6.3 Viscosity Theory

Einstein derived the specific viscosity for a dilute solution of hard spheres. His result is

$$\eta_{sp} = 2.5 \frac{N_B V_\eta}{V} \quad (6.9)$$

where  $N_B$  is the number of particles (hard spheres),  $V_\eta$  is the hydrodynamic volume of each sphere, and  $V$  is the total volume. For a first approximation to polymer solutions, we will use Einstein's theory and assume each polymer to be a hard sphere with  $V_\eta$  equal to some effective hydrodynamic volume. Letting moles of polymer be  $n_B = N_B/L$ , we get

$$\eta_{sp} = 2.5 \frac{n_B V_\eta L}{V} \quad (6.10)$$

We begin with a monodisperse polymer solution with concentration  $c = n_B M/V$  where  $M$  is molecular weight. We can rewrite  $\eta_{sp}$  as

$$\eta_{sp} = 2.5 \frac{n_B M}{V} \frac{V_\eta L}{M} = 2.5 c \frac{V_\eta L}{M} \quad (6.11)$$

or

$$\frac{\eta_{sp}}{c} = 2.5 L \frac{V_\eta}{M} \quad (6.12)$$

This result is for an ideal solution. We see that  $\eta_{sp}/c$  in an ideal solution is independent of concentration. Extrapolating to zero concentration, which is trivial because  $\eta_{sp}/c$  is independent of  $c$ , the intrinsic viscosity of an ideal solution is

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = 2.5 L \frac{V_\eta}{M} \quad (6.13)$$

For a hard sphere we could take  $V_\eta$  to be the volume of that sphere or equal to  $4\pi r^3/3$ . Because a polymer is not a hard sphere, we do not have so simple a result. We can, however, probably assume that  $V_\eta$  is be proportional to root-mean-squared radius cubed —  $\left(\sqrt{\langle r^2 \rangle}\right)^3$ . Writing  $Q$  for the as yet unknown proportionality constant we have  $V_\eta = Q \left(\sqrt{\langle r^2 \rangle}\right)^3$ . Lumping the proportionality constant along with other constants in the above equation results in:

$$[\eta] = \Phi \frac{\langle r^2 \rangle^{\frac{3}{2}}}{M} = \Phi \left( \frac{\langle r^2 \rangle}{M} \right)^{\frac{3}{2}} M^{\frac{1}{2}} = \Phi \left( \frac{\langle r^2 \rangle_0}{M} \right)^{\frac{3}{2}} M^{\frac{1}{2}} \alpha^3 \quad (6.14)$$

where  $\Phi = 2.5 L Q$ . In the last step of the above equation we rewrote the root-mean-squared end-to-end distance using the expansion factor  $\alpha$  and the unperturbed end-to-end distance:

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_0 \quad (6.15)$$

In a theta solvent the expansion factor is 1 ( $\alpha = 1$ ) and the above equation tells us that  $[\eta]$  is proportional to the square root of molecule weight and the 3/2 power of  $\langle r^2 \rangle_0/M$

$$[\eta] = \Phi \left( \frac{\langle r^2 \rangle_0}{M} \right)^{\frac{3}{2}} M^{\frac{1}{2}} \quad (6.16)$$

But, both  $\langle r^2 \rangle_0$  and  $M$  are proportional to the number of bonds or  $n$ . Thus  $\langle r^2 \rangle_0/M$  is a constant for a particular polymer that is independent of molecular weight. We get in the simplest form

$$[\eta] = KM^{\frac{1}{2}} \quad (6.17)$$

where  $K$  is a constant.

