Viscometric measurement of the thermodynamic properties of dilute polystyrene solutions

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We have investigated the use of the viscometric method for measuring the Flory interaction parameters for dilute polystyrene solutions in a range of solvents. Two 'single point' methods were used to estimate the intrinsic viscosity and these agreed well with the more conventional method of extrapolating results over a range of concentrations. Also, the interaction parameters derived from these intrinsic viscosity values showed good agreement with literature results. Values of the Flory interaction parameters are presented for 11 solvents, some of which have not previously been published.

(Keywords: intrinsic viscometry; thermodynamics of solutions; polystyrene; interaction parameters)

Introduction

As part of our research programme investigating the effects of ultrasound on dilute polymer solutions[1], we needed information on thermodynamic properties such as second virial coefficients, B, and Flory interaction parameters, χ, for polystyrene in a range of solvents. These parameters are connected by the expression

$$B = (0.5 - \chi)/\rho^2 V_1 \qquad (1)$$

where ρ is the density of the polymer and V_1 the molar volume of the solvent. Although there are a number of convenient techniques for investigating concentrated polymer solutions[2,3], the usual methods for studying dilute solutions are membrane osmometry or light scattering, both of which require specialist apparatus. A number of workers have used viscometric methods to estimate B via the intrinsic viscosity, $[\eta]$, a quantity usually measured in connection with the viscometric determination of molecular weight using the Mark–Houwink equation

$$[\eta] = KM^{\alpha} \qquad (2)$$

K and α being constants listed in the literature. The attraction of the methods in terms of economy and convenience are obvious, the main drawback of the technique being that measurements must be made on a number of solutions, making it somewhat tedious and time consuming. Several alternatives have been proposed whereby a single measurement may be used, greatly increasing the speed and utility of the method. In the results presented here, we have investigated the use of these methods for polystyrene solutions in 11 solvents. First, we compared two 'single point' methods for calculating $[\eta]$ by comparing with the usual method of extrapolating results from a series of concentrations. Following this, we investigated the calculation of χ to establish the potential accuracy of the method.

Theory

Single point measurement of $[\eta]$. The primary measurement in solution viscometry is the relative viscosity, η_r, given by the ratio of capillary flow times for a solution and the pure solvent. The intrinsic viscosity of the polymer is then found by finding η_r for solutions over a range of concentrations, c, and using

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_r - 1}{c} \right) \qquad (3)$$

To avoid use of this extrapolation procedure, a number of 'single point' methods have been suggested[4–6] but most of these have referred to a particular polymer system and were not proposed for general applicability. However, two have been proposed for more widespread use. Soloman and Ciuta[7], by combining the Huggins[8] and Kraemer[9] equations and making certain assumptions, suggested that $[\eta]$ could be found from a single measurement of η_r using

$$[\eta] = [2(\eta_r - 1 - \ln \eta_r)]^{1/2}/c \qquad (4)$$

This worked for a range of polymer–solvent systems provided that a solution concentration in the region of 0.2% was used.

Rudin and co-workers[10,11] pointed out that equation (4) was applicable only under certain conditions and proposed a method of wider applicability that was also of use in predicting relative viscosities in more concentrated solutions. From consideration of Newtonian flow of large spheres in a solution, they showed that

$$\eta_r^{-1} = 1 - 2.5\phi + 11\phi^5 - 11.5\phi^7 \qquad (5)$$

where ϕ is the volume fraction of swollen polymer molecules at a solution concentration c. They further showed that, for concentrations in the appropriate range, $[\eta]$ could be found from

$$[\eta] = \frac{2.5\phi(0.524\rho - c)}{\rho c(0.524 - \phi)} \qquad (6)$$

where ρ is the density of the amorphous polymer at the solution temperature. Thus, from a single measurement of η_r, ϕ and hence $[\eta]$ may be calculated.

Calculation of χ. Although originally proposed to account for energetic interactions in polymer solutions,

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χ is now generally regarded as a residual free energy function[12] but it is often used as an empirical parameter describing the thermodynamic quality of a solvent for a polymer. As such, it determines the conformation adopted by chains in solution due to interaction with solvent molecules and hence affects the viscosity.

