Solution properties of polystyrene in cosolvent systems

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At 293 K, intrinsic viscosities $[\eta]$ have been measured for polystyrene samples of different relative molar mass M in mixtures of two poor solvents. These solvents were ethyl acetate and cyclohexane. Upon mixing these two poor solvents, thermodynamically better solvents could be obtained. The cosolvency was detected from the viscosity measurements. Several graphical procedures have been utilized for deriving the unperturbed dimensions of polystyrene expressed as K_θ (in the relation $[\eta]=K_\theta M^{1/2}\alpha^{1/3}$, where α is the expansion factor). It was found that the unperturbed polymer dimensions were not constant and differed from those measured in the single θ-solvent (*trans*-decalin) in which K_θ was found to be $81\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$.

(Keywords: solution properties; polystyrene; cosolvent systems; viscosity)

INTRODUCTION

In some previous communications[1-4] published by one of the authors of the present article, it was reported that the unperturbed dimensions of polystyrene were constant and independent on the type of solvent used. This finding was in contrast to other data published in this respect[5-10]. The effect of temperature has been satisfactorily[11,12] accounted for by changes with temperature of the short-range intermolecular interactions. However, it seems that solvent effects on the unperturbed dimensions are more difficult to interpret. The effect of both polymer–solvent and solvent–solvent (in a binary solvent mixture) interactions on the unperturbed dimensions has been studied by Dondos and Benoit[13].

The addition of a second liquid to a binary liquid polymer system to produce a ternary system is used widely for a variety of purposes. If the second liquid is a poor solvent, or a precipitant for the polymer, the dissolving potential of the liquid medium can be reduced and eventual phase separation may even occur. This does not necessarily take place in every event and sometimes mixtures of two relatively poor solvents can even produce an enhanced solvent power[14]. The mixed solvent is then said to exhibit a synergistic effect, which is manifested as a maximum in the limiting viscosity number $[\eta]$ curve when measured as a function of the mixed solvent composition[15]. Dondos and Patterson[16] have shown that the sign and magnitude of the solvent–solvent interaction parameter χ_{12} could be considered as a guide to possible cosolvency. Thus, for a mixture of two nonsolvents, when χ_{12} was relatively large and positive, they might act as cosolvents for the polymer. The mixture of two solvents was unlikely to dissolve the polymer when χ_{12} was negative.

The main aim of the present investigation was to study the effect of solvent on the unperturbed dimensions of polystyrene (PS) in a series of mixed solvents exhibiting a synergistic effect. This effect was tested for the system ethyl acetate/polystyrene/cyclohexane.

EXPERIMENTAL

Materials

Ethyl acetate (EA) and cyclohexane (CH) were dried over anhydrous $MgSO_4$ and distilled at atmospheric pressure. The solvent mixtures were prepared by mixing appropriate volumes of pure solvents.

Five PS samples were obtained from Polymer Laboratories, Church Stretton, Shropshire, England. The quoted relative molar masses M were 1.06×10^5, 2.94×10^5, 4.20×10^5, 6.40×10^5 and 9.60×10^5 for samples PS1, PS2, PS3, PS4 and PS5, respectively. The polydispersity indices $\bar{M}_w/\bar{M}_n$ for all the polymer samples under study were $\leqslant 1.09$.

Techniques

Details of the preparation of binary mixtures and polymer solutions as well as measurements of $[\eta]$ have been described elsewhere[17,18].

RESULTS AND DISCUSSION

Results

Table 1 shows the values of $[\eta]$ for samples PS1–PS5 in EA and in binary mixtures of EA/CH having compositions expressed in terms of the volume fraction ϕ_{CH} of CH at 293 K. The data obtained in pure *trans*-decalin are also included in this table.

Mark–Houwink plots according to the equation

$$[\eta]=K_m M^a \tag{1}$$

are not reproduced here, but the derived values of the constants K_m and a also are listed in *Table 1*. The variation

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of a with the composition of the mixed solvent expressed as ϕ_{CH} is illustrated in *Figure 1*.

