the latter being nearly independent of molecular weight.

Clearly, the molecular weight is not an important factor in this range of M. We have to consider that the adsorbing power of a D-PS segment onto silica gel is slightly higher than that of an H segment. This suggests an intrinsic energetic difference between deuterium and proton, although we are unable to explain why it is so. This point should be confirmed by experiments for other polymers as well as low-molecular-weight compounds.

In summary, the TLC experiments of both the types have shown that isotopically different PS's are not identical thermodynamically. In practice, the differences between them may not be large enough to urge any modification for the interpretation of neutron scattering experiments[5] but are still large enough for one polymer to be isolated almost perfectly from the other. For separation purposes, adsorption TLC may be especially suitable since it is independent of molecular weight. We have recently constructed a rotating-disk-type TLC apparatus, in which a centrifugal field is employed to shorten the developing time, for the purpose of polymer fractionation on a semipreparative scale.[12] In a preliminary experiment with this apparatus, approximately 100 mg of a mixture of D- and H-PS's was nearly completely separated into the pure components within an hour when the same developer as used in the adsorption TLC experiments reported above was used.

Acknowledgment. We thank Professor G. Allen and Dr. A. Maconnachie of Imperial College, London, for kindly offering the deuterated polystyrene D-16.

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Linear Relation between Preferential Solvation and Intrinsic Viscosity of a Polymer in a Binary Solvent Mixture

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Received June 5, 1979

In previous papers[1-3] we proposed a relation between the coefficient of preferential solvation of a linear polymer and the segment density existing in the interior of the polymer coil. In this note we exhibit a linear relation between the coefficient of preferential solvation λ' and the segment density of samples dissolved in a solvent mixture of a given composition for the entire domain of molecular weights. Moreover, a better correlation of experimental results is achieved with a plot covering not only the entire domain of molecular weights but also the entire domain of compositions of the solvent mixture.

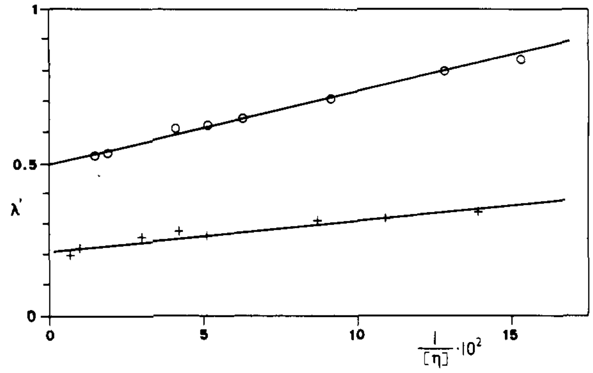

Figure 1. Application of eq 4 to linear PS samples in the mixture CCl_4 (solvent 1)/methanol (solvent 2): (+) $u_2 = 0.10$; (○) $u_2 = 0.21$.

A unique curve was obtained with linear and branched samples, even for the entire domain of compositions of the solvent mixture, plotting λ' as a function of a difference of segment density.[4-6] However, this relation was relatively complicated and knowledge of the intrinsic viscosity of each sample in a pure solvent of reference was necessary. The experimental results in this note, obtained by the light scattering technique, are taken mainly from our preceding papers. The method of treatment of these results is new.

Here the composition of the solvent mixture will be always expressed by the volume percentage of the second solvent (u_2) and the coefficient of preferential solvation λ' will be expressed, as in our preceding papers,[1,2] by the relation $\lambda' = (x_1/M)\bar{V}_1$, where x_1 is the number of molecules of solvent 1 absorbed in excess per macromolecular chain, M is the molecular weight of the chain, and $\bar{V}_1$ is the partial molar volume of solvent 1. The intrinsic viscosity will be expressed in cm^3/g.

Starting from the idea that the mean coefficient of preferential solvation λ' of a macromolecular chain is the normalized sum of the coefficients of each monomer unit and that the distribution of the monomers in the interior of the coil is Gaussian, we obtained[1,2]

$$\lambda' = \lambda'_\infty + a\left(\frac{3}{4\pi}\right)^{3/2}\left(\frac{N}{\langle R^2\rangle^{3/2}}\right) \qquad (1)$$

and knowing that $\langle R^2\rangle = b^2N\alpha^2$, we have

$$\lambda' = \lambda'_\infty + a\left(\frac{3}{4\pi b^2}\right)^{3/2}\left(\frac{1}{N^{1/2}\alpha^3}\right) \qquad (2)$$

In the above relations, λ'_∞ represents the value of the preferential solvation coefficient for an infinite chain, N the number of monomer units of the chain, b the length of monomer unit, R the radius of gyration, α the expansion coefficient, and a a constant.

Since it was known that N is proportional to the molecular weight M of the chain, relation 2 was fitted[1-3,7,8] to the experimental results, plotting $\lambda' M^{1/2}$ against $M^{1/2}$. This application is most nearly correct near the Θ point, where we have $\alpha \simeq 1$. If now we plot λ' as a function of $M^{-1/2}$, we observe that the points obtained with the samples of low molecular weight ($M < 15000$) do not fit on the

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straight line obtained with the samples of higher molecular weight, even at Θ conditions.[7] The deviation begins generally at the same molecular weight where we also observe a lowering of the Θ point. It is again in the same domain of molecular weights in which we obtained[9] a deviation of the points when $[\eta]M^{-1/2}$ [9] was plotted.[10] The unique explanation that we could give for the nonlinear relation between $\lambda' M^{1/2}$ and $M^{1/2}$ in the domain of low molecular weights is that in this domain we have a variation of the coefficient α with the molecular weight even when we are at Θ conditions.[9]

