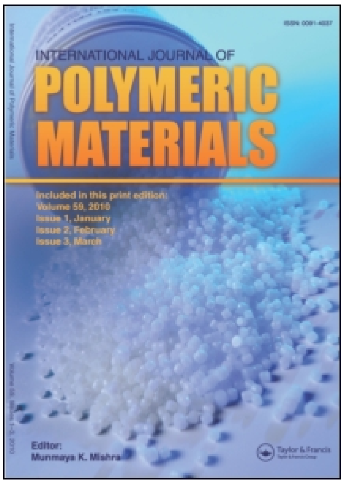

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Preferential Solvation in the Ternary System Polystyrene-Benzene-Methanol†

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The preferential sorption coefficient λ in the ternary system polystyrene (3)-benzene (1)-methanol (2) has been determined in dilute solutions by light scattering. A series of linear (especially of low molecular weight) and well defined comb-like and star-shaped polystyrenes has been studied. The solvation is very strongly dependent upon polymer segment density (or volume fraction $<v_3>$ of polymer inside the coil)

$$\lambda = \lambda_\infty + a<v_3> + b<v_3>^2 + \ldots$$

where coefficients a and b depend mainly on the thermodynamical interaction parameters, and λ_∞ is the preferential sorption coefficient of polystyrene with an infinite molecular weight. The conclusions of this study have been extended to moderately concentrated polystyrene solutions.

1 INTRODUCTION

Several experimental and theoretical studies have shown that the behavior of polymers in mixed solvents is generally affected by the preferential sorption of one of the two solvents on the polymer. This solvation phenomenon is due to the difference in affinity of each solvent with regards to the polymer, and leads to composition variations of the mixed solvent in the vicinity of the macromolecule.

A number of experimental methods can be used to study the preferential sorption in ternary systems, in dilute state and also in more concentrated

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mixtures and gels (light scattering, sedimentation, differential refractometry or densimetry after dialysis, spectroscopical methods, etc.).

In the present work, different aspects are considered of preferential solvation in ternary mixture of polymer (3)-solvent (1)-solvent (2), as a function of molecular weight, structure and concentration of the polymer. This study deals with the polystyrene (3)-benzene (1)-methanol (2) system. In this case benzene is a good solvent and methanol a strong precipitant for polystyrene (PS).

2 DILUTE TERNARY MIXTURES. INFLUENCE OF INTRAMOLECULAR SEGMENT DENSITY

Supposing that solvent (1) is preferentially adsorbed to the polymer in an infinitely dilute ternary mixture, the local concentration v_i (expressed as volume fractions) of low molecular weight components inside the polymer coil can be written as

$$\begin{aligned} v_1 &= (u_1 + \epsilon)(1 - v_3) \\ v_2 &= (u_2 - \epsilon)(1 - v_3) \end{aligned} \qquad (1)$$

where u_1 and u_2 are the volume fractions of solvent (1) and (2) far from the polymer coil (in the present case these volume fractions are identical to the volume fractions u_{10} and u_{20} of solvents without polymer); ϵ coefficient is the excess volume fraction of solvent (1) in a small volume element dV inside the coil, and v_3 is the polymer volume fraction (proportional to the segment density) in this volume element.

Thermodynamical equilibrium condition between the solvent outside and the solvent inside the coil leads to a relation that expresses ϵ as a function of thermodynamic interaction parameters and the volume fractions of components[1,2]

$$(1 - v_3)\,\epsilon = A_1(u_1)v_3 + A_2(u_1)v_3^2 + \ldots \qquad (2)$$

$A_1(u_1)$ and $A_2(u_1)$ are functions of the second and third derivatives of the free enthalpy of mixing ΔG_M, related to the unit volume of mixed solvent contained in the ternary phase, with respect to the volume fractions. Integration of ϵ over the whole volume occupied by the macromolecule, supposing the distribution of segments around the center of mass is Gaussian, yields the experimentally measurable adsorption parameter λ of dilute solution [expressed in ml of solvent (1) per g of polymer][3,4]

$$\lambda = A_1\bar{v}_3 + 2C_M V_1 A_2/(\alpha^3 M^{1/2}) + \ldots \qquad (3)$$

$\bar{v}_3$ is the partial specific volume of polymer, α its expansion coefficient, V_1 the molar volume of solvent (1) and C_M the classical constant

$$C_M = \frac{27\bar{v}_3^2}{2^{5/2}(6\pi)^{3/2}N_A V_1}\left(\frac{M}{<R^2>_0}\right)^{3/2}$$

where $<R^2>_0$ is the mean square radius of gyration of the polymer in "theta" conditions and M its molecular weight.

