statistical segments use the following form for the chromophore pair correlation function of an ideal chain:[3]

$$g(\vec{r}) = \frac{N}{\bar{N}(\bar{N}-1)} \sum_{\substack{i=1\\ i\neq j}}^{\bar{N}} \sum_{j=1}^{\bar{N}} P_{ij}(\vec{r}) \qquad \text{(B1)}$$

In this expression N is the number of chromophores on the chain, $\bar{N}$ is the number of statistical segments in the chain, and the bond probabilities are taken to be Gaussian[2,22]

$$P_{ij}(\vec{r}) = \left(\frac{3}{2\pi a^2|i-j|}\right)^{3/2} \exp\left(\frac{-3r^2}{2a^2|i-j|}\right) \qquad \text{(B2)}$$

The statistical segment length is denoted by a.

Based on a value of C_∞ of 8.65 for PMMA,[17] the statistical segment length was calculated to be 16 Å with 6.3 monomers per statistical segment. To calculate the chromophore pair correlation function for a 20 000 molecular weight PMMA chain, the sum in eq B1 was performed numerically with $\bar{N} = 32$. To calculate the pair correlation function for an infinite chain, we performed the sum in eq B1 with successively larger values of N until the result converged.

The correlation function implicit in the EF theory was calculated by first obtaining the pair correlation function for N chromophores randomly distributed in a sphere with a second moment of R_g. (See eq 9 of ref 1.) This result, designated $g(\vec{r},R_g)$, is

$$g(\vec{r},R_g) = \frac{3N}{64\pi(5/3)^{3/2}R_g{}^3}\left[16 - \frac{12r}{(5/3)^{1/2}R_g} + \frac{r^3}{(5/3)^{3/2}R_g}\right]\Theta(2(5/3)^{1/2}R_g - r) \qquad \text{(B3)}$$

where $\Theta(x) = 1$ for $x > 0$ and zero for $x < 0$.

To obtain the final result we average over the distribution function of R_g

$$g(\vec{r}) = \int_0^\infty \mathrm{d}R_g\, P(R_g)g(\vec{r},R_g) \qquad \text{(B4)}$$

where $P(R_g)$ is given by eq A2.

Registry No. PMMA (homopolymer), 9011-14-7; PEMA (homopolymer), 9003-42-3; (vinylnaphthalene)·(methyl methacrylate) (copolymer), 53640-71-4.

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Excess Volume of Polystyrene Related to the Expansion of the Coil

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ABSTRACT: Loss of chain volume for polystyrene in solution was studied by means of density measurements using the vibrating-tube method. The issue of prime concern was the apparent specific volume decrease as assessed by the chain length or by the solvent and the temperature. The principal result was that in solution the apparent specific volume follows the expansion α of the coil. Modification of Flory's bifluid theory taking into account a cooperative effect of the solvent with the expansion α gives an acceptable fit of our experimental data. The occurrence of a microstructure within the chain relating to variations in the expansion α of the chain is also discussed.

Simple lattice theory[1] based on the thermodynamic approach of Hildebrand et al.[2] appears to be inadequate for explaining experimental data of thermodynamic excess quantities after mixing. The appreciable change of volume upon mixing of nonpolar molecules is largely beyond the predictions of any theory dealing with solutions. This is why Flory et al.[3,4] developed a theory of liquid mixtures able to better account for differences between two components in a mixture and better suited for polymer solutions. Some binary mixtures of alkanes and polymer–

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Table I
Parameters of Polystyrenes

polymer	initiator	M_w	M_n	M_w/M_n
1903	α-methylstyrene tetramer	4990	4150	1.2
1770	sodium naphthalide	1.4×10^5		
1	potassium cumyl	1.4×10^5	1.35×10^5	1.04
1749	butyllithium	1.4×10^6		
PSD$_3$ II[a]	phenyllithium	1.32×10^6	0.94×10^6	1.4
3	potassium cumyl	7×10^5	6.6×10^5	1.1
PSDT 7[b]	starlike, 4 branches	8.7×10^5		1.2

[a] Synthesized by J. Marchal. [b] Synthesized by J. Herz.