The polymer size is determined by the ratio of the mean-squared unperturbed end-to-end distance and its molecular weight. In terms of  $K$  and  $\Phi$ , the result is

$$\left( \frac{\langle r^2 \rangle_0}{M} \right) = \left( \frac{K}{\Phi} \right)^{\frac{2}{3}} \quad (6.18)$$

Recall that characteristic ratio is defined as the ratio of the mean-squared end-to-end distance,  $\langle r^2 \rangle_0$ , to the freely-jointed chain mean-squared length,  $nl^2$ . The characteristic ratio can thus be written as

$$C_n = \frac{\langle r^2 \rangle_0}{nl^2} \quad \text{or} \quad C_n = \frac{\langle r^2 \rangle_0}{M} \frac{M_b}{l^2} \quad (6.19)$$

where  $M_b$  is the molecular weight per bond or  $M/n$ . Inserting this result into the previous result gives  $C_n$  in terms of  $K$  and  $\Phi$ .

$$C_n = \left( \frac{K}{\Phi} \right)^{\frac{2}{3}} \frac{M_b}{l^2} \quad (6.20)$$

The viscosity constant  $\Phi$  can be evaluated from theory. For polymers it is typically assumed to be  $2.5\text{--}2.66 \times 10^{21}$  (when  $r$  is in cm and  $[\eta]$  is in dl/g). Therefore a measurement of  $[\eta]$  for a polymer of known molecular weight in a theta solvent will give  $K$ , which in turn can be used to give a direct measurement of the characteristic ratio. These types of experiments were used to check early work on the conformations of polymers and calculations of end-to-end distances.

For polymers in non-theta solvents,  $\alpha$  will no longer be one and we lose the square-root dependence of  $[\eta]$  on molecular weight. We instead have

$$[\eta] = KM^{\frac{1}{2}}\alpha^3 \quad (6.21)$$

where  $\alpha$  may have molecular weight dependence of its own. It is usually acceptable to treat non-theta solvent results by lumping the molecular weight dependence of  $\alpha$  into one molecular weight term to get

$$[\eta] = KM^a \quad (6.22)$$

where  $a$  is some constant that depends on the polymer-solvent pair and on temperature. Values of  $a$  are typically between 0.5 and 0.8. Close to 0.5 represents near theta solvent conditions. Farther away from 0.5 represents large deviations from a theta solvent.

## 6.4 Viscosity Experiments

It is usually not convenient to work in theta solvents. We thus next discuss how to use viscosity experiments in non-theta solvents to measure molecular weight. The key experimental property is intrinsic viscosity —  $[\eta]$ . You measure  $[\eta]$  by measuring  $\eta_{sp}$  at several different concentrations and extrapolating to zero concentration (we will discuss the extrapolation further below). Once  $[\eta]$  is known, it is related to molecular weight through two unknown constants —  $K$  and  $a$ . These constants must have been previously determined by a calibration experiment. For a particular polymer-solvent pair,  $K$  and  $a$  can be measured by measuring  $[\eta]$  on a several batches of that polymer with different, and known, molecular weights. The molecular weights might be known by some other experimental technique such as osmotic pressure experiments. Plotting  $\log [\eta]$  *vs.*  $\log M$  will easily give  $K$  and  $a$  for that polymer-solvent pair. Many  $K$ 's and  $a$ 's for common polymer-solvent pairs can be found in handbooks of polymer science. Once  $K$  and  $a$  are known, a measurement of  $[\eta]$  on a polymer of unknown molecular weight can be used to measure the molecular weight. We note that this viscosity technique for measuring molecular weight is not an absolute technique as was osmotic pressure. It requires calibration experiments using samples with known molecular. To avoid errors resulting from the type of average molecular weights determined by osmotic pressure or viscosity experiments, accurate calibration experiments should be done with monodisperse polymers.

### 6.4.1 Polydisperse Polymers

We next consider experiments on polydisperse polymers. How do we use viscosity experiments to measure an average molecular weight? What sort of average molecular weight do we measure? We cannot be as rigorous as we were for osmotic pressure on polydisperse polymers. We can, however, make some reasonable assumptions and get a reasonable result. We make the following three assumptions

$$1. \quad \eta_{sp} = \sum_i (\eta_{sp})_i \quad (6.23)$$

$$2. \quad (\eta_{sp})_i = [\eta]_i c_i \quad (6.24)$$

$$3. \quad [\eta]_i = K M_i^a \quad (6.25)$$

The first assumption says that the total specific viscosity is the sum of the specific viscosities for each components (*i.e.*, each molecular weight of the polymer). The second assumption says that the specific weight of each component can be calculated from the intrinsic viscosity due to that component. The third assumption says that the relation between intrinsic viscosity and molecular weight is independent of molecular weight; *i.e.*,  $K$  and  $a$  are independent of molecular weight.

