polymer communications

Lattice coordination number in polystyrene solutions

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Intrinsic viscosities of five polystyrene samples of molar masses *ca.* 10^5–10^6 have been measured at 34.5°C in cyclohexane (θ-solvent), 1,2,3,4-tetrahydronaphthalene (good solvent) and in binary mixtures of these two liquids. Experimental values of α^5–α^3 (where α is the expansion factor) were compared with values calculated on the basis of two theories which assume the lattice coordination number Z to be infinite and finite respectively. $Z=\infty$ greatly overestimates α^5–α^3, whilst good accord is obtained if $Z=3$ or 4 according to molar mass and solvent power.

Keywords Polystyrene; cyclohexane; 1,2,3,4-tetrahydronaphthalene; lattice coordination number; intrinsic viscosity; interaction parameter

Introduction

At 34.5°C, cyclohexane (CH, subscript 3) is a θ-solvent for polystyrene (PS, subscript 2), whereas 1,2,3,4-tetrahydronaphthalene (TET, subscript 1) is a thermodynamically good solvent for the polymer[1]. Hence, by altering the composition of the TET/CH binary mixtures, it is possible to effect changes in overall solvent power at constant temperature. The solvent power is expressed as the excluded parameter $\alpha^5 - \alpha^3$ in which α is the viscometric expansion factor given by equation (1).

$$\alpha = ([\eta]/[\eta]_\theta)^{1/3} \qquad (1)$$

In equation (1), $[\eta]$ is the intrinsic viscosity of the sample in the particular solvent and $[\eta]_\theta$ is the corresponding value in CH, both quantities relating to 34.5°C.

Hydrodynamic and other aspects of these systems are being investigated currently. Here we wish to utilize certain of the findings, which have a direct bearing on two existing theories of polymers in binary solvents, and thereby assess their validity experimentally.

Experimental Part

Materials. Five PS samples of nominal polydispersity indices $\bar{M}_w/\bar{M}_n \leqslant 1.09$ were obtained from Polymer Laboratories Ltd., Church Stretton, Shropshire, UK. They are designated here as PS1, PS2, PS3, PS4 and PS5, the quoted molar masses M being 1.06×10^5, 2.94×10^5, 4.20×10^5, 6.40×10^5 and 9.60×10^5 g mol^{-1} respectively. Solvents were dried over sodium wire and distilled at atmospheric pressure.

Techniques. Densities of TET, CH and five TET/CH mixtures as well as the intrinsic viscosities of the PS samples in these media were measured according to procedures described previously[1-3] for similar systems.

Theory

The Flory–Fox theory[4] relates α^5–α^3 in a single solvent to the corresponding polymer–solvent interaction parameter χ:

$$\alpha^5 - \alpha^3 = 2C_m M^{\frac{1}{2}}(\tfrac{1}{2} - \chi) \qquad (2)$$

$$C_m = [27/(2^{5/2}\pi^{3/2} N_A)][(\bar{v}_2^2/V)(\Phi_0/K_\theta)] \qquad (3)$$

Here, N_A is the Avogadro number and Φ_0 is the Flory viscosity constant; $\bar{v}_2$ is the partial specific volume of the polymer in solution and V is the molar volume of the solvent; K_θ is the viscosity constant in the relationship $[\eta] = K_\theta M^{\frac{1}{2}} \alpha^3$.

In a binary solvent, interactions among the components can influence $[\eta]$ and hence $\alpha^5 - \alpha^3$. However, on the assumption of an infinite lattice coordination number Z, Shultz and Flory[5] proposed that equation (2) should still remain valid, provided that the factor $(\tfrac{1}{2} - \chi)$ within it is replaced by an effective thermodynamic factor $Y_{(\phi)}$. The exact form of $Y_{(\phi)}$ is not reproduced here, where it suffices to state that it comprises the volume fractions of solvents φ_1 and φ_3, the polymer–solvent interaction parameters χ_{12} and χ_{23} the solvent–solvent interaction parameter χ_{13} and the ratio V_1/V_3 of the molar volumes of the solvents. Hence, at any particular solvent composition, the Shultz–Flory treatment enables $\alpha^5 - \alpha^3$ to be obtained from the amended form of equation (2) by using C_m in conjunction with the calculated $Y_{(\phi)}$.