In order to avoid the coefficient α, the determination of which is very difficult for the low molecular weight samples, we propose to use the intrinsic viscosity, instead of $N^{1/2}\alpha^3$, in eq 2. For this we use the well-known Flory–Fox equation

$$[\eta] = K_\Theta M^{1/2}\alpha^3 \tag{3}$$

Thus eq 2 becomes

$$\lambda' = \lambda'_\infty + a\left(\frac{3}{4\pi b^2}\right)^{3/2}\left(\frac{K_\Theta m^{1/2}}{[\eta]}\right)$$

and knowing that $(K_\Theta/\phi_0)^{2/3} = A^2 = b^2/m$, we finally obtain

$$\lambda' = \lambda'_\infty + a\left(\frac{3}{4\pi}\right)^{3/2}\left(\frac{\phi_0}{m[\eta]}\right) \tag{4}$$

In the above relations m is the molecular weight of a monomer unit and ϕ_0 is the Flory constant. It is obvious that $\phi_0/[\eta]$ represents the average segment density in the coil, $M/\langle R^2\rangle^{3/2}$, because we have the equation

$$[\eta] = 6^{3/2}\phi_0\langle R^2\rangle^{3/2}/M$$

In Figure 1 we plot the experimental results obtained with the PS/CCl_4/methanol system according to eq 4. When the solvent mixture contains 21% methanol (u_2 = 0.21) the polymer is at Θ conditions. As we can see in Figure 1 we obtain good straight lines for the entire domain of molecular weights. On the contrary, for the same system we do not obtain straight lines for the entire domain of molecular weights when λ' is plotted as a function of $1/M^{1/2}$ according to eq 2. A deviation for low molecular weight samples is also obtained when plotting λ' as a function of $1/M^{1/2}$ in the PS/benzene/methanol system containing 22% methanol.[7] The extrapolation to $[\eta] = \infty$ in Figure 1 gives the same value for λ'_∞ as that obtained when $\lambda' M^{1/2}$ is plotted as a function of $M^{1/2}$.[1]

In the following we give a graphical representation of the relation between λ' and $1/[\eta]$ of a polymer/solvent 1/solvent 2 ternary system for the entire domain of solvent composition and the entire domain of molecular weights. For this, the λ' value of each polymer sample dissolved in a mixture of two solvents is plotted vs. $(1/[\eta]) + ku_2$, where u_2 is the volume fraction of the solvent 2 and k is an arbitrary constant. Two examples of such plots are shown in Figures 2 and 3.

The straight lines a, b, c, ... represent the variation of λ' as a function of $1/[\eta]$ according to eq 4 for different compositions of the solvent mixture. The curves 1, 2, 3, ... give the variation of λ' as a function of the solvent composition for each sample of the polymer of a given molecular weight. The 0 curve shows the variation of λ'_∞ with the solvent composition and is obtained by extrapolation of straight lines a, b, c, ... to $1/[\eta]$ = zero.

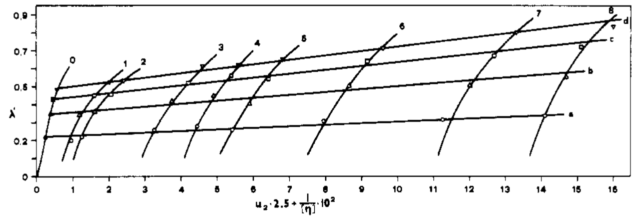

Figure 2. Double correlation of λ' as a function of volume fraction of solvent 2 and of the inverse of intrinsic viscosity, for linear PS samples in the solvent mixture CCl_4 (solvent 1)/methanol (solvent 2): a, u_2 = 0.10; b, u_2 = 0.15; c, u_2 = 0.185; d, u_2 = 0.21. M_w: (1) 700 000; (2) 400 000; (3) 76 000; (4) 47 500; (5) 32 500; (6) 16 000; (7) 8000; (8) 4800. The 0 curve corresponds to infinite molecular weight.

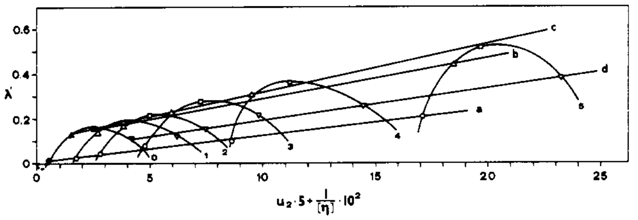

Figure 3. Double correlation of λ' as a function of u_2 and $1/[\eta]$ for PS samples in the solvent mixture benzene (solvent 1)/cyclohexane (solvent 2): a, u_2 = 0.10; b, u_2 = 0.30; c, u_2 = 0.50; d, u_2 = 0.85. M_w: (1) 260 000; (2) 104 000; (3) 40 000; (4) 14 000; (5) 3500. The 0 curve corresponds to infinite molecular weight.

The 0 curve in Figure 3 gives the variation of values of λ'_∞ of PS for the entire composition of the solvent mixture and these values are about the same as the values obtained according to eq 2[11] ($\lambda' M^{1/2}\alpha^3$ as a function of $M^{1/2}\alpha^3$).

In conclusion, we have found a linear relation between the coefficient of preferential solvation of a polymer dissolved in a solvent mixture and the intrinsic viscosity determined in the same solvent mixture, and we propose a plot giving a relation between λ' and $1/[\eta]$ for the entire domain of compositions of the solvent mixture.

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