DETERMINATION OF MOLECULAR WEIGHT OF POLYMER WITH LOW DEGREE OF POLYMERIZATION

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Molecular weights of polycarbonate fractions in the range 5,000 to 22,000 have been determined by vapour pressure osmometer. The results are within 5% of the viscosity average molecular weights. Moreover, agreement between the molecular weights calculated from Raoult's law and from the Flory–Huggins treatment is of the same order. The polymer–solvent interaction parameter is somewhat higher, probably indicating the concentration dependence.

It is not possible to determine polymer molecular weights less than 25,000 either by osmometer[1] or by light scattering method.[2] Polymer molecules in this range of molecular weights are permeable to osmometer membrane[3] and small amount of impurities cause much greater interference to the scattered light. Of the other methods, vapour pressure osmometer is convenient. It is, in fact, a vapour pressure lowering method in which the sensitivity is increased manifold by thermoelectric appliances. Vapour pressure lowering in polymer solutions is very small, of the order of 4×10^{-3} mm of Hg. Measurements of such small differences require a very sensitive appliance.

Vapour pressure osmometer offers an indirect method of determining vapour pressure lowering. This thermoelectric osmometer based on the apparatus described by Hill[4] and Baldes,[5] measures the steady state of temperature difference arising from different rates of solvent evaporation from solvent and solution. The temperature difference is assumed to be proportional to the difference in the vapour pressure which, in turn, is related to the molecular weight of the solute. The use of thermistors[6] enables detection of a very small temperature difference and rapid attainment of equilibrium. The theory of the method has been discussed by Tomlinson et al.[7] and van Dam.[8]

Raoult's law and the Flory–Huggins treatment[9] are the theoretical basis of molecular weight determination by this method. The vapour pressure lowering due to a solute, according to Raoult's law, is expressed by,

$$(p_I/p_0) = (W_I/M_I)/(W_I/M_I + W_2/M_2) \qquad (1)$$

where p_0 and p_I are vapour pressures of solvent above solvent and solution respectively and W and M refer to weight and molecular weight with subscripts 1 and 2 denoting solvent and polymer. However, Raoult's law does not hold even for dilute polymer solutions but equation 1 can be used to obtain apparent molecular weights for different concentrations, the extrapolation of which to zero concentration gives the true molecular weight.

The Flory-Huggins treatment[9] is,

$$[\ln(p_I/p_0) - \ln \phi_I]/\phi_2 - 1 = -V_I/V_2 + \chi_I \phi_2 \qquad (2)$$

where ϕ is the volume fraction, V the molar volume, subscripts 1 and 2 referring to solvent and polymer respectively and χ_I is the polymer–solvent interaction parameter. A plot of the left hand side of equation 2 against ϕ_2 should be rectilinear with an intercept $(-V_I/V_2)$ and a slope χ_I. The molecular weight can be calculated from the intercept.[10]

Experimental and Results

The apparatus and its operation have been described elsewhere.[11,12] This is not an absolute method and the instrument must first be calibrated using a pure substance of known molecular weight in the solvent to be used in the determination of polymer molecular weight. Recrystallized benzil was used in chloroform with molar concentrations m in the range 0.001 to 0.006 for calibration. The lowering of vapour pressure is read as a difference in resistance ΔR in ohms. The values of ΔR obtained are plotted against m to get the calibration curve for the solvent (Fig. 1).

Fractionation of bisphenol A polycarbonate (makrolon 3,000) has been described in previous papers.[13,14] Values of ΔR for polycarbonate solutions in chloroform in the concentration range 0.5 to 1.75 g/dl. were obtained. The experiment was carried out at 37°C and in all cases equilibrium values of ΔR were taken. For benzil solutions

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equilibrium values were attained within 4 min but polymer solutions took 10 min to reach reasonably constant values. This could be attributed to higher viscosities of polymer solutions.[15] The solutions used for calibration were very dilute and could be assumed to be ideal. It is also assumed that ΔR is directly proportional to the vapour pressure difference between solvent and solution. The assumption of ideality, of course, will not apply to polymer solutions except at infinite dilution. Values of ΔR for polycarbonate solutions were used to obtain, from the calibration curve, apparent molecular weights. These were then plotted against polymer concentrations (Fig. 2) and extrapolated to zero concentration to obtain $\bar{M}_n$, the number average molecular weight.

An alternative method of treating the results is the Flory–Huggins treatment.[9] Assuming that a particular value of ΔR, for a given solvent, corresponds to the same vapour pressure difference whatever be the solute, such differences can be calculated from the calibration data by use of Raoult's law since the solutions used in the calibration are assumed to be ideal. Thus values of (p_1/p_0) are obtained for polymer solutions and used in equation 2. Plot of the left hand side of equation 2 against ϕ_2 are given in Fig. 3. $\bar{M}_n$ is obtained from the intercept and χ_1 from the slope.