Table II
Equation-of-State Data and Characteristic Parameters for Benzene and Polystyrene (PS)

			PS	
	benzene	cyclohexane	$M_w = 10^4$	$M_w = 10^6$
v_s, $\bar{v}_2$, cm^3 g^{-1}	1.1444	1.2905	0.932	0.926
α_d, deg^{-1}	1.223×10^{-3}	1.223×10^{-3}	5.72×10^{-4}	5.72×10^{-4}
γ, J cm^3 deg^{-1}	1.262	1.073	1.379	1.379
P^*, J cm^{-3}	630	533	528	528
T^*, K	4700	4700	8300	8290
v^*, cm^3 g^{-1}	0.886	0.999	0.823	0.818

solvent have been treated successfully in this way, and the excess volumes calculated for these systems are in good agreement with those observed using theoretical adjustable parameters. In this approach the properties of the pure polymers and of the mixtures are independent of molecular weight and the conformation of the polymer. Moreover, mixing is assumed to be a random process.

Still, a series of experimental works leads to the conclusion that even for a chain of sufficient length where end effects are negligible the specific volume of the pure liquid polymer and the apparent specific volume of the polymer in dilute solution[5-7] decrease with increasing molecular weight. A related quantity, the refractive index increment of the polymer, also varies with molecular weight as expected from additivity rules.[8] In an earlier work,[9] we explained this behavior by the variation of the intramolecular segment density inside the coil. This assumption was refined by Khokhlov[10] and by des cloizeaux using scaling calculations for the probabilities of segment–segment contacts.[11] Moreover, other assumptions suggested that the molecular weight dependence of the apparent specific volume occurs with local order in polymer solutions and pure polymer[12] with variation of the number of rotational isomers in a chain with the expansion factor, α, of the coil.[13]

The purpose of the present paper is to present new results for the excess volume of mixing for polystyrene over a wide range of molecular weight and concentration in solutions in good and Θ solvents and to compare them with the Flory theory.

Experimental Section

The values of the weight-average molecular weight, M_w, and the polydispersity index of the samples used in this work are given in Table I. The sample PSDT, synthesized by Hert et al.,[14] is a starlike polystyrene with four branches.

The experiments were performed on a DMA 02 densimeter, improved in our laboratory by the design of a new cell[15] which is now able to give an accuracy of 5×10^{-6} g cm^{-3} on the density measurement.

The value of the apparent specific volume (ASV), Φ_2, is calculated from the relationship

$$\Phi_2 = v_s + (v_{12} - v_s)c_w^{-1} \tag{1}$$

where v_s is the specific volume of the solvent, v_{12} is the specific volume of the polymer solution, and c_w is the weight fraction of the polymer.

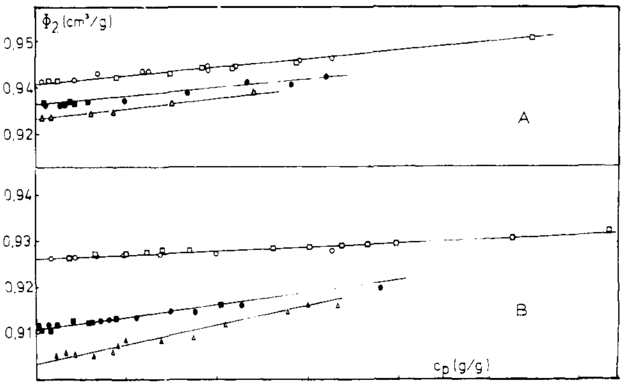

Figure 1. Plot of the ASV, Φ_2, vs. concentration for linear and starlike polystyrene: (A) in solution in a Θ solvent (cyclohexane at 34.5 °C); (B) in solution in benzene at 25 °C. (○) PS 1903; (□) PS 1770; (■) PS 1; (△) PS 1749; (▲) PS 1.32×10^6; (●) PSDT 7.

Results

The variations of the ASV, Φ_2, vs. the weight fraction of polymer are plotted in Figure 1, A and B, for our linear and starlike polystyrenes in solution respectively in cyclohexane at 34.5 °C (Θ solvent) and in benzene at 25 °C.

The concentration dependence of the ASV in benzene is found to depend strongly on the molecular weight and the structure of the polymer. The mean slope of this variation is equal to 2.7×10^{-2} cm^3 g^{-1} for a linear polystyrene of $M_w = 1.4 \times 10^6$, which can be compared with the value 7.5×10^{-3} cm^{-3} g^{-1} found for a sample of $M_w = 1.4 \times 10^4$.

