Novel approach to Mark–Houwink–Sakurada constants and related parameters of polystyrene solutions

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Intrinsic viscosity data of a polystyrene sample in various good and poor solvents have been employed to estimate the Mark–Houwink–Sakurada constants by a novel expression. Two simple models are also proposed to deduce the values of the polymer–solvent interaction parameter and the solubility parameter of the polymer in agreement with those in the literature. It is shown empirically that the viscometric behaviour of polystyrene in its best solvent can be predicted. The merits of the present analysis are discussed.

(Keywords: polystyrene solutions; Mark–Houwink–Sakurada constants; polymer–solvent interaction parameter; solubility parameter of polymer; best solvent prediction)

INTRODUCTION

Dilute-solution viscometry serves as a convenient and effective tool for monitoring the molecular weight of linear polymers[1]. However, this particular approach involves the formidable task of calibrating the system. The present paper describes a simplified version of this classical practice. More importantly, it further explores a new route to other relevant physical constants of flexible polymers.

DEVELOPMENT OF METHOD

The intrinsic viscosity, hereafter designated as $[\eta]$, is accessible by measuring the relative viscosities of dilute polymer solutions[2]. It is related to the viscosity-average molecular weight, $\bar{M}_v$, by the Mark–Houwink–Sakurada (MHS) equation:

$$[\eta] = K\bar{M}_v^a \qquad (1)$$

where K and a are empirical constants. Equation (1) provides a simple means to compute an average molecular weight of polymers. However, the values of K and a can be obtained only by using well characterized polymer fractions[1]. In this connection, we have recently utilized whole polymer samples for the same purpose by invoking the following equation instead[3]:

$$\ln[\eta] + C = \ln K + a \ln \bar{M}_w \qquad (2)$$

where

$$C = -a \ln\left[1 - \left(\frac{1-a}{2}\right)\left(1 - \frac{\bar{M}_n}{\bar{M}_w}\right)\right]$$

with $\bar{M}_w$ and $\bar{M}_n$ being the weight- and number-average molecular weights, respectively.

In fact, the MHS constants are interrelated by[4]:

$$K = \frac{K_\theta M_0^{1/2-a}}{2(1-a)} \qquad (3)$$

where K_θ is the unperturbed parameter and M_0 is a characteristic molecular weight uniquely connecting the empirical and theoretical values of $[\eta]$. Combining equations (2) and (3) leads to

$$a = 1 - \left\{\left[1 - \left(\frac{1-a}{2}\right)\left(1 - \frac{\bar{M}_n}{\bar{M}_w}\right)\right]\tilde{M}\right\}^a \Big/ 2[\tilde{\eta}] \qquad (4)$$

where $\tilde{M}$ and $[\tilde{\eta}]$ are reduced parameters defined by

$$\tilde{M} = \bar{M}_w / M_0$$

$$[\tilde{\eta}] = [\eta]/[\eta]_{0\theta}$$

with

$$[\eta]_{0\theta} = K_\theta M_0^{1/2}$$

In the present study, the constant a is computed by an iteration algorithm using equation (4) as the recursion formula, and $a = \frac{1}{2}$ as the first approximation.

It has been proved that the polymer–solvent interaction parameter, χ, is a function of constant a (ref. 4), i.e.

$$\chi = \tfrac{1}{2} - Ax \qquad (5)$$

where

$$x = \bar{V}_1\left(\frac{2a-1}{1-a}\right)$$

$$A = \frac{1.59K_\theta}{C_1 v_2^2 M_0^{1/2}} \qquad (5a)$$

where $\bar{V}_1$, v_2 and C_1 being, respectively, the molar volume of the pure solvent, the specific volume of the polymer and a numerical constant evaluated theoretically as 1.55. An alternative expression for χ at temperature T is given by the solubility parameter theory[5] as:

$$\chi = \chi_s + \frac{\bar{V}_1}{RT}(\delta_1 - \delta_2)^2 \qquad (6)$$

where χ_s is due to the entropy contribution, R is the gas constant and δ_1 and δ_2 are the solubility parameters of solvent and polymer, respectively. Assuming that the χ_s

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term is negligible, equation (6) is classically treated by the linear least-squares method[6]. In this work, we resort to the more rigorous non-linear least-squares (NLLS) treatment outlined in the Appendix to derive the values of χ_s and δ_2.