Relation (3) shows the molecular weight influence (or more exactly the segment density influence) on the preferential sorption coefficient. A recent experimental work of Dondos and Benoît has confirmed this result.[5] These authors have proposed the following expression representing the experimental data

$$\lambda M^{1/2} = \lambda_\infty M^{1/2} + A \tag{4}$$

λ_∞ being the preferential sorption coefficient for an infinite molecular weight polymer and A a parameter describing the segment density influence on λ.

In the first part of this work, the segment density influence due to the lowering of molecular weight is considered. This study has been performed by means of light scattering,[6] recalling that the λ coefficient can be calculated from the apparent molecular weight $M_w{}^*$ of the polymer in the mixed solvent, its true molecular weight M_w and the optical properties

$$\lambda = \left[\left(\frac{M_w{}^*}{M_w}\right)^{1/2} - 1\right]\frac{(dn/dc)_k}{dn_0/du_1} \tag{5}$$

where $(dn/dc)_k$ is the refractive index increment at constant solvent composition and dn_0/du_1 is the variation of the solvent index with composition. Optical properties of the considered system (PS-benzene-methanol) are given elsewhere.[7]

The dependence of λ on the volume fraction of methanol u_2 for some linear PS samples is given in Figure 1; as shown, there is a noticeable influence of molecular weight on the λ coefficient in this system. In particular, the mixture characterized by $u_2 = 0.22$ (for this system, the second virial coefficient is equal to zero at room temperature) has been studied for more samples. Figure 2 represents the variation of λ as a function of $M^{-1/2}$. According to relation (4), this variation should be linear with an intercept equal to λ_∞ and a slope equal to A. Practically the variation is linear down to molecular weights of 10,000 (with $\lambda_\infty = 0.365$ and $A = 16$) but in the lower range of molecular weights, there is an important deviation from linearity; this shows that the relation $\lambda = \lambda_\infty + A/M^{1/2}$ is only a first approximation and fails to hold when the effect of the segment density becomes more important. If a third term $A_3 v_3{}^3$ is taken into account in Eq. (2), the following relation can be obtained for λ

$$\lambda = \lambda_\infty + A/M^{1/2} + B/M \tag{6}$$

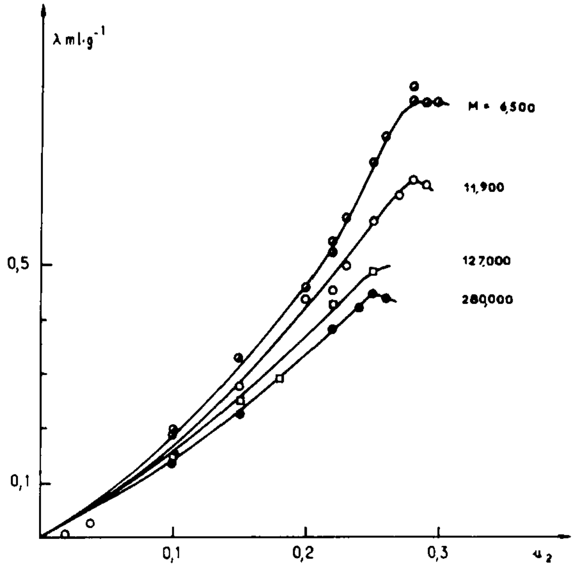

FIGURE 1 Plot of λ coefficient *versus* volume fraction of methanol u_2 in the system linear PS-benzene-methanol. Data by M. Hert, C. Strazielle and H. Benoît, *Makromol. Chem.*, **172**, 169 (1973). Reprinted by courtesy of Hüthig & Wepf Verlag.