The unperturbed dimensions are normally expressed in terms of $(\langle r^2\rangle_0/M)^{1/2}$, where $\langle r^2\rangle_0$ is the mean square end-to-end distance in the unperturbed state. Under θ-conditions, $K_m = K_\theta$ and, therefore,

$$K_\theta = \Phi_0(\langle r^2\rangle_0/M)^{3/2} \tag{2}$$

where Φ_0 is the Flory constant. In *trans*-decalin, the value of K_θ could be derived directly from the Mark–Houwink plot. In the other solvents, indirect methods were applied to derive K_θ. The full equations relevant to these methods are summarized in *Table 2* together with the corresponding references[19–23], and are designated as A, B, C, D and E. These procedures utilize various plots involving $[\eta]$ and M which allowed K_θ, for each solvent, to be derived from the intercept. The resultant values are summarized in *Table 3*.

Table 1 Intrinsic viscosities at 293 K for PS samples of different molar mass in EA/CH mixtures and in *trans*-decalin

Solvent[a]		$[\eta]$ ($dm^3\ kg^{-1}$)						
No.	ϕ_{CH}	PS1	PS2	PS3	PS4	PS5	$K_m \times 10^2$ ($dm^3 kg^{-1}$)	a
1	0.00	30.6	55.5	68.3	87.4	110.7	3.60	0.583
2	0.05	31.6	58.4	72.3	93.2	119.0	2.98	0.602
3	0.10	33.2	62.3	77.6	100.7	129.4	2.60	0.618
4	0.15	34.8	66.0	82.6	107.8	139.5	2.38	0.630
5	0.20	36.2	69.7	87.6	114.8	148.9	2.15	0.642
6	0.25	36.9	71.5	90.1	118.5	154.1	2.02	0.649
7	0.30	37.8	73.7	93.1	122.6	159.9	1.93	0.655
8	0.35	38.9	75.9	96.0	126.7	165.9	1.92	0.658
9	0.40	39.5	77.8	98.6	130.4	170.7	1.82	0.664
10	0.45	39.7	78.5	99.5	131.8	172.6	1.79	0.666
11	0.50	39.8	78.7	99.9	132.3	173.5	1.75	0.668
12	0.55	39.5	78.6	99.4	131.3	171.8	1.76	0.668
13	0.60	39.4	77.7	98.5	129.9	169.9	1.83	0.663
14	0.65	39.2	77.1	97.7	129.0	168.8	1.85	0.662
15	0.70	38.4	74.9	94.7	125.0	163.2	1.89	0.658
16	0.75	37.5	72.5	90.0	119.5	155.5	2.15	0.645
17	0.80	36.1	68.5	85.7	111.8	144.2	2.49	0.629
18	0.85	34.5	63.2	78.3	101.1	130.0	3.27	0.601
19	0.90	31.3	55.9	68.5	87.0	109.5	4.38	0.538
trans-decalin		26.4	43.9	52.5	64.8	79.4	8.10	0.500

[a] ϕ_{CH} is the volume fraction of CH

For molar masses of samples PS1–PS5, see 'Experimental' part

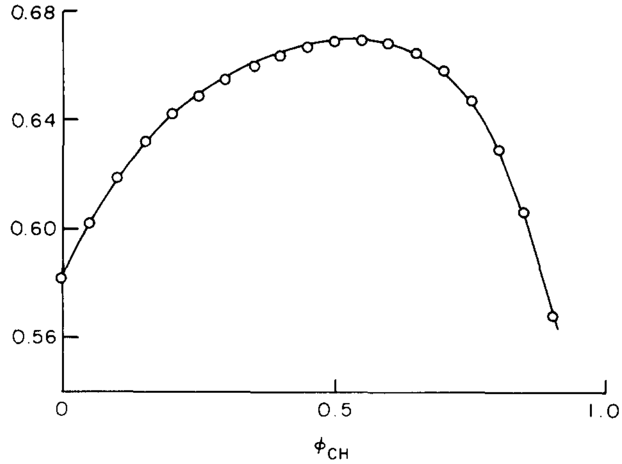

Figure 1 Dependence of a on the composition of the EA/CH binary mixtures expressed as volume fraction of CH, ϕ_{CH}, at 293 K

Table 2 Coordinates and intercept relating to extrapolation procedures used to determine K_θ