We previously showed that grafted polystyrenes do not behave like their linear homologues but that their ASV is near that of a sample of a lower molecular weight. It is obvious from Figure 1 that PSDT 7 with $M_w = 8.7 \times 10^6$ has the same concentration dependence as the linear sample with $M_w = 1.4 \times 10^5$. We note that for the ASV of low molecular weight samples, we have subtracted the influence of the chain ends according to the procedure described in an earlier work[16]

$$\Phi_{2M} = \Phi_2 + K/M_n \tag{2}$$

where Φ_2 is the ASV of the main chain, Φ_{2M} is the ASV measured and calculated from relation 1, K is a constant that depends on the nature of the chain ends, and M_n is the number-average molecular weight. We assumed that K did not depend on concentration; in our discussion, we deal with the behavior of the ASV, Φ_2, related to the chain unit and with the excess volume, ΔV, defined as

$$\Delta V = \delta V / V^0 \tag{3}$$

where $\delta V = \varphi_2(\Phi_2 - \bar{v}_2)$, V^0 is the initial volume, $\bar{v}_2$ is the specific volume of the monomer unit in the pure liquid polymer extrapolated to 25 °C, and φ_2 is the volume fraction of the polymer. For polystyrene, one generally uses $\bar{v}_2 = 0.933$ cm^3 g^{-1}, whatever the molecular weight, assuming that relation 2 is valid over the entire range of molecular weight. Yet in the case of dilute solution of polymer, the variation of the ASV Φ_{2M} with reciprocal molecular weight departs up to 2×10^4 from this linearity. We have also shown,[6] in agreement with Rudin et al.,[5] that this relation is valid in the liquid state only for low molecular weight samples. This result is supported by the analysis of measurements made by different authors. If we consider that $\bar{v}_2$ depends on the molecular weight, we find the following extrapolated values of $\bar{v}_2$ at 25 °C: $\bar{v}_2$

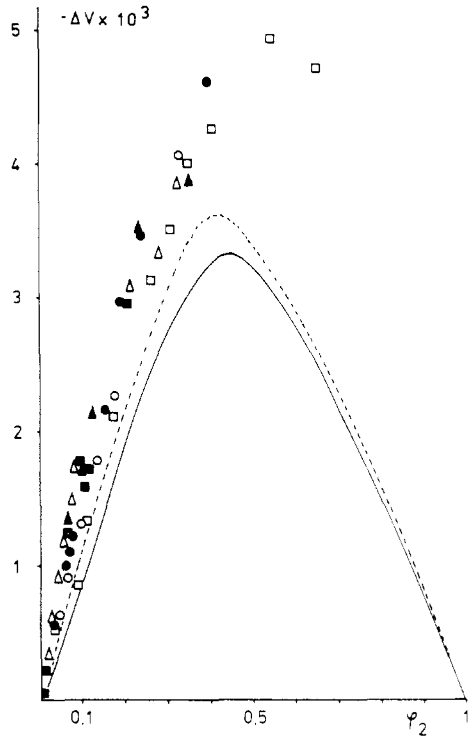

Figure 2. Plot of the excess volume ΔV vs. concentration in benzene with a $\bar{v}_2$ value depending on molecular weight and extrapolated for each sample separately from its liquid state above T_g. (□) PS 1770 ($\bar{v}_2 = 0.933$); (■) PS 1 ($\bar{v}_2 = 0.930$); (△) PS 1749 ($\bar{v}_2 = 0.926$); (○) PS 1903 ($\bar{v}_2 = 0.933$); (●) PSDT 7 ($\bar{v}_2 = 0.928$); (▲) PS 1.32×10^6 ($\bar{v}_2 = 0.926$). Also shown are calculated values from eq 14 with $k' = 10^{-3}$ and $X_2 = -8$ cal cm^{-3}: (—) for $M_w = 10^4$; (- - -) for $M_w = 10^6$.

$= 0.926$ for $M_w = 10^6$, $\bar{v}_2 = 0.930$ for $M_w = 10^5$, and $\bar{v}_2 = 0.933$ for $M_w = 10^4$. By using the constant Flory value, $\bar{v}_2 = 0.933$, one obtains large negative excess values of up to -6×10^{-3} for high molecular weight (10^6), which is very different (-4×10^{-3}) from that obtained for low molecular weight (10^4). Likewise, we have plotted excess volume vs. concentration calculated with $\bar{v}_2$ values depending on the molecular weight. This plot is shown in Figure 2 and gives a lower excess volume at its maximum than previously (-5×10^{-3}). On the other hand, differences from a unique representation of ΔV vs. molecular weight are diminished. There are still differences in ΔV between molecular weights for the low volume fractions of the polymer in solution, as can be seen better in Figure 3. Here we have plotted the relative differences (RD) of ΔV corresponding to two different molecular weights (10^6 and 10^5) against the concentration φ_2, with a reference at molecular weight 10^4. This ratio tends to 0 for φ_2 greater than 40%.