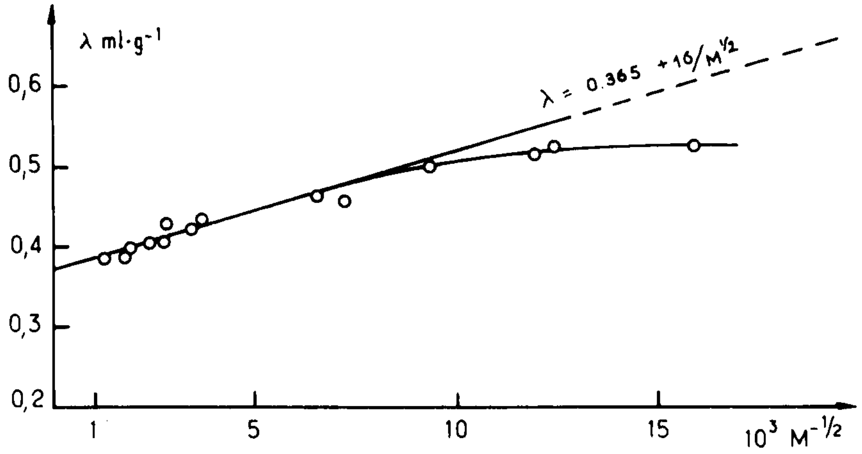

FIGURE 2 Dependence of the λ coefficient on the molecular weight for linear PS in the mixed solvent benzene (78 %)-methanol (22 %). Data by M. Hert, C. Strazielle and H. Benoit, *Makromol. Chem.*, **172**, 169 (1973). Reprinted by courtesy of Hüthig & Wepf Verlag.

Such a relation (with a negative B coefficient) explains the observed dependence and it may also be written as

$$\lambda = \lambda_\infty + a < v_3 > + b < v_3 >^2 \tag{7}$$

where $< v_3 >$ is the average volume fraction of polymer in the coil; in the case of a uniform segment distribution inside the sphere of radius $\alpha < R^2 >_0^{1/2}$, the volume fraction $< v_3 >$ would be equal to

$$< v_3 > = \frac{3\bar{v}_3}{4\pi \mathrm{N_A}} \left(\frac{M}{< R^2 >_0} \right)^{3/2} \frac{1}{\alpha^3 M^{1/2}} \tag{8}$$

The effect observed for low molecular weight linear PS should also occur in branched PS that can present very high segment densities even at high molecular weights.

3 BRANCHED POLYSTYRENE

Two kinds of anionic branched PS prepared in our laboratory have been studied.[10–12]

The first structure corresponds to star-shaped PS with a definite number of branches p ($p = 3$ and $p = 4$) and variable branch length for different samples.

The second kind of branched PS has comb-like structure with variable structural parameters (these parameters are the number p of branches all having the same length, and the ratio r of the branch length to the distance between two neighbour branches on the backbone). It is well known that in "theta" conditions the radius of gyration $< R^{*2} >_0^{1/2}$ of a branched polymer is related to the radius of gyration $< R^2 >_0^{1/2}$ of an identical molecular weight linear polymer by the relation $< R^{*2} >_0 = g < R^2 >_0$; g is the structural parameter which depends on the kind of branching and the number of bonds in the random-flight chain.[8] At the limit of infinite number of bonds, g is equal to $(3p - 2)/p^2$ for star-shaped polymers with branches of equal length, and for comb polymers which have a high number p of branches the parameter g is given by Orofino's relation[9]

$$g = (3/p)r^2/(1 + r)^2 + 1/(r + 1)$$

The molecular and structural parameters as well as the average $< v_3 >_0$ values of the studied branched PS are given in Table I. The g values have been calculated for the infinite limit; this assumption may introduce errors which are neglectable with regard to experimental accuracy.

TABLE I
Molecular and structural parameters of branched polystyrenes
Star-shaped PS

Sample	p	g	M_w	$< \nu_3 >_0 \times 10^{+2}$
PSTT 1	3	0.778	12,600	17.5
PSTT 2	3	0.778	37,000	10.2
PSTT 3	3	0.778	79,000	7.0
PSTT 4	3	0.778	153,000	5.0
PSTT 5	3	0.778	270,000	3.8
PSTT 6	3	0.778	980,000	2.0
PSDT 1	4	0.625	312,000	4.9
PSDT 2	4	0.625	575,000	3.6
PSDT 3	4	0.625	870,000	2.9
PSDT 4	4	0.625	2,210,000	1.8