Using the above three assumptions we derive

$$\frac{\eta_{sp}}{c} = \frac{\sum_i K c_i M_i^a}{c} = \frac{\sum_i K \frac{N_i M_i}{V} M_i^a}{\sum_i \frac{N_i M_i}{V}} = \frac{\sum_i K N_i M_i^{1+a}}{\sum_i N_i M_i} \quad (6.26)$$

Assumption two implies we are considering the limit of zero concentration. Thus we remove the constant  $K$  from the summation terms and state the zero-concentration limit to get

$$\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = K \overline{M}_v^a \quad (6.27)$$

where

$$\overline{M}_v = \left( \frac{\sum_i N_i M_i^{1+a}}{\sum_i N_i M_i} \right)^{\frac{1}{a}} \quad (6.28)$$

$\overline{M}_v$  is known as the viscosity average molecular weight (for obvious reasons). When  $a = 1$ ,  $\overline{M}_v$  is equal to the weight average molecule weight,  $\overline{M}_W$ ; otherwise  $\overline{M}_v$  is between the weight average molecule weight and the number average molecule weight,  $\overline{M}_N \leq \overline{M}_v \leq \overline{M}_W$ . For typical  $a$ 's (0.5 to 0.8),  $\overline{M}_v$  is closer to  $\overline{M}_W$ . This result is to be expected because viscosity properties are expected to be a function of size and not just the number of polymers.

### 6.4.2 Experimental Procedures

We next discuss the experimental procedures and the equipment used to measure solution viscosity. The experiments are simple and can all be done with a relatively simple and relatively inexpensive piece of glassware called a viscometer (see Fig. 6.3). The experiment is to fill the viscometer such that the level on the left side is at point  $C$  and the level on the right side is at point  $A$  (*i.e.*, a certain volume of liquid depending on the volume of the viscometer). Because of the height difference between  $C$  and  $A$  ( $h$ ), there is a hydrostatic head or driving pressure to cause the liquid to flow through the capillary or narrow diameter section of the viscometer. The experiment is to measure the time it takes the liquid to flow from point  $A$  to  $B$ . In other words the time it takes the volume of liquid between  $A$  and  $B$  to flow through the capillary.

Flow of a Newtonian fluid through a capillary is relatively easy to analyze. The result can be found in many fluids books. If we ignore kinetic energy terms, the time is proportional to the solution viscosity through the following relation:

$$\eta = \frac{\pi r_c^4 \Delta P}{8 V_f L} t = A \rho t \quad (6.29)$$

where  $r_c$  is the radius of the capillary,  $V_f$  is the volume of liquid that flows (*i.e.*, the volume between points  $A$  and  $B$ ),  $\Delta P$  is pressure difference, and  $L$  is the length of the capillary. When flowing due to gravity only in a tube of length  $h$ ,  $\Delta P = \rho g h$  where  $\rho$  is the solution density. The physical constants of the viscometer can be then lumped into a single constant denoted above as  $A$ . If  $A$  is

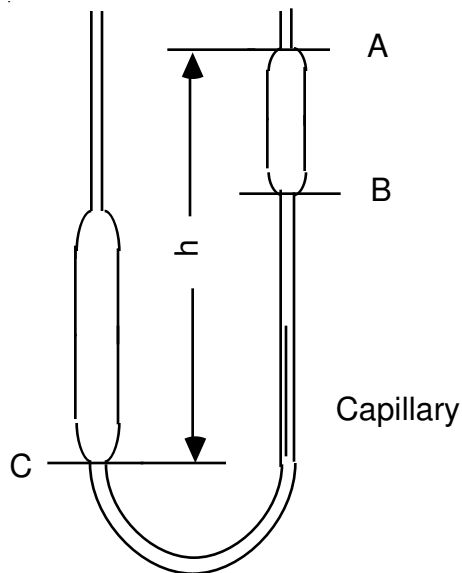


Figure 6.3: Simple viscometer.

known for a particular viscometer, a measurement of flow time and solution density can be used to determine solution viscosity.