Kok and Rudin[13–15] developed a model showing that the second virial coefficient could be calculated from

$$B=\frac{16\pi[\eta]}{M[15.44+4\pi c([\eta]-[\eta]_\theta]}\left(1-\frac{[\eta]}{[\eta]_\theta}\right) \quad (7)$$

where M is the polymer molecular weight and $[\eta]_\theta$ its intrinsic viscosity under θ conditions, calculated from

$$[\eta]_\theta=K_\theta M^{0.5} \quad (8)$$

In equation (8), $K_\theta = 72.03\ \mathrm{dm^3\,g^{-1}}$ for polystyrene[16]. The Flory interaction parameter can then be calculated from equation (1). Although this did not account for the variation of χ with solution concentration, it did account for dependence on molecular weight and agreement was found with literature results to within an average of 2.0%.

Tseng and Lloyd[17] employed an alternative approach for calculating χ from $[\eta]$. They showed that, by combining the Flory–Huggins lattice model of polymer solutions with the Fox–Flory treatment of solution viscosity[18], the interaction parameter was given by

$$\chi=0.5-\frac{V_1}{4.8\times10^{-3}M}\left(\frac{[\eta]^{1.66}}{[\eta]_\theta^{0.66}}-[\eta]\right) \quad (9)$$

where all the symbols have the same meaning as above and V_1 is the molar volume of the solvent. The constant terms refer to a temperature of 25°C. They also derived a similar equation using a modified viscosity treatment due to Kurata *et al.*[19] designed to take into account the non-Gaussian shape of the polymer chains in solution.

$$\chi=0.5-\frac{V_1}{4.8\times10^{-3}M}\times\left[\left(\frac{[\eta]^5}{[\eta]_\theta^{2.57}}\right)^{1/2.43}-\left(\frac{[\eta]^3}{[\eta]_\theta^{0.57}}\right)^{1/2.43}\right] \quad (10)$$

Experimental

The polystyrene used was a secondary standard (Aldrich Ltd) with a number average molecular weight of 145 000, viscosity average molecular weight of 245 000 and polydispersity of 2.1, measured by g.p.c. in toluene using polystyrene standards. Solutions were prepared to concentrations between 2 g dm^{-3} and 12 g dm^{-3}, filtered and their flow times measured together with that of the pure solvents using an Ubbelohde 'A' viscometer in a water bath thermostatically controlled at 25 ± 0.1°C. The only exception was cyclohexane which was used at 34°C to give a solution under θ conditions. The solvents, listed in *Table 1*, were reagent grade or better and were obtained from various suppliers. These were chosen to range from thermodynamically good to poor solvents for polystyrene.

Results and discussion

Single point measurement of $[\eta]$. Intrinsic viscosities were measured for the polystyrene sample in each of the solvents by the conventional extrapolation method. Some of the plots are shown in *Figure 1*, the others having been omitted for clarity. The values of $[\eta]$ are shown in *Table 1* along with those from the two 'single point' methods being considered here. The values from the Soloman–Ciuta equation were calculated using the experimental results for the lowest concentration studied and were in each case lower than the recommended maximum. To apply the Rudin method, we again used the lowest concentration values of c and η_r. The corresponding value for ϕ was calculated from equation (4) using a Newton–Raphson type iterative procedure with the experimental η_r; in each case only one real root of equation (4) in a reasonable range was found. This was then used in equation (5) with $\rho = 1.047\ \mathrm{g\,cm^{-3}}$ to calculate $[\eta]$.

