

A HIGH POLYMER EXPERIMENT FOR PHYSICAL CHEMISTRY

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IN RECENT years the physical chemistry of such macromolecular substances as proteins and high polymers has become of great interest and value. The purpose of this communication is to describe an experiment which is in successful use in the elementary physical chemistry course at the University of Wisconsin.

THEORY

Information as to the size and shape of high polymer molecules in solution may be obtained from viscosity measurements. The theoretical background for this method starts with Einstein's derivation(3), in 1906, of an equation relating the viscosity of dilute suspensions of small rigid spheres to the volume fraction of the spheres. Einstein's equation is

$$\eta = \eta_0 (1 + 2.5 \phi), \quad (1)$$

where

η = viscosity of suspension
 η_0 = viscosity of solvent
 ϕ = volume of spheres per unit volume of suspension

This equation may be rearranged to give

$$\frac{\eta - \eta_0}{\eta_0} = 2.5 \phi \quad \text{or} \quad \frac{\eta}{\eta_0} - 1 = 2.5 \phi$$

Because of the high molecular weight of polymeric materials the usual techniques of physical chemistry for the determination of molecular weight (*i.e.*, freezing point lowering, boiling point elevation, and vapor pressure lowering) are not applicable, and special methods have been developed. The molecular weights of high molecular weight substances may be determined with the equilibrium and velocity ultracentrifuges of Svedberg (11), the light scattering method of Debye (2), and the classical osmotic pressure method. Although the apparatus and technique required for these methods are beyond the scope of the elementary physical chemistry laboratory, the viscosity method of Staudinger (10), which must be calibrated by one of the preceding methods, may be satisfactorily carried out by the student using only simple apparatus. In our opinion, it is a valuable addition to the laboratory work in physical chemistry.

The ratio η/η_0 is the familiar *relative viscosity* of the suspension. The quantity $(\eta/\eta_0) - 1$ is of frequent occurrence in viscosity studies and has come to be known as *specific viscosity*, with the symbol η_{sp} . It should be remembered that neither relative viscosity

nor specific viscosity are actually viscosities but are dimensionless numbers.

The Einstein equation, while valid for rigid spheres, proved to be inapplicable to solutions of linear polymers, in which the solute molecules are usually thread-like and flexible rather than rigid spheres. For such molecules the viscosity coefficient is greater than 2.5 and Staudinger, in 1930, found it to be approximately proportional to the molecular weight of the polymer. He wrote a new equation

$$\frac{\eta_{sp}}{c} = KM \quad (2)$$

where

c = concentration
 K = constant for a class of similar polymers
 M = molecular weight

It was found that for many substances η_{sp}/c varies with concentration; therefore the value extrapolated to infinite dilution, termed the intrinsic viscosity, $[\eta]$, is used

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} = \lim_{c \rightarrow 0} \frac{\ln \eta/\eta_0}{c} \quad (3)$$

In the low concentration range the plot of η_{sp}/c vs. c is quite linear, and it may be shown the plot of $1/c \ln \eta/\eta_0$ extrapolates to the same limit at zero concentration. The use of the double extrapolation makes it possible to determine the intrinsic viscosity with a high degree of precision.

The Staudinger equation now becomes

$$[\eta] = KM \quad (4)$$

This relation proved satisfactory in certain cases, yielding molecular weights in good agreement with those obtained by other methods mentioned in the introduction. However, in some instances very pronounced errors were observed, and it was proposed by Mark (8) that the data could be better represented by an equation of the type

$$[\eta] = KM^a \quad (5)$$

where a is a function of the geometry of the molecule, varying from 0.5 for tightly curled polymer molecules to 2 for rigidly extended molecules.