A more accurate calculation of solution viscosity in terms of flow time would account for kinetic energy of the moving liquid. The result with kinetic energy is

$$\eta = A\rho \left( t - \frac{B}{At} \right) \quad (6.30)$$

where  $B$  is a constant. If the flow occurs rapidly ( $t$  is small), the liquid is moving fast and there can be significant kinetic energy. In this case it is important to correct for kinetic energy. If the flow is slow ( $t$  is large) the kinetic energy term, which is proportional to  $1/t$ , gets small. Physically the liquid is moving slowly and has little kinetic energy. In practice, it is simplest to use long flow times and ignore the kinetic energy term.

For most accurate results, there are several important considerations. First, the viscometer must be clean. Any contamination from previous solutions might add to the current solution and change its viscosity. A clean tube also means a tube that is free from dust particles. Dust particles can add to the solution as hard spheres with a large hydrodynamic volume. They can increase the solution viscosity and affect the results, especially when working with very dilute solutions. Third, it is best to choose a viscometer such that the flow time is greater than 100 seconds. When  $t > 100$  seconds, it is permissible to ignore the kinetic energy terms. It is then a simple matter to calculate relative viscosity and specific viscosity by comparing the flow time of the solution,  $t$ , to the flow time of the pure solvent,  $t_0$ :

$$\eta_r = \frac{t}{t_0} \quad \text{and} \quad \eta_{sp} = \frac{t - t_0}{t_0} \quad (6.31)$$



To adjust flow times, viscometers are available with different radius capillaries. The smaller the capillary, the longer the flow time. You thus select a viscometer to give good flow times in the expected viscosity range for your solutions.

To measure intrinsic viscosity requires extrapolation of  $\eta_{sp}/c$  to zero concentration. As with osmotic pressure, we are faced with the problem of how to extrapolate. The simplest approach is to do a simple linear extrapolation:

$$\frac{\eta_{sp}}{c} = [\eta] + kc \quad (6.32)$$

Experience shows that a linear extrapolation works well as long as  $\eta_r$  is restricted to less than 2. Another consideration for viscosity experiments, therefore, is to keep the relative viscosity less than 2.

Experimental results with polymer solutions has revealed that the slope of the  $\eta_{sp}/c$  vs.  $c$  curve,  $k$ , depends on molecular weight of the polymer. Huggins found that a plot of  $k$  versus  $[\eta]^2$  was linear and passed through the origin. In other words

$$\frac{d\left(\frac{\eta_{sp}}{c}\right)}{dc} = k'[\eta]^2 \quad (6.33)$$

Integrating this empirical result gives the Huggins' equation:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (6.34)$$

The new constant,  $k'$ , is a function of the polymer/solvent/temperature of the system, but is independent of molecular weight. Therefore once  $k'$  is known, a single relative viscosity measurement at one concentration can be used to get the viscosity average molecular weight. The following steps are used:

1. Measuring  $\eta_r$  leads to  $\eta_{sp}/c$  which using  $k'$  gives  $[\eta]$
2. With known  $K$  and  $a$ , the measured  $[\eta]$  gives  $\overline{M}_v$  or the viscosity average molecular weight.

If  $k'$  is not known, the typical viscosity experiment is to measure  $\eta_{sp}/c$  at several concentrations and do a linear extrapolation to zero concentration to get  $[\eta]$ . With known  $K$  and  $a$ , the measured  $[\eta]$  gives  $\overline{M}_v$ .