$$\mathrm{RD} = (\Delta V_{\mathrm{M}} - \Delta V_{10^4})/\Delta V_{10^4}$$

The behavior of polystyrene in cyclohexane at 34.5 °C (Θ point) is shown in Figure 1A. It is obvious from this figure that the concentration effect on ASV depends more slightly on the molecular weight than for polystyrene in benzene. Moreover, the molecular weight effect on ASV seems to be less important at low polymer concentration ($\varphi_2 \sim 0$) in cyclohexane, in which the chain has its unperturbed dimensions. This is characteristic of the Θ region, since by increasing the temperature above the Θ point we found again a stronger molecular weight dependence of ASV for polystyrene in cyclohexane.[18] The excess volumes ΔV measured near the Θ point were almost zero until $\varphi_2 = 0.2$. These results were not predicted by Flory and co-workers.

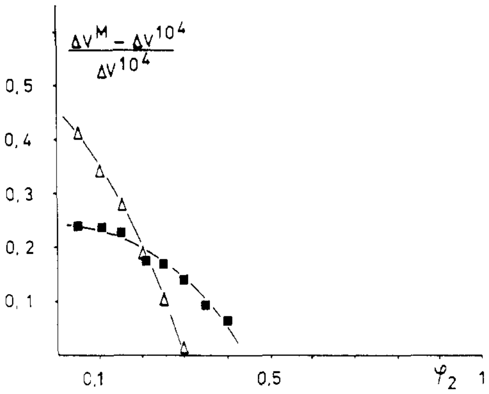

Figure 3. Evidence for the variation of the excess volume ΔV^M vs. the molecular weight against the concentration, starting from ΔV^{10^4} as a reference in this calculation. (△) PS 1749; (■) PS 1.

These results lead us to the following remarks.

The variation of ASV vs. concentration prevents us from explaining the molecular weight dependence of Φ_2 by the sole variation of the intramolecular segment density, related to a change in the number of segment–segment contacts. Indeed, according to such a hypothesis, we could expect the same variation of ASV vs. the intra- or intermolecular volume fraction of polymer, ν_2 and φ_2, respectively. In fact, the mean slope of the variation with ν_2, $\mathrm{d}\Phi_2 = 1.4$, is found to be much greater than $\mathrm{d}\Phi_2/\mathrm{d}\varphi_2 = 0.34$ for $M_w = 10^6$. In addition, the lower molecular weight effect on the ASV of polymer in dilute solution as the Θ point is approached[18] or as the concentration is increased leads us to invoke a cooperative effect of the solvent inside the coil vs. the expansion α of the coil.[7] This assumption could explain the different magnitude in the slope of the ASV variation much higher in the dilute regime than in the concentrated regime vs. the molecular weight. This can be seen in Figure 4.

Discussion

It is well-known that as the polymer concentration increases, the conformation of a chain in solution in a good solvent changes from an expanded coil with excluded volume effect to a statistical coil. To the contrary we cannot expect any variation in the chain dimensions with concentration in a Θ solvent since a polymer maintains a statistical conformation even in the pure state, as shown by neutron scattering experiments.[19] One could understand our present results by considering the suggestions of Khokhlov,[10] who assumes that the expansion factor α is the driving parameter of the molecular weight dependence of Φ_2, through variation of the number of rotational isomers in a chain with α. Furthermore, calculations of Mattice et al.[20] show that the chain swelling does not change this number but modifies the length of the sequences of each rotational isomer. These two complementary ideas were extensively discussed in a previous paper,[7] and we will argue later on these assumptions. For now, let us keep the idea that the expansion coefficient α is the main factor and let us try to verify this by reexamining all our previous results where we studied the variations of Φ_2 with molecular weight, grafting, temperature, and concentration. Can the ASV changes be related to this sole parameter?

$$\alpha = R_g/R_{g\Theta} \qquad (4)$$

where R_g is the radius of gyration under the given conditions and $R_{g\Theta}$ is the unperturbed radius of gyration.

