

Polymers in mixed solvents: application of the new representation of viscosity data as a function of molecular weight

Anastasios Dondos

Centre de Recherches sur les Macromolécules (CNRS), 6, rue Boussingault, F 67083 Strasbourg Cedex, France

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The relation proposed between the intrinsic viscosity and the molecular weight of a polymer^{1,2} ($1/[\eta]$ versus $1/M^{1/2}$), has been applied in this paper in cases when the polymer is dissolved in a binary solvent mixture. We have then shown that even in this case we can calculate in a very accurate way the molecular weight of the polymer from its intrinsic viscosity, especially in the molecular weight range where the Mark–Houwink–Sakurada equation is the least applicable ($M_w < 150\,000$).

It is well known that the published values of the K and a coefficients of the Mark–Houwink–Sakurada equation (MHS) are quite scattered for a given polymer/solvent system even when one takes into account experimental errors. We believe that this observation can be attributed to the fact that the $\log[\eta] - \log M$ representation is not justified, especially in the range of small molecular weights. The slope obtained in this kind of diagram depends on the domain of the molecular weights considered which explains the large deviations observed. A K – a couple of values depends strongly on the range of molecular weight for which it has been determined.

In the previous papers^{1,2} we proposed an empirical relation between the intrinsic viscosity of a polymer dissolved in a good solvent and its molecular weight. This relation was applicable for polymers of molecular weight from 3000 to 250 000.

After transforming the first relation¹, one obtains the new formula²:

$$\frac{1}{[\eta]} = -A_2 + \frac{A_1}{M^{1/2}} \quad (1)$$

where A_1 and A_2 are specific constants for a particular polymer–solvent system. If this formula is correct one should obtain straight lines when plotting $1/[\eta]$ versus $1/M^{1/2}$: this diagram should be a more satisfactory way to represent the relation between $[\eta]$ and M than in the 'classical' $\log[\eta] - \log M$ representation. We have shown that our representation is valid experimentally in the molecular weight range from oligomers up to 400 000. We have shown that, in a certain way, equation (1) is quite similar to the Stockmayer–Fixman–Burchard^{3,4} relation (SFB) which is an indirect justification of its validity.

In the case when the polymer is dissolved in a binary solvent mixture, the points obtained for relatively low molecular weight samples in the MHS and SFB plots are far away from the straight line obtained for higher molecular weight samples. This has been explained by the change of the preferential solvation of polymers with low molecular weight^{5–7}.

In this paper we show that equation (1) can be applied in a satisfactory manner even in cases when the polymer is dissolved in a binary solvent mixture.

In Figure 1 we have plotted $\log[\eta]$ versus $\log M$ for polystyrene (PS) samples in solution in two different binary solvent mixtures: one of these binary mixtures is made of 81.5% of carbon tetrachloride and 18.5% of methanol and the other one is made of a 50/50 vol% benzene–heptane mixture. PS in both mixtures is under intermolecular Θ conditions⁸

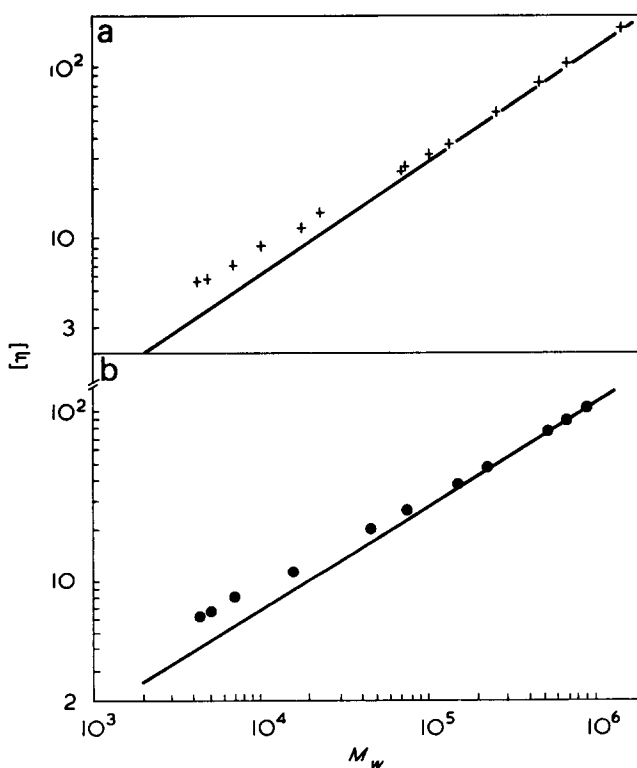


Figure 1 Plot of $\log[\eta]$ versus $\log M$ for PS samples in (a) 50/50 benzene/heptane mixture; (b) 81.5% CCl_4 /18.5% methanol mixture $T = 25^\circ\text{C}$