Procedure				
Designation	Ref.	Ordinate	Abscissa	Intercept on ordinate
A	19	$[\eta]M^{-1/2}$	$M^{1/2}$	K_θ
B	20	$[\eta]M^{-1/2}$	$M^{7/20}$	K_θ
C	21	$[\eta]M^{-1/2}$	$M^{7/20}$	$(\Phi_\varepsilon/\Phi_0)K_\theta$
D	22	$[\eta]M^{-1/2}$	$M^{1/2}-\tilde{D}M$	K_θ
E	23	$\log[2K_m(1-a)]$	$a-\frac{1}{2}$	$\log K_\theta$

Table 3 Values of 10^3K_θ (in $dm^3\ kg^{-1}$) derived from different extrapolation procedures for PS in different mixed solvents 1–19 and in *trans*-decalin

Solvent No.[a]	Method					
	A	B	C	D	E	F
1	86	78	91	85	80	74
2	86	77	92	84	80	73
3	89	77	95	86	80	73
4	91	77	97	87	80	71
5	93	77	100	88	80	74
6	94	77	100	88	80	74
7	95	77	101	89	80	75
8	97	78	103	90	80	77
9	98	77	103	90	80	77
10	98	77	103	89	80	76
11	98	77	103	89	80	76
12	98	77	104	92	80	76
13	98	78	104	94	80	76
14	98	77	103	91	80	76
15	96	77	102	89	80	76
16	96	79	102	90	80	76
17	95	81	102	91	80	77
18	94	84	100	92	80	80
19	90	83	94	89	80	80
trans-decalin	81	81	81	81	80	81

[a] For composition of solvents, see *Table 1*

It is to be noted that procedure E differs from the others in the respect that its plot invokes values of K_m and a for each of the solvents used. Consequently, only one value of K_θ is yielded. In this procedure, the simplified form of the original equation suggested by Abdel-Azim and Huglin[3] was used.

Another method F not involving extrapolation was employed as well. This method is considered as a semiempirical interpretation of equation (1). In this method, Munk and Halbrook[24] proposed the following equation:

$$K_\theta = Q^{3/(4-2a)} \tag{3}$$

where

$$Q = (K_m)(\Phi_0^{(1-2a)/3})(N_0^{1/2}M/L)^{2a-1} \tag{4}$$

In (4), (M/L) is the molar mass of polymer per unit length of chain, which was calculated by Munk and Halbrook[24] to be $4.14 \times 10^9\ g\ mol^{-1}\ cm^{-1}$ for PS. These authors postulated that there is no thermodynamic interaction among polymer segments within a short section of a chain with characteristic number of segments N_0. The value of N_0 was estimated[24] to be ~ 9. Invoking $\Phi_0 = 2.87 \times 10^{23}\ mol^{-1}$, K_θ could be evaluated separately for each solvent from (4). A random variation between $71\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$ and $80\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$ was obtained, leading to an average value of $76\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$. This method is omitted from *Table 2* since an extrapolation technique to give the required intercept is not involved. Equation (3) was previously modified[3] in the form

$$\log Q=[(4-2a)/3)]\log K_\theta \qquad (5)$$

Hence, the plot of $\log Q$ *versus* $(4-2a)/3$ should be linear, passing through the origin and having a slope of $\log K_\theta$. The actual plot (not reproduced here) displayed some scatter and the value of K_θ derived via least-squares analysis was $76\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$, exactly the same as that of the average of the individual values calculated for each solvent.

Discussion

In *Figure 1*, the tabulated values of exponent a are plotted as a function of the composition of the solvent. It is clear that a maximum is obtained at ϕ_{CH} between 0.5 and 0.55. This maximum was to be expected at ϕ_{CH} of 0.5 if the two solvents were of the same power. The slight shift from 0.5 seems to be due to the poverty of CH with respect to EA. Moreover, the obtained maximum illustrates clearly the synergistic effect. These findings are in good accord with the results obtained by Munk *et al.*[15] for the same system.