In contrast, Patterson and co-workers[6] replaced the factor $(\tfrac{1}{2} - \chi)$ in equation (1) by an effective thermodynamic factor $Y_{(x)}$, viz:

$$\alpha^5 - \alpha^3 = 2C_m M^{\frac{1}{2}} Y_{(x)} \qquad (4)$$

$Y_{(x)}$ differs from $Y_{(\phi)}$ in the respects that (a) solvent composition is expressed in terms of mole fractions x_1 and x_3, (b) V_1/V_3 is taken to be unity and, most importantly (c) Z is taken to be finite. In connection with (c) the interaction parameters (now distinguished by an asterisk) become

$$\chi_{12}^* = [\chi_{12} - (1/Z)][Z/(Z-2)]^2 \qquad (5)$$

$$\chi_{23}^* = [\chi_{23} - (1/Z)][Z/(Z-2)]^2 \qquad (6)$$

However, solvent–solvent interaction is uninfluenced by the polymer lattice coordination number and therefore

$$\chi_{13}^* = \chi_{13} \qquad (7)$$

The expression for $Y_{(x)}$ is as follows

$$Y_{(x)} = [(Z-2)/Z]^2[(Z-2)^{-1} +$$

$$(1-2)x_1\chi_{12}^* - 2x_3\chi_{23}^* + Dx_1x_3)/$$

$$(1-2x_1x_3\chi_{13}^*)] \qquad (8)$$

where

$$D = 2(\chi_{12}^*\chi_{13}^* + \chi_{13}^*\chi_{23}^* + \chi_{12}^*\chi_{23}^*)[(\chi_{12}^*)^2 + (\chi_{23}^*)^2 + (\chi_{13}^*)^2]$$

Hence, at any particular solvent composition, the treatment of Patterson and co-workers enables $\alpha^5 - \alpha^3$ to be obtained from equation (4) *via* equations (5)–(8) and, as is evident from equations (5), (6) and (8), the resultant value is dependent on the value selected for Z.

Results and Discussion

Parameters required for calculations. To evaluate C_m from equation (3) the requisite quantities were as follows: Literature data[7] on amorphous PS were interpolated to give $\bar{v}_2 = 0.9387$ cm^3 g^{-1}. Molar volumes V of mixed solvents were obtained from equation (9) using experimental values of $V_1 = 137.9$ cm^3 mol^{-1} and $V_3 = 110.3$ cm^3 mol^{-1}

$$V = x_1V_1 + x_3V_3 \qquad (9)$$

A value of $K_\theta = 85 \times 10^{-3}$ cm^3 g$^{-3/2}$ mol$^{\frac{1}{2}}$ was used throughout, since the independence of K_θ on solvent composition has been established[8]. The value of $\Phi_0 = 2.5 \times 10^{23}$ mol^{-1} has recently been asserted to be definitive[9] and was adopted here. The resultant values of C_m ranged between 3.22×10^{-2} g$^{-\frac{1}{2}}$ mol$^{\frac{1}{2}}$ (at $x_1 = 0.082$) and 2.76×10^{-2} g$^{-\frac{1}{2}}$ mol$^{\frac{1}{2}}$ (at $x_1 = 0.762$). Details of the determination of the interaction parameters are to be published[8]; the relevant values are $\chi_{12} = 0.41$, $\chi_{23} = 0.50$ and for χ_{13}, values varying between 0.52 at $x_1 = 0$ and 0.24 at $x_1 = 1$.

Comparison of theories. For each PS sample the experimental values of $\alpha^5 - \alpha^3$ increased smoothly with content of the good solvent, i.e. with increasing x_1. This is illustrated for samples PS1 and PS5 in *Figures 1* and 2 respectively, which also show the calculated values of $\alpha^5 - \alpha^3$. On the basis of $Z = \infty$ the Shultz–Flory theory clearly overestimates the chain expansion and also indicates a region of maximum solvent power, which is absent in practice. Implementation of the treatment of
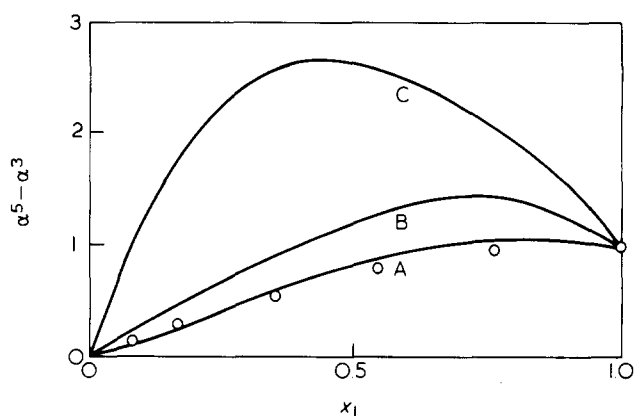

Figure 1 Experimental values (open circles) of α^5-α^3 as a function of solvent composition for sample PS1. Curves calculated on the basis of (A) Z = 3, (B) Z = 4 and (C) Z = ∞
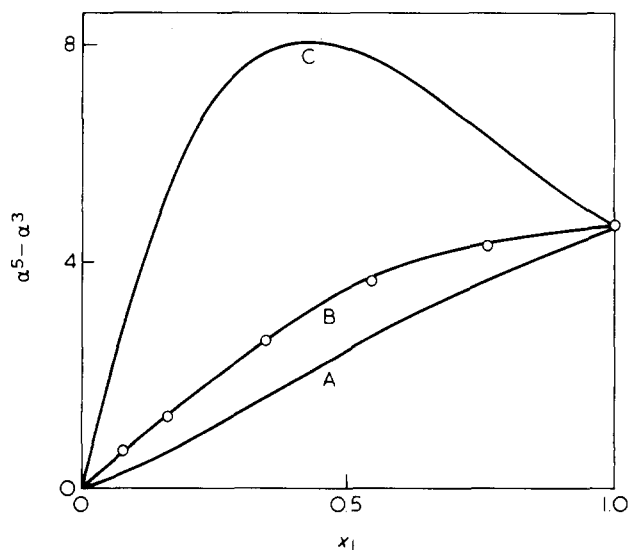