(1) The variation of α vs. molecular weight for a swollen chain in benzene at 25 °C in the dilute regime as well for

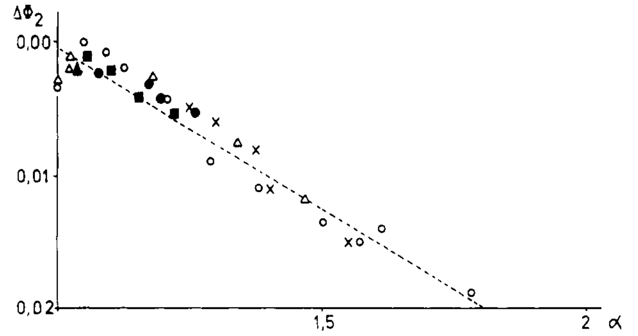

Figure 4. Variation of the ASV deviation, $\Delta\Phi_2$, with expansion coefficient α of the coil at 25 °C in a good solvent: (○) linear chain; (△) grafted chain; (×) PS 1749 at different concentration φ_2. Variation of $\Delta\Phi_2$ with α above a Θ solvent at 34.5 °C: (●) PS 1749 in cyclohexane at different temperatures above the Θ point; (■) PS 7 × 10^5 in cyclohexane at different temperatures above the Θ point; (▲) PS 1 in cyclohexane.

cyclohexane at 34.5 °C is obtained from well-known experimental relations.[21]

(2) α for a Grafted Sample. We used some previous results obtained on comblike polystyrene. For such polymers, it has been shown[22] that the skeleton and each branch have the same expansion coefficient as that of their linear homologues. We can assume that the mean expansion coefficient $\bar\alpha$ for the whole molecule is given by

$$\bar\alpha = \alpha_s\frac{M_s}{M_t} + \alpha_b\frac{n_bM_b}{M_t} \tag{5}$$

Indices b and s are respectively used for branches and skeleton, M_t is the whole molecular weight, and n_b is the number of branches.

(3) α above the Θ Point in Cyclohexane. We have collected different experimental data given by Decker,[21] Candau,[23] Zilliox,[24] Carpenter et al.,[25] and Slagowski[26] for a large range of temperature and molecular weight and we found an equation that fits better than 4% the experimental variations.[18]

(4) α vs. Concentration in a Good Solvent. If the concentration is higher than the concentration of overlapping chains ($c > c^*$), α must vary as $c^{-1/8}$.[27] At concentrations lower than c^*, α is generally assumed to remain constant and equal the value calculated in ref 21.

In Figure 4, we have plotted the variations of $\Delta\Phi_2$ as a function of α, where $\Delta\Phi_2$ is the absolute variation of the ASV calculated from a reference state corresponding to a molecular weight lower tha 2 × 10^4, under which Φ_2 does not vary and α is near 1.[28,29] This reference state is an experimental determination at each thermodynamic condition already studied in early works subtracting the influence of the chain end volume. It clearly appears from Figure 4 that all the experimental points can be fitted by a simple straight line, which constitutes a good proof of the hypothesis which attributes the ASV changes to variations of the chain swelling. One understands that the variation of Φ_2 with M in a Θ solvent is negligible.

We could then imagine a model according to which the change in the length of the sequences of the cis and trans rotational isomers, occurring when the polymer coil expands, perturbs the organization of the solvent molecules around the chain; we must assume that such an effect tends to decrease the "hole" volume. This hypothesis should be in agreement with our experimental observations: (i) Φ_2 is a quasi-linear function of the molar volume of the solvent and (ii) the molecular dependence of Φ_2 becomes negligible when the molar volume of the solvent is sufficiently low (the case for aqueous solutions).

The "hole" volume being generally related to the size of the molecules, one easily conceives that this hypothetical effect of the chain conformation increases with increasing volume of solvent molecules. In such a model the form of the molecules must also play an important role.

Now we want to introduce this hypothesis into Flory's theory,[3,4] keeping the same formalism. The partition function for a binary mixture takes the form

$$Z = \text{const} \times Z_{\text{comb}}(\tilde v^{1/3} - 1)^{3rNc} \exp(-E_0/kT) \tag{6}$$

for N molecules, each molecule being subdivided into r_i segments that have a "hard-core" volume v^* and an external area of interaction s_i. Z_{comb} is the combinatorial factor for intermixing the two component species. $3c$ is the mean value of the number $3c_i$ of external degrees of freedom per segment of type i

The energy E_0 of the mixture is written

$$E_0 = A_{11}\eta_{11} + A_{22}\eta_{22} + \tfrac{1}{2}(A_{12}\eta_{12} + A_{21}\eta_{21})v^{-1} \tag{7}$$

where A_{ij} is the number of ij contacts, each contact being characterized by an energy $-\eta_{ij}/v$.