The θ-temperature of PS in *trans*-decalin was determined experimentally by using the method of Cornet and Van Ballegooijen[25] and was found to be 293 K. This temperature seems to agree well with that previously found by Fukuda *et al.*[26] and Munk *et al.*[15]. Bazuaye and Huglin[12] and Inagaki *et al.*[27] have afforded higher values for the θ-temperature, 295.4 and 296.4 K respectively.

The plots obtained by the different methods given in *Table 2* afforded good linearity in general (*Figures 2–4*). Some of these plots were selected in view of the fact that they exhibited a behaviour widely different from that previously obtained under other conditions[3]. For instance, in the Stockmayer–Fixman plot (method A), the downward deviation from linearity could be interpreted as being a result of solvent power. This deviation occurred at the highest M, but only for $a\geqslant0.7$. However, in the present system, the maximum power of the solvent mixture afforded $a=0.58$ and consequently this deviation, as expected, disappeared. Similarly, by applying method D on the same previous system[3], an upward deviation was observed at the highest M. This could be attributed[3] to an excessive reduction of $M^{1/2}$ by the factor $\tilde{D}M$ when the exponent a within $\tilde{D}$ was greater than 0.80. In the present system, a did not exceed 0.80 and hence the factor $\tilde{D}$ was not excessively large, so that perfect linearity could be obtained.

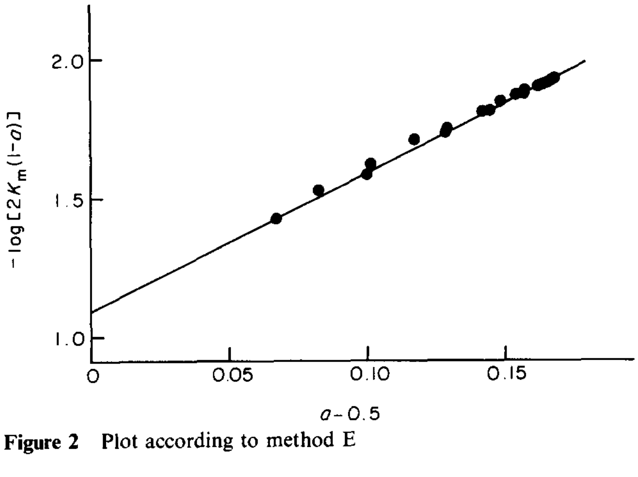

Figure 2 Plot according to method E

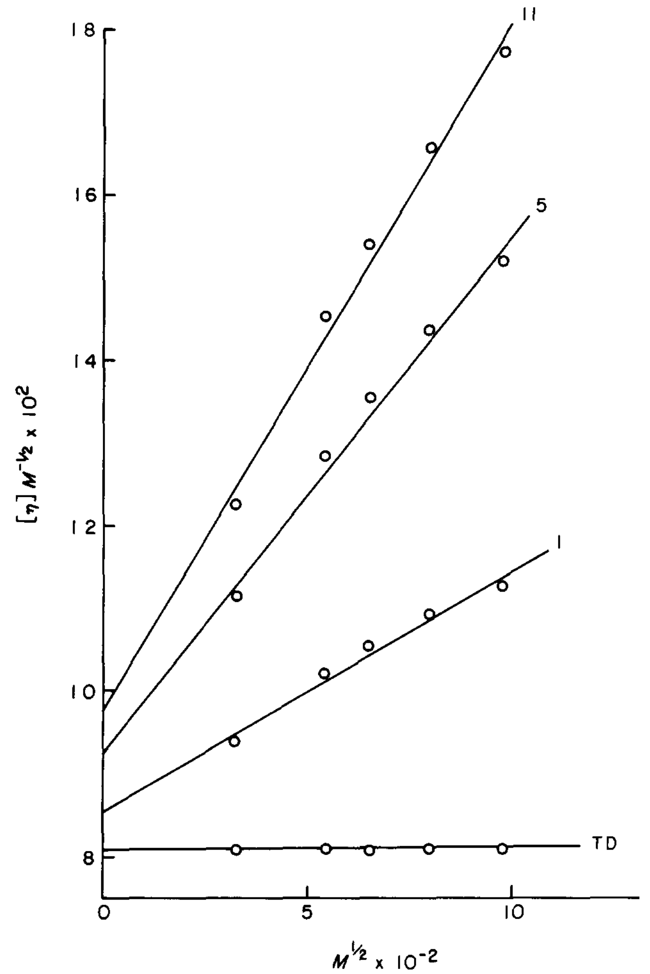

Figure 3 Stockmayer–Fixman plots (method A) for PS in *trans*-decalin (TD) and in mixed solvents 1, 5 and 11 (for compositions of mixed solvents, see *Table 1*)