The results are given in Tables 1 and 2. The viscosity average molecular weights $\bar{M}_v$ calculated from the relationship[14] $[\eta] = 1.12 \cdot \bar{M}_v^{0.82}$ in chloroform at 25°C are included in Table 1 for comparison.
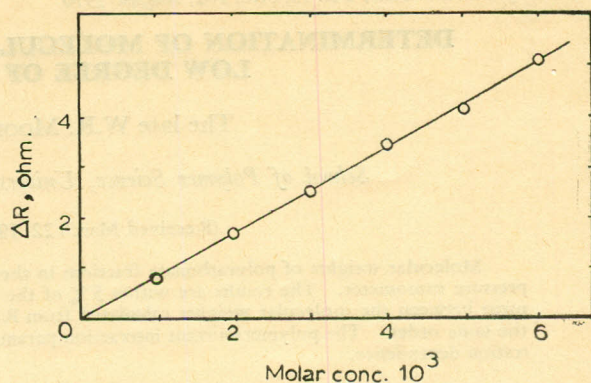

Fig. 1.—Calibration curve for benzil in chloroform.
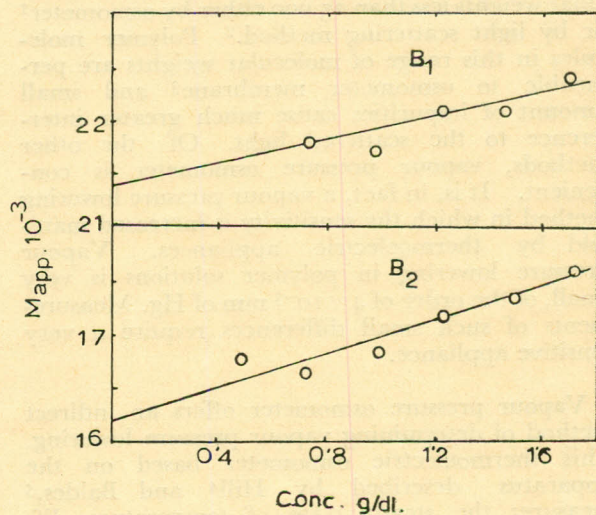

Fig. 2.—Plots of apparent molecular weight against concentration, figures indicate fractions.
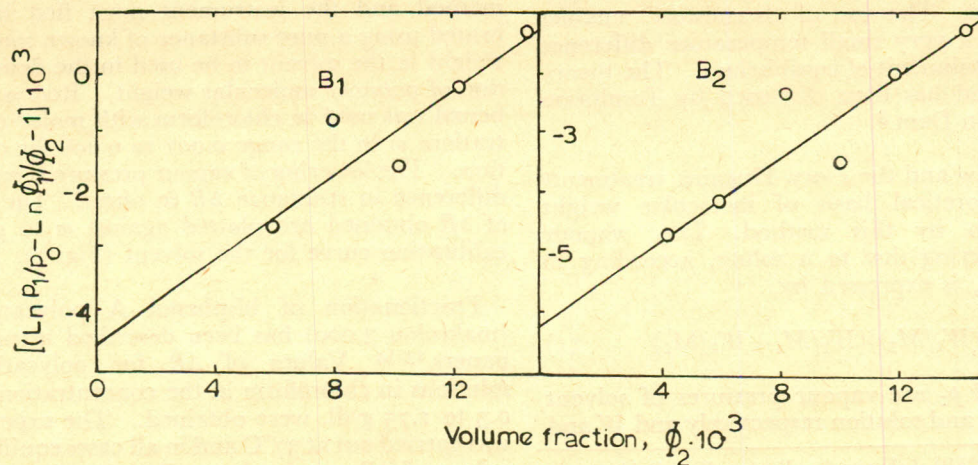

Fig. 3.—Plots of the left hand side of equation 2 against the volume fraction of polymer.

TABLE 1.—MOLECULAR WEIGHTS OF POLYCARBONATE FRACTIONS.

Method	Fraction A1	Fraction A2	Fraction A3	Fraction A4
Viscosity	21,000	15,000	9,600	6,300
Thermoelectric vapour pressure lowering	20,000	12,000	9,060	5,900

TABLE 2.—MOLECULAR WEIGHTS OF POLYCARBONATE FRACTIONS.

Fraction	Molecular weights by		χ_1
	Raoult's law	Flory–Huggins treatment	
B1	21,400	21,400	0.36
B2	16,200	15,600	0.35
B3	9,500	8,800	0.36
B4	6,900	6,500	0.34

Discussion

The determination of molecular weights by vapour pressure osmometer is reasonably rapid. The upper limit of molecular weight capable of accurate determination is about 25,000. Modifications have been described which extended this to 40,000 and accuracies of 4–5% have been reported.[16] For polycarbonate fractions, number average molecular weights compare well with the viscosity average molecular weights in the same solvent as shown in Table 1. The lower values of number average molecular weights reflect the difference between the two averages. The molecular weights obtained from equations 1 and 2 are also in agreement but χ_1 values appear to be somewhat higher. Lower values of χ_1 in chloroform for higher molecular weight fractions of polycarbonate have been obtained from osmotic and light scattering measurements.[14] These higher values may reflect the concentration dependence[17] of χ_1 as more concentrated solutions were used for vapour pressure osmometry.

Ohama[18] suggested that the second virial coefficient can be obtained directly from the slope of the plots of apparent molecular weight against concentration (Fig. 2). This suggestion seems unreasonable since the nature of the slope has been found to change in many cases.[19-22] However, information regarding association and dissociation of polymer in solutions can be obtained by determining molecular weights in a number of solvents of varying solvent power.[11]

This method of molecular weight determination has been reviewed by Billmeyer[16] and Moore et al.[11] The method seems to be valuable for the determination of molecular weights below 25,000 and to be free from many of the limitations and disadvantages. This is, of course, limited to polymers soluble in liquids which are volatile and have relatively low heats of vaporization. A temperature difference of 10^{-4}°C can be measured with good reproducibility.[23] The volatility of solvents is, therefore, a factor determining the sensitivity of the process; the more the volatility, the better is the sensitivity.[24]

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