Comb-like PS

Sample	p	r	g	M_w	$< \nu_3 >_0 \times 10^2$
PS 2A	20	1.14	0.51	1,500,000	3.0
PS 3A	70	4.0	0.23	3,550,000	6.5
PS 4A	195	11.1	0.10	8,500,000	14.6
PS 1752 F_3	30	5.5	0.23	170,000	29.2
PS 1751 F_2	44	10.8	0.17	392,000	30.8
PS 1752 F_1	90	5.4	0.18	480,000	25.5

The $< \nu_3 >_0$ values have been determined according to the relation

$$< \nu_3 >_0 = \frac{3\bar{\nu}_3}{4\pi N_A} \left(\frac{M}{< R^2 >_0} \right)^{3/2} g^{-3/2} M^{-1/2} \tag{9}$$

on the assumption that there is a uniform segment distribution in the sphere of radius $< R^{*2} >_0^{1/2} = g^{1/2} < R^2 >_0^{1/2}$. The suffix "o" indicates that $< \nu_3 >_0$ is the value in "theta" conditions ($\alpha = 1$). The coefficient λ of preferential solvation has been determined by the light scattering method for all these samples, in the benzene-methanol mixture containing 22% methanol. Experimental results are listed in Table II and compared with λ values of the corresponding linear PS calculated from the experimental relation $\lambda = 0.365 + 16/M^{1/2}$ established in the same conditions.

In the first place, we observe that for equivalent molecular weights, the branched PS has a higher coefficient λ than the linear PS. Figure 3 gives the variation of λ with $1/M^{1/2}$ for the two series of star-shaped PS ($p = 3$ and $p = 4$) and also for linear PS. The relation (3) which applies to the linear polymer,

TABLE II
Preferential sorption coefficient of branched polystyrenes in the mixed solvent benzene (78 %)-methanol (22 %)

Sample	M_w	$<\nu_3>_0$	λ_{exp} ml/g	$\lambda_{eq\,lin}$ ml/g
PSTT 1	12,600	17.5	0.516	0.507
PSTT 2	17,000	10.2	0.491	0.448
PSTT 3	79,000	7.0	0.459	0.422
PSTT 4	153,000	5.0	0.432	0.406
PSTT 5	270,000	3.8	0.415	0.395
PSTT 6	980,000	2.0	0.413	0.380
PSDT 1	312,000	4.9	0.425	0.393
PSDT 2	575,000	3.6	0.407	0.386
PSDT 3	870,000	2.9	0.410	0.382
PSDT 4	2,210,000	1.8	0.400	0.375
PS 2A	1,500,000	3.0	0.402	0.378
PS 3A	3,550,000	6.5	0.455	0.374
PS 4A	8,500,000	14.6	0.485	0.370
PS 1752 F_3	170,000	29.2	0.428	0.403
PS 1751 F_2	392,000	30.8	0.407	0.390
PS 1752 F_1	480,000	25.5	0.455	0.388

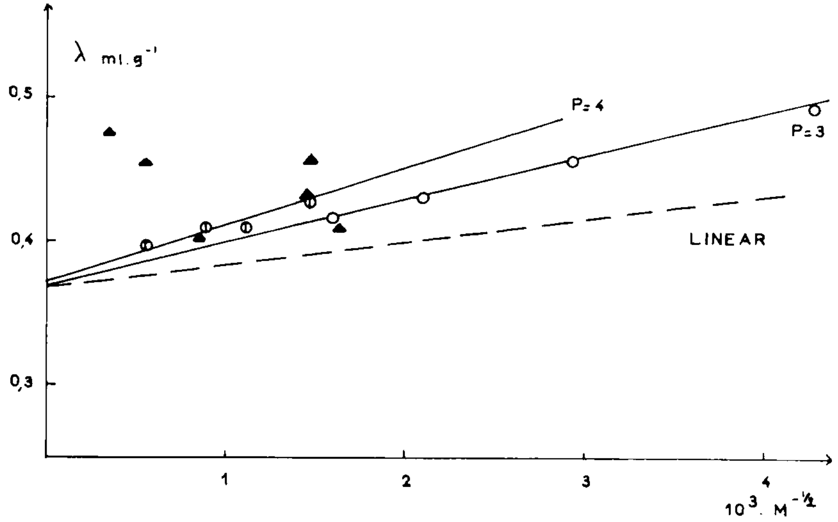

FIGURE 3 Plot of λ coefficient *versus* $M^{-1/2}$ for linear and branched PS in the mixed solvent benzene (78 %)-methanol (22 %). (▲) comb molecules, (○) three-branch star molecules, (⦶) four-branch star molecules.