We can now introduce the concept of a local composition[30] of the solvent near the chain, which depends on the expansion factor of the macromolecule. Let us assume that the local external area of interaction is a function of α, and in a first approach, varies linearly with α. This approach is driven by experimental considerations associating the average area of interaction s_2 with the structure of the polymer solution.

$$s_2' = s_2 + k_1(\alpha - 1) \tag{8}$$

where k_1 is a positive constant depending on the molar volume of the solvent. In a Θ solvent $s_2' = s_2$.

From this hypothesis it follows that

$$2A_{22} + A_{21} = r_2N_2(s_2 + k_1(\alpha - 1)) \tag{9}$$

$$2A_{11} + A_{12} = r_1N_1s_1 \tag{10}$$

N_i is the total number of molecules of type i. The number of contacts $A_{ij} = A_{ji}$ can be expressed by the two relations

$$A_{12} = s_1r_1N_1(1 + k_1(\alpha - 1)/s_2)\theta_2 \tag{11}$$

$$A_{21} = s_2r_2N_2(1 + k_1(\alpha - 1)/s_2)\theta_1 \tag{12}$$

where θ_i is the site fraction of each species i:

$$\theta_1 = 1 - \theta_2 = s_1r_1N_1/srN \tag{13}$$

The reduced equation of state that follows from these hypotheses and from the assumption that α does not depend on pressure but varies slightly ($\partial\alpha/\partial\tilde v \sim 0$) with the volume at one temperature is

$$\frac{\tilde P\tilde v}{\tilde T} = \frac{\tilde v^{1/3}}{\tilde v^{1/3} - 1} - \frac{1}{\tilde T\tilde v} - \frac{Ak'(\alpha - 1)}{\tilde v} \tag{14}$$

Equation 17 differs from Flory's equation of state in the third term on the right side in which

$$A = \varphi_2(P_2^* - X_2\theta_1) \tag{15}$$

and

$$k' = k_1v^*/s_2c\mathbf{k}T$$

where $\mathbf{k}T$ is the thermal energy and P^* is the characteristic pressure:

$$P^* = \varphi_2P_2^*\left(1 + \frac{k_1(\alpha - 1)}{s_2}\right) + \varphi_1P_1^* - \varphi_2\theta_1X_2\left(1 + \frac{k_1(\alpha - 1)}{s_2}\right) \tag{16}$$

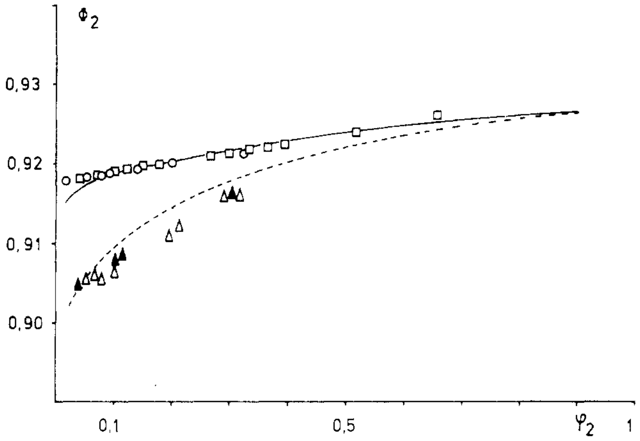

Figure 5. Theoretical values of the ASV calculated from eq 14 for two different chain lengths and with the following parameters: $X_2 = 2$ cal cm^{-3}, $k' = 2 \times 10^{-3}$, and $\bar{v}_2 = 0.926$. (—) For $M_w = 10^4$; (- - -) for $M_w = 10^6$. With the equivalent experimental ASV: (□) PS 1770; (○) PS 1903; (△) PS 1749; (▲) PS 1.32 × 10^6.