By analogy with the swelling relationship for network rubbers, it has been suggested[7] that $[\eta]$ is a Gaussian function of δ_1, i.e.

$$[\eta]=[\eta]_m \exp[-\kappa \bar{V}_1(\delta_1-\delta_2)^2] \tag{7}$$

where $[\eta]_m$ is the maximum intrinsic viscosity and κ is an empirical constant. Combining equations (5)–(7) yields:

$$\ln[\eta]=\ln[\eta]_m-\kappa RT(\tfrac{1}{2}-\chi_s)+\kappa RTAx \tag{8}$$

Equation (8) indicates that a plot of $\ln[\eta]$ *versus* x would result in a straight line whose intercept and gradient supply the data for computing $[\eta]_m$.

RESULTS AND DISCUSSION

Streeter and Boyer[8] have determined the $[\eta]$ data of a polystyrene sample in various solvents at 25°C with the results exhibited in *Table 1*. For the polystyrene–chloroform mixture at 25°C, it has been discovered that $a=0.76$ and $K=7.16\times10^{-3}$ ml g^{-1} (ref. 9). Substituting these figures into equation (1) furnished $\bar{M}_v=4.0\times10^5$ for this particular sample whose $\bar{M}_w$ is 3.7×10^5. This allows us to assume $\bar{M}_w=\bar{M}_n$ for the present analysis, since the average molecular weight is basically independent of the constant a (ref. 10).

Previous investigation performed on the viscometric data of polystyrene has concluded that $K_\theta=0.083$ ml g^{-1} and $M_0=1.59\times10^5$. Details of these calculations are elaborated in ref. (4). On the basis of these findings, we acquired the values of a and K via equations (4) and (3) respectively. *Table 1* displays the results. The reliability of these computations is best tested by the ensuing exercises.

For polystyrene at 25°C, $\bar{v}_2=0.92$ ml g^{-1} (ref. 4), then equation (5a) renders $A=2.52\times10^{-4}$ mol ml^{-1}. The $\bar{V}_1$ data are collected in *Table 1*. We now proceed to compute the values of χ by equation (5). Clearly, these estimates are indeed consistent with the literature values, as demonstrated in *Table 1*.

The data for δ and χ tabulated in *Table 1* are fitted into equation (6) and processed by the NLLS algorithm (see Appendix) to obtain $\delta_2=18.4$ (J ml^{-1})$^{1/2}$ and $\chi_s=0.42$. Here a spectrum of solvents with δ_1 varying from 17 to 20 (J ml)$^{1/2}$ is studied. For polystyrene, Sosa *et al.*[14] have reported $\delta_2=18.6$ (J ml^{-1})$^{1/2}$ using a different technique. On the other hand, an average value of $\delta_2=18.1$ (J ml^{-1})$^{1/2}$ was cited by Sheehan and Bisio[11]. Again, our result is in good agreement with theirs. However, the standard error of the estimate of χ is found to be 0.08, reflecting the approximate nature of equation (6), as expected.

Figure 1 shows the plot of $\ln[\eta]$ *versus* x. The intercept and gradient of the least-squares regression line are found to be 3.99 and 4.0×10^{-3} mol ml^{-1} respectively, and the correlation coefficient is 0.9539, confirming the validity of equation (8) statistically. Consequently, we obtain $[\eta]_m=196.2$ ml g^{-1} based on the foregoing χ_s value. It