Both of the methods give very good prediction of $[\eta]$, the average percentage differences from the extrapolated values being 1.3% for equation (4) and 1.1% for equations (5) and (6). This is within the experimental error introduced by the extrapolation of the concentration series results so that, for polystyrene, both 'single point' methods are suitable. Although not shown here, we also calculated $[\eta]$ by both methods using the most concentrated solution employed in the concentration series and, as might be expected given their derivations, the Rudin model gave better results. However, using the

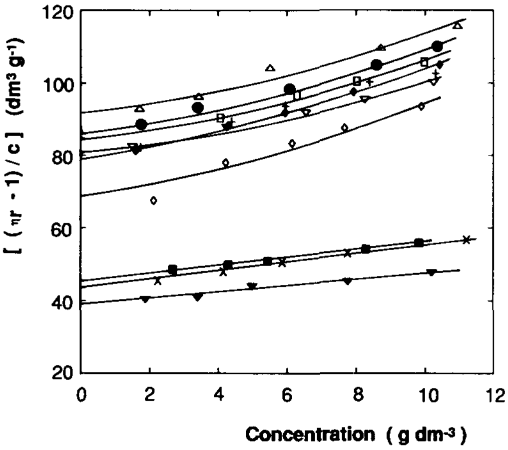

Figure 1 Calculation of intrinsic viscosity for polystyrene solutions: (△) benzene; (□) toluene; (●) tetrahydrofuran; (▽) ethyl benzene; (+) xylene; (◆) tetrachloromethane; (◇) dichloromethane; (■) 2-butanone; (×) ethyl acetate; (▼) cyclohexane

Table 1 Comparison of extrapolated with 'single point' intrinsic viscosity (dm^3 g^{-1}) values for polystyrene solutions at 25°C

Solvent	Extrapol. $[\eta]$	Soloman–Ciuta $[\eta]$	Soloman–Ciuta $\Delta/\%^a$	Rudin $[\eta]$	Rudin $\Delta/\%^a$
Toluene	85.8	85.8	0.0	86.9	1.3
Benzene	89.4	88.6	0.9	89.4	0.0
Cyclohexane[b]	39.1	39.4	0.8	39.5	0.1
o-Xylene	80.8	78.6	2.7	79.2	2.0
Ethyl benzene	80.2	79.3	1.1	79.9	0.4
Dichloromethane	69.1	70.8	2.5	71.9	4.0
Chloroform	85.6	84.6	1.2	85.3	0.4
Tetrachloromethane	78.8	79.0	1.0	78.6	0.3
Ethyl acetate	44.4	44.1	0.7	44.3	0.4
Butan-2-one	46.4	46.6	0.3	46.8	0.9
Tetrahydrofuran	87.0	84.5	2.9	85.3	2.0

[a] Percentage difference between the extrapolated and single point values of $[\eta]$

[b] At 34°C

Table 2 Comparison of interaction parameters for polystyrene solutions at 25°C

Solvent	Rudin	Lloyd 1[a]	Lloyd 2[b]	Lit.	Ref.
Toluene	0.435	0.448	0.417	0.44	3
Benzene	0.442	0.451	0.422	0.455	3
Cyclohexane[c]	0.495	0.500	0.500	0.50	3, 20
o-Xylene	0.434	0.450	0.423	0.41	20
Ethyl benzene	0.432	0.450	0.422	0.45	3
Dichloromethane	0.473	0.484	0.476	0.42	20
Chloroform	0.450	0.458	0.433	0.43	20
Tetrachloromethane	0.448	0.462	0.459	0.46	20
Ethyl acetate	0.488	0.497	0.496	0.49	3, 20
Butan-2-one	0.484	0.495	0.494	0.49	3
Tetrahydrofuran	0.449	0.459	0.434		

[a] Equation (9)
[b] Equation (10)
[c] At 34°C

more dilute solutions required for the Soloman–Ciuta method should not present any experimental difficulties and it is computationally more straightforward.

Calculation of χ. Since we had shown that $[\eta]$ could be accurately estimated from 'single point' methods, we were next interested in the accuracy with which χ could be calculated from these values of $[\eta]$. *Table 2* shows the values of χ employing the three equations described above, obtained using $[\eta]$ from the conventional, concentration series experiments.