P_1^* and P_2^* are the characteristic pressures for the pure components. The characteristic temperature T^* of the mixture is given by

$$1/T^* = (\varphi_2 P_2^*/T_2^* + \Phi_1 P_1^*/T_1^*)/P^* \qquad (17)$$

The characteristic temperature and pressure of each component i are defined by

$$T_i^* = s_i \eta_{ii}/2v^* c_i k \qquad (18a)$$

$$P_i^* = s_i \eta_{ii}/2v^{*2} \qquad (18b)$$

The interaction parameter X_2 is

$$X_2 = s_2 \Delta\eta/2v^{*2} \qquad (19)$$

$\Delta\eta$ being

$$\Delta\eta = \eta_{11} + \eta_{22} - \eta_{12} - \eta_{21} \qquad (20)$$

We are mainly interested by the equation of state at $P = 0$:

$$1/\tilde{T} = (\tilde{v}^{4/3}/\tilde{v}^{1/3} - 1) - Ak'(\alpha - 1) \qquad (21)$$

Using the assumption that α does not vary with temperature in a good solvent over a small range of temperature leads to

$$\tilde{v}^{1/3} - 1 = (\alpha_d T/3)(1 + 2\alpha_d) \qquad (22)$$

where the thermal dilatation coefficient α_d is

$$\alpha_d = (\partial \ln v/\partial T)_{P=0} \qquad (23)$$

These expressions are used to determine $\tilde{v}$ and $\tilde{T}$ for pure polystyrene.

Because the core volume v^* is common to both components by hypothesis, one obtains the foregoing relationship by using additivity rules for the volume:

$$\tilde{v}^0 = \varphi_1 \tilde{v}_1 + \varphi_2 \tilde{v}_2 \qquad (24)$$

The excess volume is $\tilde{v}^E = \tilde{v} - \tilde{v}^0$ and then $\delta V/V^0 = \tilde{v}^E/\tilde{v}^0$, from which it follows that

$$\phi_2 = (\tilde{v}^E/\tilde{v}^0)(v_2 + (\varphi_1/\varphi_2)v_1) + v_2 \qquad (25)$$

At this time it is possible to fit a set of experimental data with the two adjustable parameters X_2 and k'.

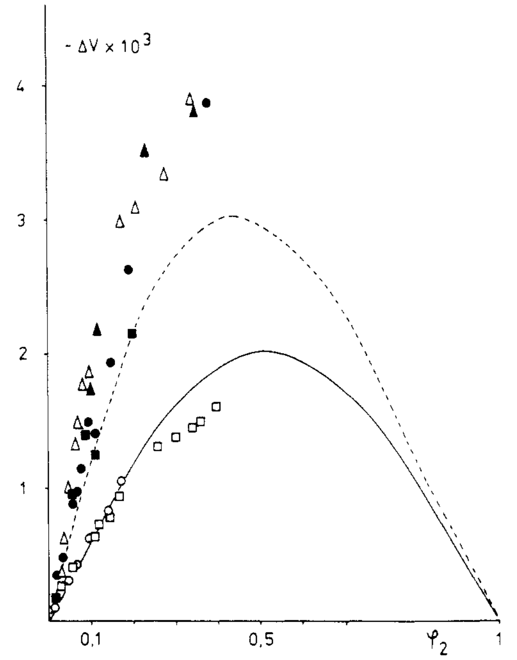

Figure 6. Plot of the calculated excess volume ΔV with the parameters of Figure 5.

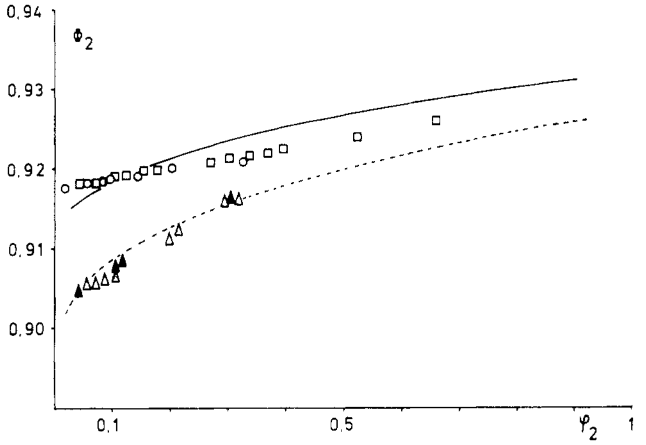

Figure 7. Theoretical values of the ASV calculated from eq 14 with the high molecular weight effect extrapolated at 25 °C from the liquid polymer and with the following constants: $X_2 = -8$ cal cm^{-3}, $k' = 10^{-3}$, $\bar{v}_2 = 0.933$ for $M_w = 10^4$, and $\bar{v}_2 = 0.926$ for $M_w = 10^6$. With the equivalent experimental ASV: (□) PS 1770; (○) PS 1903; (△) PS 1749; (▲) PS 1.32 × 10^6.