The constants a and K depend upon the type of polymer, the solvent, and the temperature of the viscosity determinations. Their values are determined experimentally by measuring the intrinsic viscosities of poly-

mer samples for which the molecular weight has been determined by an independent method, such as osmotic pressure. Since equation (5) may be written in logarithmic form, the evaluation of the constants is usually accomplished by graphing $\log [\eta]$ versus $\log M$ and determining the slope, a , and intercept, $\log K$, of the straight line plot.

$$\log [\eta] = \log K + a \log M \quad (6)$$

Table 1 (6) lists values of K and a which have been determined for various polymer-solvent systems.

TABLE 1

Polymer	Solvent	Temperature	K	a
Cellulose acetate	Acetone	25°	1.49×10^{-4}	0.82
Polyisoprene	Toluene	25°	5.02×10^{-4}	0.67
Polystyrene	Toluene	25°	3.7×10^{-4}	0.62
GR-S copolymer	Toluene	30°	5.4×10^{-4}	0.66
Methyl methacrylate	Benzene	25°	0.94×10^{-4}	0.76
Polyisobutylene	Toluene	20°	3.6×10^{-4}	0.64

Since most synthetic high polymers are polydisperse, the molecular weights obtained by the viscometric method are average values. Flory (5) has shown that this is generally neither a weight average nor a number average weight but is given by

$$M_v = \left[\frac{\sum N_i M_i^{a+1}}{\sum N_i M_i} \right]^{1/a} \quad (7)$$

where a is the constant in equation (5). He terms this value the *viscosity average* molecular weight. The viscosity average molecular weight is intermediate between a number average and a weight average molecular weight, being identical with the latter than $a = 1$.

It has been noted that the values of K and a for a given polymer depend upon the solvent as well as the

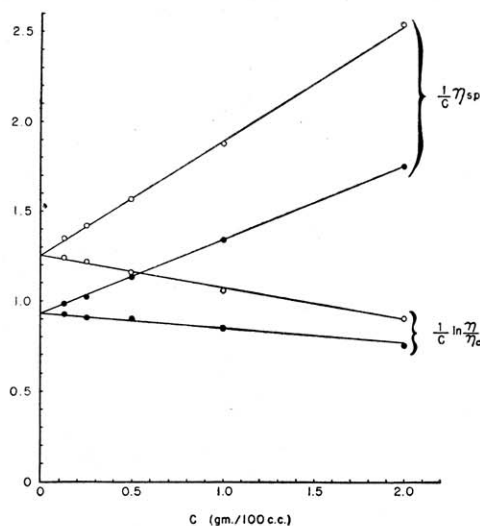


Figure 1. Determination of the Intrinsic Viscosity of Polystyrene PS-65 in Toluene (●) and in 15% Methanol-85% Toluene (●)

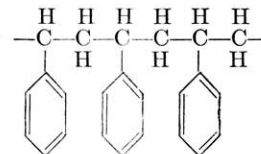


Figure 2. Structure of Styrene Polymer

solute. Thus, the intrinsic viscosity of a given polymer sample is different in different solvents. This phenomenon gives us some insight into the general form of polymer molecules in solution (1). A long chain molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly rolled up mass and a rigid linear configuration. Presumably all possible degrees of curling may be displayed by any one molecule, owing to the internal Brownian movement of the flexible chains. There will be, however, an average configuration, which will depend upon the solvent. In a "good" solvent, that is, one which shows a zero or negative heat of mixing with the polymer, the polymer molecule is fairly loosely extended, approximating a random spatial arrangement, and the intrinsic viscosity is high. In a "poor" solvent, that is, one in which the polymer dissolves with the absorption of heat (positive heat of mixing), the segments of the polymer molecule attract each other in solution more strongly than they attract solvent molecules, and the result is that the molecule assumes a more compact configuration and the solution has a lower intrinsic viscosity.

A dilute solution of high polymer in a solvent-non-solvent mixture would, therefore, be expected to exhibit a lower intrinsic viscosity than a solution of the same polymer in a good solvent.