can be generalized in the first approximation, for both types of branched and linear polymers by the following expression

$$\lambda = \lambda_\infty + A/(M^{1/2}g^{3/2}) \qquad (10)$$

In representation (10), only the term expressing the slope has been modified by the structural parameter g and its value should permit the evaluation of this parameter (provided that the thermodynamic coefficient A is not modified as a result of branching: $A = 16$ for $u_2 = 0.22$); the g values determined in this way for three and four branched PS are 0.74 and 0.69 respectively whereas the theoretical values are 0.778 and 0.625. The results corresponding to comb-like PS are also given in Figure 3; the points related to the comb-like PS are always higher than those for linear PS but the increase does not permit a determination of the structure parameter g because (a) Eq. (10) is only the first approximation, (b) these samples do not belong to a homologous series with constant g.

To see the effect of structure, the representation of λ versus $\langle \nu_3 \rangle_0$ [Eq. (7)] has been given in Figure 4 for all the samples. Two ranges of $\langle \nu_3 \rangle_0$ values corresponding to the differences in adsorption behavior are obvious:

i) In the range of small $\langle \nu_3 \rangle_0$ values ($\langle \nu_3 \rangle_0 < 0.13$) the λ coefficient varies linearly with $\langle \nu_3 \rangle_0$ for all samples. In this range, λ is given by the relation

$$\lambda = 0.365 + 1.1 \langle \nu_3 \rangle_0 \tag{11}$$

According to the definition of $\langle \nu_3 \rangle_0$ [see Eq. (9)] λ coefficient at a given mixture composition depends only on molecular weight and g factor of the polymer

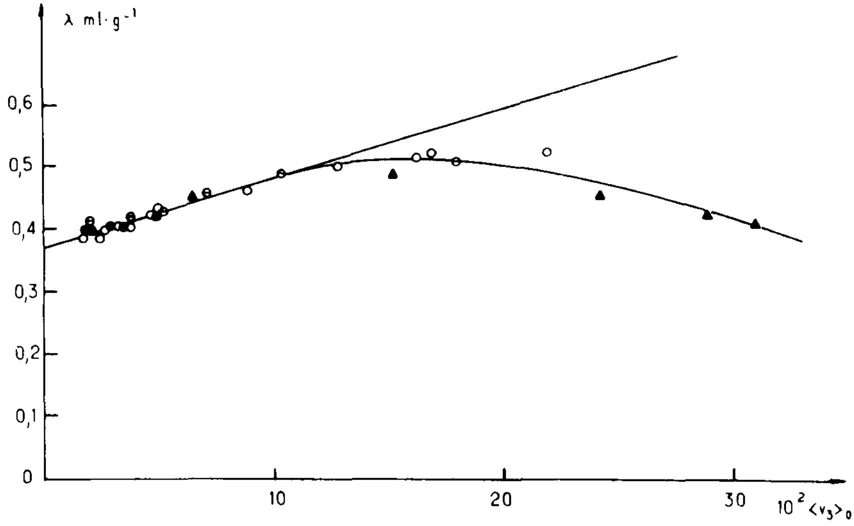

FIGURE 4 The λ coefficient as a function of $\langle \nu_3 \rangle_0$ for linear and branched PS in the mixed solvent benzene (78%)-methanol (22%). (○) linear molecules, (⊖) three-branch star molecules, (●) four-branch star molecules, (▲) comb molecules. Data by M. Hert, C. Strazielle and H. Benoît, *Makromol. Chem.*, **172**, 185 (1973). Reprinted by courtesy of Hüthig & Wepf Verlag.

ii) For higher $<\nu_3>_0$ values ($<\nu_3>_0 > 0.13$), a departure occurs from linearity given by relation (11); the effect of $<\nu_3>_0$ on the λ coefficient is decreasing, since λ reaches a maximum value and decreases slowly with increasing $<\nu_3>_0$. Though it is possible to obtain a single generalized dependence for all the samples, the scatter of experimental points is larger than in the range of small $<\nu_3>_0$ values. The reason for these fluctuations can be due to the definition of $<\nu_3>_0$ itself given by relation (9). Now, if the Gaussian distribution of segments around the mass center is assumed for evaluation of the average volume fraction of polymer, the new $<\nu_3>_0$ is proportional to the value of relation (9), but departure from the Gaussian segment distribution at higher local segment densities will introduce a mean square fluctuation term dependent on the structure in the square value $<\nu_3>^2$.