The calculation presented here predicts contribution of the expansion of the coil α to the variation of the ASV vs. molecular weight and concentration, as is shown in Figure 5. The scatter of the experimental data above $\varphi_2 \sim 0.02$ suggests a precision of 2×10^{-3} on the ASV for the high molecular weight and a very good agreement with the molecular weight of 10^4. For the very low concentration, theory fails because of the very low accuracy in the determination of the excess volume and because of the mean field approximation. Thus in Figure 5 we give the experimental and the calculated values of the ASV issued from eq 25 with the following parameters: $X_2 = +2$ cal cm^{-3}, with a unique value of $\bar{v}_2 = 0.926$ cm^3 and with a driving factor of the expansion $k' = 2 \times 10^{-3}$. Nevertheless, as shown in Figure 6, the calculated excess volume ΔV for low molecular weight gave a better description of the experimental excess volume than for high molecular weight.

Thus we have to include in our calculation the high molecular weight effect in the extrapolated values of $\bar{v}_2 = f(M_w)$.[6] Figure 7 shows the final calculations carried out with a $\bar{v}_2$ extrapolated from the liquid state vs. the molecular weight and with the interaction coefficient $X_2 = -8$ cal cm^{-3} and $k' = 1 \times 10^{-3}$. The fit of the excess volume ΔV is then better for the whole range of molecular weight as is seen in Figure 2. In Figure 2 the calculated curves and the experimental points of the excess volume depend

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less on molecular weight when we take into account the variation of the specific volume $\bar{v}_2$ of the pure liquid polymer vs. their molecular weight. It is then obvious that relation 14 describes very well the behavior of the excess volume over the entire range of molecular weight. Concerning the behavior of the ASV, Figure 7 shows that the scatter of the experimental points is also less for high molecular weight than previously and that the agreement between calculation and the experimental data of the ASV is excellent.

Conclusion

We have presented a modified version of the bifluid theory using the nonrandom mixing approximation to fit the ASV behavior of polystyrene vs. concentration and molecular weight in the dilute and semidilute regimes. Introducing the local organization of the solvent driven by the expansion coefficient α and by the length of the conformer sequences,[20] we were able to describe our data with only two parameters, X_2 and k'. This modification does not affect Flory's equation of state for pure components but that of the mixture. Some restrictions of these calculations are due to the determination of the crossover concentration or c^*, where the expansion α of the coil has a different scaling law vs. molecular weight. These variations of α with the molecular weight was computed as in the asymptotic region and may explain the discrepancy observed for the excess volume ΔV in the concentrated regime.

Registry No. Polystyrene (homopolymer), 9003-53-6.

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Counterion Condensation in Polyelectrolyte Solution: A Theoretical Prediction of the Dependences on the Ionic Strength and the Degree of Polymerization

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ABSTRACT: As an extension of Manning theory, we propose, without explicit consideration of the condensed phase, a free energy minimization treatment for the estimation of the degree of counterion condensation in polyelectrolyte solutions. The theory is compared with those of Manning, Iwasa et al., Ramanathan et al., and Delville and with experimental data on counterion activity coefficients. The agreement with the data is satisfactory.

Introduction

Manning theory, which first appeared in 1969[1] based on Mayer's cluster theory, predicts the degree of counterion condensation, θ, of polyelectrolyte assumed as an infinitely long linear charge array

$$\nu\theta = 1 - \xi_0/\xi \qquad (1)$$

$$\xi = e^2/DkTb \qquad (2)$$

where ν is the valence of the counterion, e the electronic charge, D the dielectric constant of the bulk solvent, T the Kelvin temperature, b the axial charge spacing of the polyelectrolyte, and ξ the nondimensional charge density parameter. When $\xi > \xi_0$ counterions will condense to reduce the effective polymer charge density to ξ_0. This critical charge density is expressed as ν^{-1}. Manning has obtained eq 1 also based on a two-phase model[2] in which electrostatic energy of polyelectrolyte and mixing entropy of counterions in the condensed and the bulk phases are taken into account. In this model, a free energy minimization method was applied to infinitely long polyelectrolytes in the limit of infinite dilution under an assumption that the volume of the condensed phase V_p is a constant independent of the ionic strength. The limiting law

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