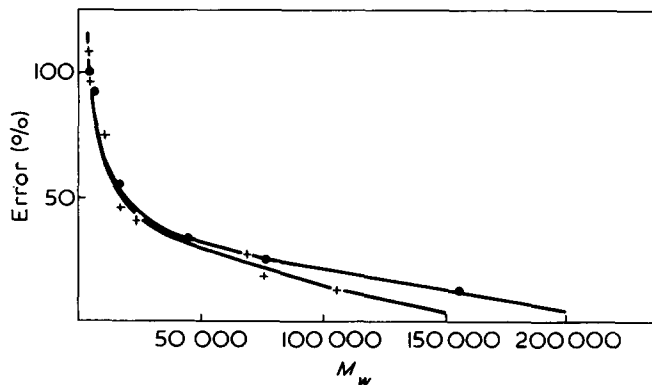


Figure 2 Error (%) in the molecular weight determination of PS samples as a function of its molecular weight taking into account the values of $[\eta]$ and the viscosity law established with samples of molecular weight higher than 150 000: +, PS in 50/50 benzene/heptane mixture; •, PS in 81.5% CCl_4 /18.5% methanol mixture

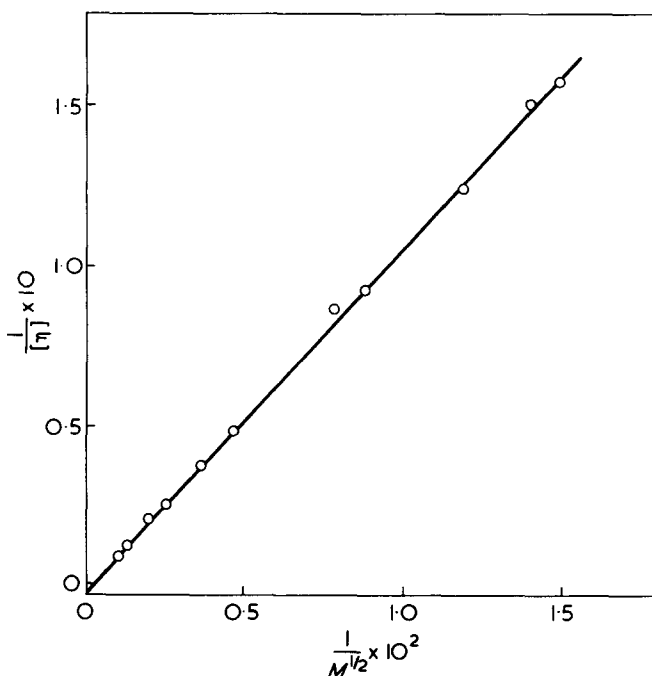


Figure 3 Plot of $1/[\eta]$ versus $1/M^{1/2}$ for PS samples in 81.5% CCl_4 /18.5% methanol mixture

(second virial coefficient equal to zero^{5,9}) and its preferential solvation changes with its molecular weight^{5,9}.

One observes that the points corresponding to molecular weights below 150 000 are located above the straight line corresponding to higher molecular weight ones. The deviation is all the more important as the molecular weights decrease. Neglecting this deviation can lead to very erroneous values for the molecular weights when one relies solely on viscosity for these determinations.

In Figure 2 we have plotted the error (%) of the molecular weight obtained from the value of $[\eta]$ and low $[\eta] = KM^a$ established from the constants obtained for molecular weight samples above 150 000. This error increases when molecular weight decreases: it is of the order of 40% for a 30 000 molecular weight sample.

If, for the same systems, we plot $1/[\eta]$ versus $1/M^{1/2}$, we obtain straight lines (Figures 3 and 4) which enable us to calculate in a very accurate way the molecular weight of a

PS sample from its intrinsic viscosity, especially for polymers of molecular weight below 150 000.