An alternate technique is to extrapolate inherent viscosity or  $\ln \eta_r/c$  to zero concentration to get  $[\eta]$ . As we approach zero concentration,  $\eta_{sp}$  will get small. Using the approximation for small  $x$  of  $\ln(1+x) \approx x - x^2/2$  we can derive

$$\ln \eta_r = \ln(1 + \eta_{sp}) \approx \eta_{sp} - \frac{\eta_{sp}^2}{2} \quad (6.35)$$

Then

$$\frac{\ln \eta_r}{c} \approx \frac{\eta_{sp}}{c} - \frac{\eta_{sp}^2}{2c^2} c \quad (6.36)$$

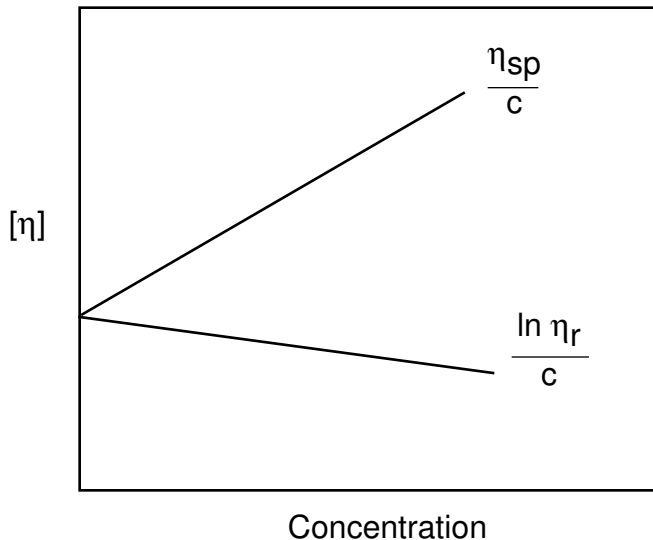


Figure 6.4: Typical plots of  $\eta_{sp}/c$  and  $\ln \eta_r/c$  as a function of concentration. The curves extrapolate to the same  $[\eta]$  at zero concentration, but approach zero concentration with different slopes.

Using Huggins' equation, this result gives:

$$\frac{\ln \eta_r}{c} \approx [\eta] + k'[\eta]^2 c - \frac{[\eta]^2 c}{2} - k'[\eta]^2 c^2 - \frac{k'^2 [\eta]^4 c^3}{4} \quad (6.37)$$

Neglecting higher order terms of order  $c^2$  or higher gives

$$\frac{\ln \eta_r}{c} \approx [\eta] + \left(k' - \frac{1}{2}\right) [\eta]^2 c = [\eta] + k'' [\eta]^2 c \quad (6.38)$$

Thus a plot of  $\ln \eta_r/c$  vs.  $c$  should be linear with slope  $k''[\eta]^2$  and intercept  $[\eta]$ . The new constant,  $k''$ , is related to  $k'$  by  $k'' = k' - 1/2$ . We see that plots of both  $\eta_{sp}/c$  vs.  $c$  and  $\ln \eta_r/c$  vs.  $c$  will both be linear and both extrapolate to  $[\eta]$  at zero concentration. The slopes of the two plots, however, will be different.

The terms  $\eta_{sp}/c$ ,  $\ln \eta_r/c$ , and  $[\eta]$  all have units of 1/concentration (e.g., a common convenient unit is deciliters per gram — dl/g). Because  $[\eta]^2 c$  also has units of 1/c,  $k'$  and  $k''$  are dimensionless. For many polymers  $k' \approx 1/3$  which makes  $k'' \approx -1/6$ . This difference in signs makes plots of both types of data useful. The two types of plots converge on the same intrinsic viscosity but from different directions — one has a positive slope and the other a negative one. Plotting of both types of data will often give a good feeling for the accuracy of the extrapolated intrinsic viscosity. Typical plots will resemble the curves in Fig. 6.4.

One final complication arises if  $[\eta]$  is large. A high intrinsic viscosity probably means that the viscosity depends on the shear rate of the test. Likewise, the extrapolation to zero concentration will also depend on shear rate. To remove shear rate effect it is sometimes necessary to get  $[\eta]$  at several shear rates and do a second extrapolation of  $[\eta]$  to zero shear rate. The zero shear-rate

intrinsic viscosity is the intrinsic viscosity that should be used in molecular weight calculations. If  $[\eta]$  is not too high, the measured value of  $[\eta]$  at some non-zero shear rate can probably be assumed to be a good estimate of the zero shear-rate viscosity.