Figure 2 Experimental values (open circles) of α^5-α^3 as a function of solvent composition for sample PS5. Curves calculated on the basis of (A) Z = 3, (B) Z = 4 and (C) Z = ∞

Patterson *et al.* [equation (4)] has been made by assigning small finite values to Z. Good agreement with experiment is apparent for the sample of lowest molar mass, PS1, when $Z = 3$ (*Figure 1*). However, the sample of highest molar mass, PS5, requires that Z be assigned a value of 4 for good accord with experiment.

For samples PS2, PS3 and PS4 also, the use of $Z = \infty$ considerably overestimates the excluded volume factor. Application of the theory of Patterson *et al.* to these systems is shown in *Figure 3*. It is seen that for PS4 a value of $Z = 4$ affords a good fit over the whole range of solvent composition. The accord with experiment is not perfect for samples PS2 and PS3. For each of these samples there is perfect agreement at high x_1 when Z is assigned a value of 3 and also at low x_1 when $Z = 4$.

All calculated values of $\alpha^5 - \alpha^3$ are dependent on Φ_0. Although the samples were reasonably monodisperse, we have corrected Φ_0 for polydispersity by the method of Bareiss[9]. However, the resultant changes in $\alpha^5 - \alpha^3$ were small enough to be discounted.

The present results support other findings[2,6,10,11] regarding the necessity to describe the behaviour of a polymer in single and binary solvents in terms of a small, finite lattice coordination number. Specifically, it appears
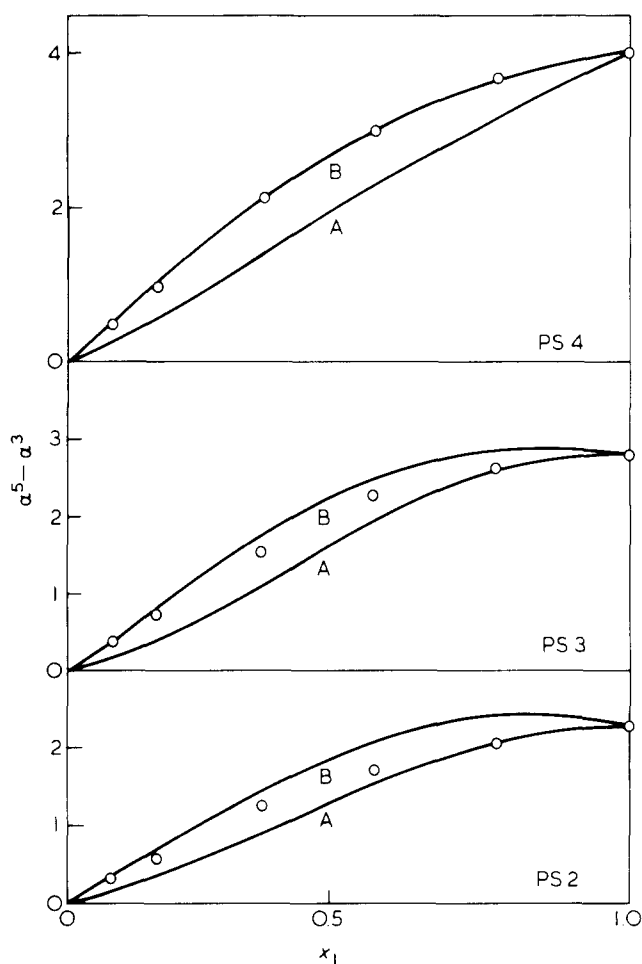
Figure 3 Experimental values (open circles) of α^5-α^3 as a function of solvent composition for samples PS2, PS3 and PS4. For each sample, curves calculated on the basis of (A) $Z = 3$ and (B) $Z = 4$

that the smaller the molar mass of polymer the lower is Z. Of the possible reasons for a small Z it has been concluded elsewhere[6] that the most feasible is the effect of back-coiling[12], viz. the probability of a segment making contact with another segment is greater than that obtaining on the assumption of random mixing. Back-coiling requires that the low value of Z be associated with the polymer itself and consequently the particular value of Z should hold at all solvent compositions. Whilst this is so for PS1, PS4 and PS5, slight deviations have been noted for the other two samples, which indicate different values of Z according to the content of TET in the binary solvent. However, since it is the region of good solvent power (and high chain expansion) which demands the lower value of Z, this is also compatible with a back-coiling effect.

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