Although the actual plots involved in methods B and C are identical (cf. *Table 2*), the difference in the values of K_θ in *Table 3* appears to be due solely to the application of the correction factor Φ_ε/Φ_0 to the intercepts obtained from method B.

The data of K_m and a, derived from measurements in all the solvent media, are embodied in a single plot (*Figure 2*), upon applying method E. This single plot gives good linearity. The obtained K_θ, $80\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$, shown in *Table 3*, agrees well with the value obtained in *trans*-decalin (single θ-solvent) which was found to be $81\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$.

In the method of Munk and Halbrook K_m and a values were also utilized but the value of K_θ obtained by applying this method (method F) was $76\times10^{-3}\,\mathrm{dm^3\,kg^{-1}}$ as mentioned above. This value is somewhat lower than that obtained in *trans*-decalin, which could be attributed to the uncertainty in N_0, Φ_0 and M/L.

CONCLUSIONS

From the study of the present system EA/PS/CH and previous ones[3,4], we can conclude that method E seems to

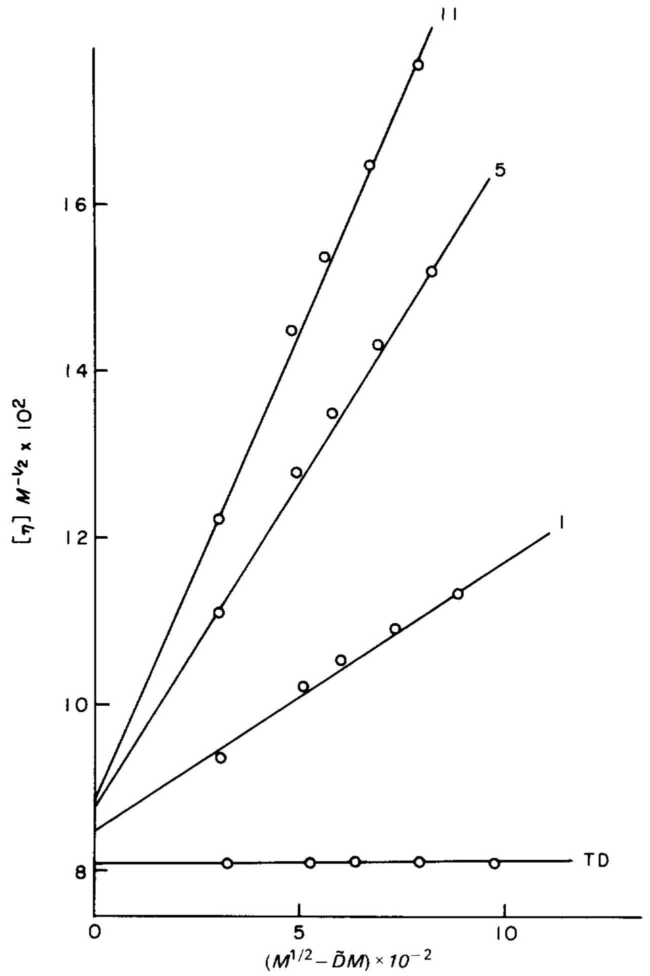

Figure 4 Plots according to method D for PS in *trans*-decalin (TD) and in mixed solvents 1, 5 and 11 (designation of solvents as in *Figure 3*)

be very reliable when several liquids of widely different solvent powers are available. If it is desired to use only one solvent, none of the considered methods would produce a constant value of K_θ, in contrast to the previous systems[3,4].

However, in view of the constancy of K_θ (and hence the unperturbed dimensions) at the particular temperature, namely 293 K in the present study, it appears that the unperturbed dimensions of polystyrene differ according to the binary solvent composition.

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