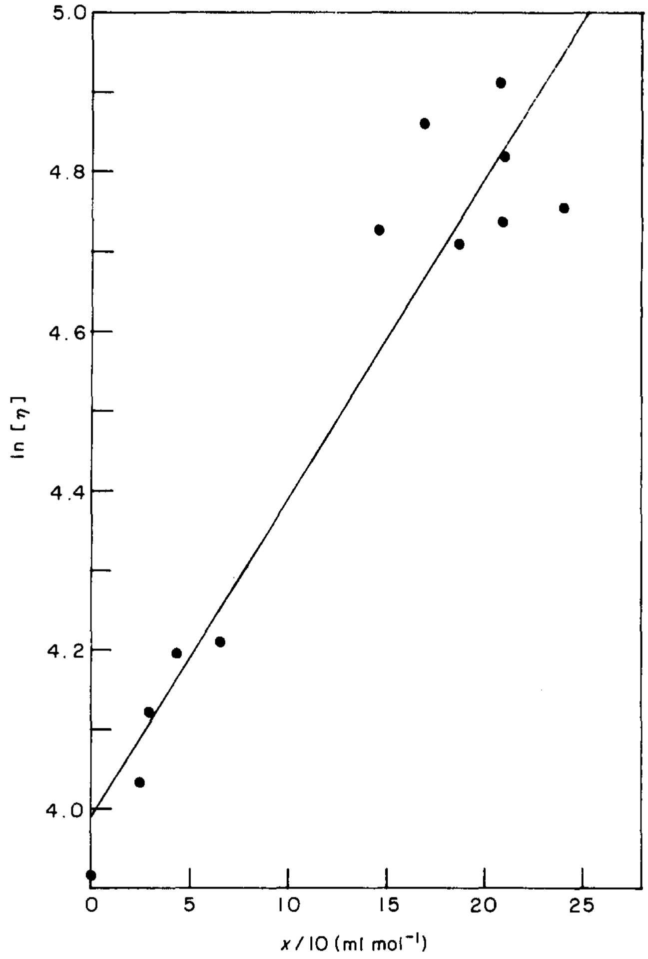

Figure 1 Plot of $\ln[\eta]$ *versus* x for polystyrene solutions at 25°C

Table 1 Values of viscometric parameters of a polystyrene in various solvents at 25°C

No.	Solvent	$[\eta]$ (ml g^{-1})	$\bar{V}_1$ (ml mol^{-1})	δ_1 (J ml^{-1})$^{1/2}$	a	$K\times10^3$ (ml g^{-1})	x (ml mol^{-1})	χ
1	Benzene	139	90	18.7	0.767	7.28	206.3	0.448 (0.446)^a
2	Chloroform	129	80	18.9	0.757	7.86	169.2	0.457
3	Toluene	124	106	18.2	0.749	8.38	210.3	0.448 (0.438)^a
4	Tetralin	116	136	19.5	0.735	9.39	241.2	0.439
5	Ethylbenzene	114	122	18.0	0.731	9.70	209.5	0.447 (0.450)^b
6	Dioxane	113	85	20.0	0.729	9.86	143.7	0.464
7	*o*-Dichlorobenzene	111	114	20.4	0.725	10.20	186.5	0.453
8	2-Heptanone	67.5	141	18.7^c	0.595	32.84	66.15	0.483
9	Butanone	66.3	98	18.6	0.589	34.76	42.44	0.489 (0.486)^b
10	Ethyl acetate	61.6	98	18.6	0.567	42.96	30.33	0.492 (0.491)^b
11	Decalin	56.4	155	18.0	0.538	56.98	25.50	0.494
12	Ethyl laurate	50.2	265	17.0^c	0.498	84.67	5.65×10^{-3}	0.500

^{a,b} Values in parentheses are literature data obtained from refs. 11 and 12 respectively
^{c} Estimated by the structural group addivity method proposed by Dunkel[13]

follows from equations (4) and (3) that the ultimate MHS constants attainable for polystyrene are $a=0.83$ and $K=4.70\times10^{-3}\,\mathrm{ml\,g^{-1}}$. The cube of the viscosity expansion factor, α, of a linear polymer is defined as:

$$\alpha^3=[\eta]/[\eta]_\theta \qquad (9)$$

where $[\eta]_\theta$ is the intrinsic viscosity under theta conditions. Accordingly, we forecast $\alpha=1.57$ when this particular polymer sample is subjected to an environment where the maximum excluded volume effect prevails. Although the prediction of constant a is slightly higher than 0.80, a figure generally accepted for flexible polymers in extremely good solvents[1], it is not unreasonable considering the remarkable effect of bulky pendant phenyl groups on the chain flexibility of polystyrene.

A distinctive merit of the present procedure, which may be readily extended to other systems, is its simplicity. This means that once the two characteristic parameters K_θ and M_0 are calibrated for a particular polymer[4], then the constants a and K for the polymer in any other solvents can be assessed directly. Practically, it implies that the lengthy listing of MHS constants for some polymer–solvent combinations[15] appears to be redundant. Moreover, it is inferred from equation (4) that the above MHS results are not very sensitive to the polydispersity ($=\bar{M}_w/\bar{M}_n$) of the polymer, particularly in good solvents. Hence, we have established a practical, dependable and rapid method for deriving a variety of important information about polymer solutions from simple viscosity measurements. Clearly, the method is limited to polymers whose unperturbed dimensions are solvent- and temperature-independent[1].