On the other hand, the expansion coefficient supposed to be equal to unity (at $u_2 = 0.22$) can also be a source of error. For highly branched polymers, a can have values greater than one at the unperturbed dimension conditions of linear homologues.[13]

4 DEPENDENCE OF THE PREFERENTIAL SOLVATION COEFFICIENT ON POLYMER CONCENTRATION

In a ternary system with initial volume fractions ν_{10}, ν_{20} and ν_3 ($\nu_3 = c\bar{\nu}_3$ where c is the polymer concentration expressed in g/cm^3), a local solvent composition variation occurs owing to the preferential sorption of component 1 into the polymer. If the thermodynamic equilibrium (by means of dialysis) is established between this ternary phase and the mixed solvent whose volume fractions are u_{10} and u_{20} [related to ν_{10} and ν_{20} by following expressions: $\nu_{10} = u_{10}\,(1 - \nu_3$ and $\nu_{20} = u_{20}\,(1 - \nu_3)$], the preferential solvation produces composition changes in both phases. In the case of volume-constant dialysis, ν_3 remains constant and the volume fractions of solvent (1) and (2) in the ternary phase at equilibrium are

$$\nu_1 = (u_1 + \epsilon)\,(1 - \nu_3)$$

$$\nu_2 = (u_2 - \epsilon)\,(1 - \nu_3)$$

where u_1 and u_2 are the volume fractions of solvents in mixed solvent in thermodynamic equilibrium with the ternary system. The ϵ coefficient has the same significance as that in the preceding chapter [excess volume of solvent (1) in ml absorbed per ml of mixed solvent], but it is now employed as a "total parameter".

This ϵ coefficient can be related to the λ parameter of infinitely dilute solutions (which is called now λ_0) by the relation

$$\lambda_0 = \left(\frac{d[\epsilon(1 - \nu_3)]}{dc}\right)_{c\to 0} = \bar{\nu}_3\left(\frac{d\epsilon}{d\nu_3}\right)_{\nu_3\to 0} \tag{13}$$

thus, λ_0 is the initial slope of the variation of ϵ with ν_3.

Differential refractometry is one of the easiest methods to detect composition changes after dialysis and consequently to evaluate the ϵ coefficient. This method is accurate only if both solvents have sufficiently different refractives indices. The coefficient ϵ can be obtained from the refractive index differences between the solution after and before dialysis ($\Delta n3$) on the one hand, and between dialysed and initial solvent ($\Delta n_0{}^*$) on the other hand

$$\epsilon = \left[\frac{\Delta n^*}{(1 - c\nu_3)(1 + ac)} - \Delta n_0{}^*\right] \Big/ (dn_0/du_1) \tag{14}$$

with

$$a = \left[\frac{d(dn/dc)_{\mathrm{K}}}{du_1}\right] \Big/ (dn_0/du_1);$$

this parameter a depends only on the optical properties of the ternary system at constant composition (before dialysis).

The variation of the excess volume fraction ϵ due to the solvation with polymer concentration has been established for a linear PS ($M_w = 80{,}000$) in the benzene-methanol mixture at different compositions. During dialysis, the volume of both phases has been held constant. The dialysis equilibrium is generally reached after six hours.[3] Refractive index differences have been measured with a Brice-Phoenix differential refractometer and the ϵ coefficient has been calculated from the relation (14). For the system PS-benzene-methanol, the parameter a is independent of concentration and its value is equal to -0.871, and the $\bar{\nu}_3$ value is 0.92 ml/g.

The variation of ϵ with ν_3 for four initial solvent compositions ($u_{20} = 0.1$, 0.15, 0.22 and 0.25) is shown in Figure 5. For small values of ν_3, ϵ increases linearly and the slope for $\nu_3 \to 0$ gives λ_0. The λ_0 values thus obtained are in good agreement with the values determined by means of light scattering on a linear PS of the same molecular weight[4] (see Table III).