EXPERIMENTAL PROCEDURE

It is apparent that the determination of molecular weights by use of equation (5) involves measurements of the relative viscosities of polymer solutions of several concentrations. These relative viscosities may be determined by using an Ostwald viscometer. The relative viscosity of the solution, η/η_0 , is given by

$$\frac{\eta}{\eta_0} = \frac{dt}{d_0 t_0} \quad (8)$$

where

d = density of solution

d_0 = density of solvent

t = time of flow of solution through capillary

t_0 = time of flow of solvent through capillary

For very dilute polymer solutions, $d \cong d_0$ so that equation (8) reduces to

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \quad (9)$$

Thus it is necessary to measure only the time of flow of the solvent and several solutions. These solutions may be best obtained by successive dilution of a 1% solution prepared by the student. All viscosity measurements should be carried out in a thermostat, since

the variation of viscosity with temperature is about 1.2% per degree for toluene at 25°C.

From the value of η/η_0 obtained as described, one may calculate η_{sp} and η_{sp}/c . The latter is plotted against the concentration, and the curve extrapolated to $c = 0$. In the low concentration ranges the curve should be linear, facilitating the extrapolation. Table 2 gives data on solutions of Dow polystyrene PS-65 in toluene and in 15% (volume percent) methanol, 85% toluene at 25°C. The graph for the determination of the intrinsic viscosity in these two solvents is shown in Figure 1.

The intrinsic viscosity of this polymer sample was 1.26 in toluene, a "good" solvent, and 0.93 in 15% methanol, 85% toluene, a "poor" solvent. Since the values of K and a for polystyrene in toluene are available in the literature (Table 1), we may calculate the average molecular weight of this particular polymer sample. Using equation (5)

$$\begin{aligned} 1.26 &= 3.7 \times 10^{-4} M^{0.62} \\ M &= 500,000 \end{aligned}$$

To obtain an estimate of the size of such a molecule we may calculate the length of the extended polymer molecule. The structure of a segment of a polystyrene molecule is illustrated in Figure 2. Since the weight of a monomer unit is 104, there are approximately 4800 monomer units in a polystyrene molecule of molecular weight 500,000. Since the length of the chain is 2.5 Å. per monomer unit, the total length of the chain is 12,000 Å. The actual extension of the polystyrene molecules in solution is intermediate between a tightly coiled form and an extended form and depends upon the solvent and temperature.

This experiment enables the student to carry out one of the standard techniques of a high polymer molecular weight determination, and provides an introduction to the physical chemistry of macromolecular substances. The effect of the solvent upon the configuration of large molecules in solution may be qualitatively demonstrated. The equipment required (Ostwald viscometer, stopwatch, and thermostat) are available in any physical chemistry laboratory.

TABLE 2
Viscosity Data on Solutions of Polystyrene PS-65

$c(\text{gm./100 cc.})$	$t(\text{sec.})$	η/η_0	η_{sp}/c	$\left(\frac{1}{c} \ln \frac{\eta}{\eta_0}\right)$
I. Polystyrene in Toluene at 25°C. ($t_0 = 98.5 \text{ sec.}$)				
1.998	598.7	6.090	2.55	0.90
0.999	282.9	2.879	1.88	1.06
0.499	175.1	1.782	1.57	1.16
0.249	133.2	1.355	1.42	1.22
0.124	114.8	1.168	1.35	1.24
II. Polystyrene in 15% Methanol, 85% Toluene at 25°C. ($t_0 = 83.3 \text{ sec.}$)				
2.000	375.9	4.515	1.76	0.75
1.000	195.0	2.342	1.34	0.85
0.500	130.6	1.569	1.14	0.90
0.250	104.5	1.255	1.02	0.91
0.125	93.5	1.123	0.98	0.93

The authors are indebted to Dr. J. W. Williams and Dr. J. D. Ferry for helpful suggestions and to the Dow Company for the samples of polystyrene resin (PS-15, PS-25, and PS-65).

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