APPENDIX

The NLLS treatment of equation (6) defines a sum of squares of a difference:

$$S=\sum[(\chi-\chi_s)-B(\delta_1-\delta_2)^2]^2 \qquad (A1)$$

where

$$B=\bar{V}_1/RT \qquad (A2)$$

Here, the summation refers hereafter to a set of n data points. By setting $\partial S/\partial\chi_s=0$ and $\partial S/\partial\delta_2=0$, we obtain respectively:

$$\chi_s=\frac{-1}{n}\left(\sum B(\delta_1-\delta_2)^2-\sum\chi\right) \qquad (A3)$$

$$\sum\{B(\delta_1-\delta_2)[(\chi-\chi_s)-B(\delta_1-\delta_2)^2]\}=0 \qquad (A4)$$

Equation (A3) estimates the value of χ_s if δ_2 is predetermined by solving equation (A4). To this end, the Newton iteration method is applied to get:

$$\delta_2''=\delta_2'-\frac{f(\delta_2')}{f'(\delta_2')} \qquad (A5)$$

where δ_2' and δ_2'' are the two successive approximations of δ_2, the function f is given by the left-hand side of equation (A4), and

$$f'=\frac{\partial f}{\partial\delta_2}=\sum B\left[2(\delta_1-\delta_2)\left(B(\delta_1-\delta_2)-\frac{1}{n}\sum B(\delta_1-\delta_2)\right)\right.$$
$$\left.-[(\chi-\chi_s)-B(\delta_1-\delta_2)^2]\right] \qquad (A6)$$

The parameter χ_s appearing in f and f' is expressed in terms of δ_2 via equation (A3) in these calculations. Equation (A5) converges rapidly to a root of δ_2 if the first approximation of δ_2 is chosen as the δ_1 corresponding to the highest value of $[\eta]$ measured.

REFERENCES

1 Bohdanecky, M. and Kovar, J. 'Viscosity of Polymer Solutions', Elsevier, Amsterdam, 1982, Ch. 2

2 Chee, K. K. *J. Appl. Polym. Sci.* 1985, **30**, 2607

3 Chee, K. K. *J. Appl. Polym. Sci.* 1985, **30**, 1323

4 Chee, K. K. *Polymer* 1986, **27** (*Commun.*), 135

5 Hildebrand, J. H. and Scott, R. L. 'The Solubility of Nonelectrolytes', 3rd Edn., Reinhold, New York, 1950

6 Dudek, T. J. and Bueche, F. *J. Polym. Sci.* (*A-2*) 1964, 811

7 Barton, A. F. M. in 'Polymer Yearbook', 1st Edn., (Eds. H.-G. Elias and R. A. Pethrick), Harwood, London, 1984, p. 149

8 Streeter, D. J. and Boyer, R. F. *Ind. Eng. Chem.* 1951, **43**, 1790

9 Oth, J. and Desreux, V. *Bull. Soc. Chim. Belges* 1954, **63**, 285

10 Chee, K. K. *J. Appl. Polym. Sci.* 1985, **30**, 1359

11 Sheehan, C. J. and Bisio, A. L. *Rubber Chem. Technol.* 1966, **39**, 149

12 Orwoll, R. A. *Rubber Chem. Technol.* 1977, **50**, 451

13 van Krevelen, D. W. and Hoftyzer, P. J. 'Properties of Polymers', Elsevier, Amsterdam, 1976, Ch. 7

14 Sosa, J. M., Rubio, A. and Perez, B. J. in 'Structure–Solubility Relationships in Polymers', (Eds. F. W. Harris and R. B. Seymour), Academic Press, New York, 1977, p. 89

15 Kurata, M., Tsunashima, Y., Iwama, M. and Kamada, K. in 'Polymer Handbook', 2nd Edn., (Eds. J. Bandrup and E. H. Immergut), Wiley-Interscience, New York, 1975, pp. iv 1–60