In Figure 5 we have plotted the variation of $1/[\eta]$ versus $1/M^{1/2}$ for PS in solution in benzene/methanol mixtures of two different composition. Here again the equation seems to be perfectly well defined. As it was shown already in our previous articles^{1,2}, A_1 , the slope of the straight lines obtained

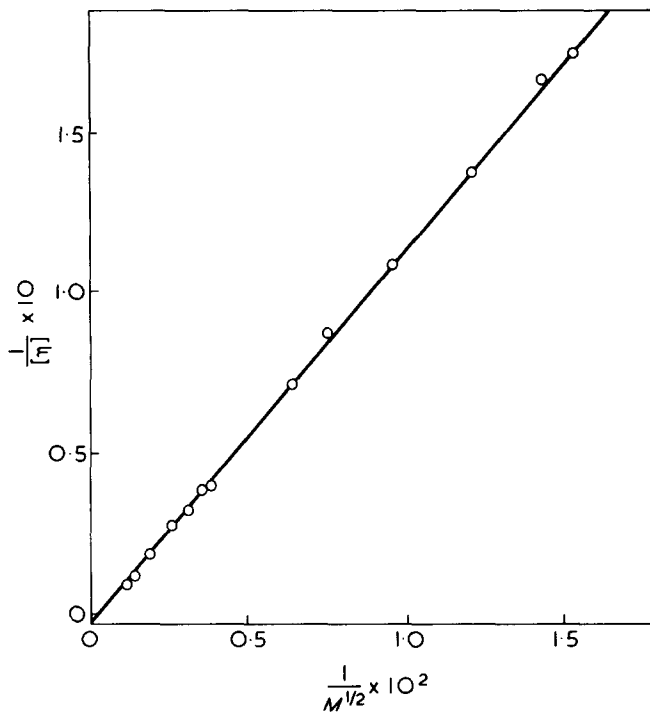


Figure 4 Plot of $1/[\eta]$ versus $1/M^{1/2}$ for PS samples in 50/50 benzene/heptane mixture

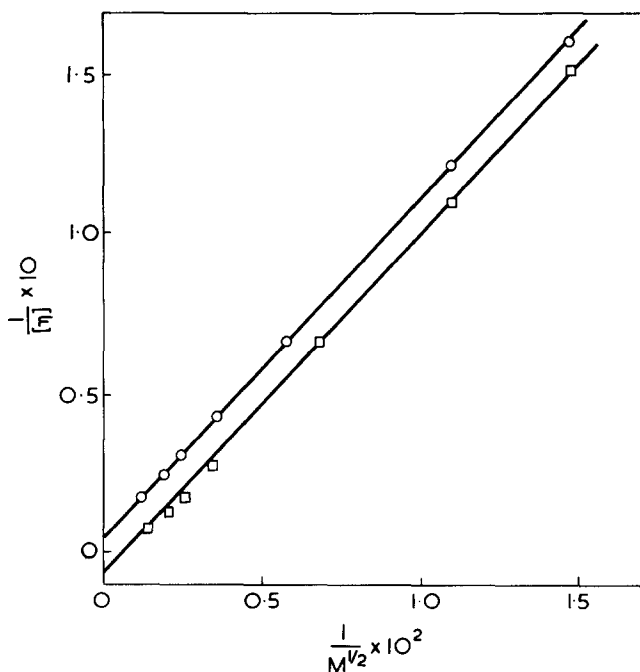


Figure 5 Plot of $1/[\eta]$ versus $1/M^{1/2}$ for samples in 90% benzene/10% methanol mixture (\square) and 74.5% benzene/25.5% methanol mixture (\circ)

when plotting equation 1, is related to the unperturbed dimensions parameter, K_θ , by the equation:

$$K_\theta = \frac{1}{A_1 + A'} \quad (2)$$

where A' is a constant of the system, determined by the empirical relation:

$$-\Delta\rho = \Delta\rho_\infty + \frac{A'}{M^{1/2}} \quad (3)$$

introduced in ref 1.

Using equation (2) and the straight lines in *Figure 5* we obtain a value for K_θ , in the case of PS, which is higher in the mixture containing 10% of methanol, though the straight lines in *Figure 5* exhibit the same slope; this is due to the lower value of the A' constant. This result is in agreement with former determinations of K_θ for PS in the same mixtures of solvents¹⁰, obtained using the SFB equation.

It is therefore impossible to determine K_θ from such a dia-

gram, if one does not know the A' parameter. In certain cases its value can reach to 10–15% of the A_1 value, which causes an error of the same order in K_θ . It follows from this that though this representation has the advantage of giving an accurate relation between $[\eta]$ and M , it has the shortcoming of preventing any direct measurements of the unperturbed dimensions.

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