## 6.5 Viscosity Summary

In summary, the work you need to do to get useful results from viscosity experiments depends on the prior knowledge you might have about the constants relevant to your particular polymer/solvent pair. We consider four situations:

1. Known  $K$ ,  $a$ ,  $k'$  (or  $k''$ ): If all these constants are all known, then measurement of  $\eta_0$  and  $\eta$  at one concentration will lead directly to  $\overline{M}_v$ . Many of these constants are tabulated for common polymers. Thus when you are working with common polymers it is relatively easy to get a good estimate of molecular weight.
2. Known  $K$  and  $a$ , but unknown  $k'$  (and  $k''$ ): Tables of  $K$  and  $a$  are common, but there is less data about  $k'$  (or  $k''$ ). When these constants are not known, you have to measure  $\eta_0$  and measure  $\eta$  at several concentrations. These results can be used to linearly extrapolate  $\eta_{sp}/c$  and  $\ln \eta_r/c$  to zero concentration to get  $[\eta]$  which will lead to  $\overline{M}_v$ . Although this situation requires more work than using a known  $k'$  (or  $k''$ ), it is less prone to errors; it is less prone to uncertainties in the tabulated values of  $k'$  (or  $k''$ ).
3. No constants known: If you are working with a new polymer or an unusual solvent, it is likely that none of the constants ( $K$ ,  $a$ ,  $k'$ , or  $k''$ ) will be known. For such polymers you can still measure  $[\eta]$  by extrapolating  $\eta_{sp}/c$  and  $\ln \eta_r/c$  to zero concentration. Although you cannot use  $[\eta]$  to determine molecular weight, you can compare values of  $[\eta]$  from the same polymer/solvent pair to get relative molecular weights. The higher the value of  $[\eta]$ , the higher the molecular weight. Relative molecular weights are often enough. If they are not enough it might be useful to do calibration experiments to find  $K$  and  $a$ . The calibration experiments will require monodisperse polymers whose molecular weight has been absolutely determined by some other method (*e.g.*, osmotic pressure or light scattering). The use of monodisperse polymers avoids problems of differences in  $\overline{M}_N$ ,  $\overline{M}_W$ , and  $\overline{M}_v$ .
4. Insoluble polymer: Solution viscosity techniques assume that you can dissolve the polymer in some solvent. Obviously the techniques cannot be used with polymers that cannot be dissolved in any solvent. For such polymers it is often possible to measure the zero shear-rate viscosity of the polymer melt. The zero shear-rate melt viscosity increases as the molecular weight increases. A crude, but standardized method of estimating melt viscosity is called the melt index. The melt index test measures the mass of material that flows through a standard

orifice in a fixed amount of time. The more material that flows, and hence the higher the melt index, the lower the melt viscosity and thus the lower the molecular weight.

## Problems

- 6-1. Two “monodisperse” polystyrenes are mixed in equal quantities by weight. One polymer has molecular weight 39,000 and the other molecular weight of 292,000. What is the intrinsic viscosity of the blend in benzene at 25°C. The Mark-Houwink constants for polystyrene/benzene at 25°C are  $K = 9.18 \times 10^{-5}$  dl/g and  $a = 0.74$ .
- 6-2. With enough predetermined constants for a particular polymer-solvent pair, it is possible to determine molecular weight of a polymer by doing only two viscosity measurements. What two viscosity measurements are required? What constants for the particular polymer-solvent pair are required and how are they used?
- 6-3. Solution viscosities for a particular polymer and solvent are plotted in the form  $(\eta - \eta_0)/(c\eta_0)$  versus  $c$ , where  $\eta$  is the viscosity of the polymer solution at concentration  $c$  in g/cm<sup>3</sup> and  $\eta_0$  is the viscosity of the pure solvent. The plot is a straight line with intercept of 1.50 cm<sup>3</sup>/g and a slope of 0.9 cm<sup>6</sup>/g<sup>2</sup>. Give the magnitude and the units for the Huggin’s constant for this polymer-solvent pair.