There is a spread of results in the literature so that those quoted in *Table 2* can be taken only as a guide and comparisons with them must be treated with caution. However, all three equations give very similar results, with those from equation (9) (Lloyd 1) being closest to those found in the literature. Since our aim was to measure accurate χ values as rapidly as possible, it was of interest to determine the difference in χ obtained using the $[\eta]$ values from the 'single point' methods. Each of the interaction parameters in *Table 2* were recalculated using the three different values of $[\eta]$ from *Table 1*. In most cases, the difference in χ was only 0.001–0.002; in no case was it more than 0.004. Since this is well within the experimental error of the method, and considerably less than the spread of results in the literature, we feel that the use of 'single point' intrinsic viscosities to calculate interaction parameters in dilute polystyrene solutions is justified.

During the course of this work, we also examined other methods for deriving χ from $[\eta]$, such as that of Chee[21,22]. However, these require knowledge of the Mark–Houwink constants for equation (2) and these were not available for all of the solvents investigated. While these can be predicted, with a limited degree of success using group contribution methods[23], the procedure yields results no better than those described in this paper.

Conclusions

It has been shown that the 'single point' methods suggested by Soloman and Ciuta and by Rudin and co-workers for measuring intrinsic viscosities of dilute polymer solutions agree well with the conventional, concentration series method for polystyrene in a range of solvents. Also, these results can be used to calculate meaningful values of the Flory interaction parameters of these systems. Thus, even though the applicability of the 'single point' methods have to be established for each particular polymer system, it seems that they will hold for a range of solvents. One further parameter that needs further investigation is to check whether this is the case in solutions where very strong interactions such as hydrogen bonding take place.

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References

1 Price, G. J. and Smith, P. F. *Polym. Int.* 1991, **24**, 159
2 Bonner, D. C. *J. Macromol. Sci. Rev. Macromol. Chem.* 1975, **C13**, 263
3 Orwoll, R. A. *Rubber. Chem. Technol.* 1977, **50**, 451
4 Elliot, J. H., Horowitz, K. H. and Hoodock, T. *J. Appl. Polym. Sci.* 1970, **14**, 2947
5 Wirick, M. G. and Elliot, J. H. *J. Appl. Polym. Sci.* 1973, **17**, 2867
6 Nero, J. R. and Sikdar, S. K. *J. Appl. Polym. Sci.* 1982, **27**, 4687
7 Soloman, O. F. and Ciuta, I. Z. *J. Appl. Polym. Sci.* 1962, **6**, 683
8 Huggins, M. L. *J. Am. Chem. Soc.* 1942, **64**, 2716
9 Kraemer, E. O. *Ind. Eng. Chem.* 1938, **30**, 1200
10 Rudin, A. and Strathdee, G. B. *J. Paint. Technol.* 1974, **46**, 33
11 Rudin, A. and Wagner, R. A. *J. Appl. Polym. Sci.* 1975, **19**, 3361
12 Flory, P. J. *Disc. Farad. Soc.* 1970, **49**, 7
13 Kok, C. M. and Rudin, A. *J. Appl. Polym. Sci.* 1981, **26**, 3575
14 Kok, C. M. and Rudin, A. *J. Appl. Polym. Sci.* 1981, **26**, 3583
15 Kok, C. M. and Rudin, A. *J. Appl. Polym. Sci.* 1982, **27**, 353
16 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Wiley Interscience, New York, 1975
17 Tseng, H. S. and Lloyd, D. R. *Polymer* 1984, **25**, 671
18 Fox, T. G. and Flory, P. J. *J. Am. Chem. Soc.* 1951, **73**, 1904
19 Kurata, M., Stockmayer, W. H. and Riog, A. *J. Chem. Phys.* 1960, **33**, 151
20 Sheehan, C. J. and Bisio, A. L. *Rubber. Chem. Technol.* 1966, **39**, 149
21 Chee, K. K. *Polym. Commun.* 1986, **27**, 135
22 Chee, K. K. *Polymer* 1987, **28**, 977
23 Van Krevelen, D. 'Properties of Polymers', 3rd Edn, Elsevier, Amsterdam, 1991