If ν_3 (or c) increases, in the case of low methanol content, a departure from linearity ($\epsilon = c\lambda_0$) in the variation of ϵ occurs. This deviation becomes more important with decreasing u_{20}. For higher methanol contents ($u_{20} = 0.22$ and 0.25), higher polymer concentrations would be required to get this effect, but demixing occurs.

These experimental results can be expressed in the same way as the results obtained in infinitely dilute solutions by the relation

$$\epsilon(1 - \nu_3) = A_1\nu_3 + A_2\nu_3{}^2 + \ldots$$

and the λ coefficient expressed in ml of solvent (1) adsorbed by unit mass of polymer can be derived from:

$$\lambda = \epsilon(1 - \nu_3)\bar{\nu}_3/\nu_3 = A_1\bar{\nu}_3 + A_2\bar{\nu}_3\nu_3 + \ldots \qquad (15)$$

In this relation $A_1\bar{\nu}_3$ represents the λ_0 parameter of the infinitely dilute polymer solution (λ_0 is a function of the segment density $<\nu_3>_0$) and ν_3 the polymer concentration in the ternary system.

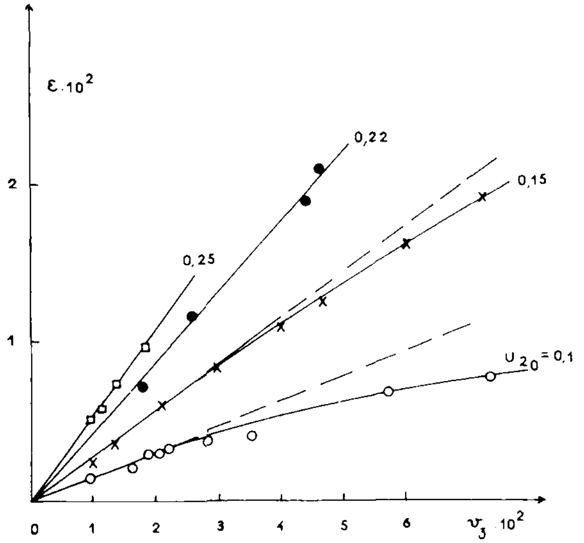

FIGURE 5 Plot of ϵ coefficient *versus* PS volume fraction ν_3 in the system linear PS (M_w = 80,000)-benzene-methanol at different mixed solvent compositions.

TABLE III

Preferential sorption coefficient for the system linear polystyrene[a]-benzene-methanol

u_2	λ_{LS}[b]	λ_R[c]
0.10	0.160	0.140
0.15	0.260	0.260
0.22	0.420	0.410
0.25	0.515	0.495

[a] M_w = 80,000.

[b] Determined in dilute solution by light scattering.

[s] Determined in moderately concentrated solution by differential refractometry.

The following relations can be derived from the curves of Figure 5

$$\lambda = 0.140 - 0.7\,\nu_3 \qquad \text{at } u_{20} = 0.1$$

$$\lambda = 0.260 - 0.4\,\nu_3 \qquad \text{at } u_{20} = 0.15$$

For higher methanol contents, dependence of λ on ν_3 is not detectable in the concentration range studied. Comparison of the experimental relations of λ as a function of the "total" concentration and of λ_0 as a function of average intramolecular segment density [Eq. (11)] shows that the concentration coefficients in both cases have not the same signs. This is not surprising, since the concentration-effect parameters are mainly due to concentration dependence of the thermodynamic interaction parameters χ; these parameters χ generally do not have the same sense of variation with the "total polymer concentration" c as with the "average intramolecular segment concentration" $<\nu_3>_0$.

References

1. A. R. Shultz and P. J. Flory, *J. Polymer Sci.* **15,** 231 (1955).
2. J. Pouchlý, A. Živný, and K. Šolc, *J. Polymer Sci., Part C* **23,** 245 (1968).
3. A. Živný, J. Pouchlý, and K. Šolc, *Collect. Czech. Chem. Commun.* **32,** 2753 (1967).
4. M. Hert, C. Strazielle, and H. Benoît, *Makromol. Chem.*, to be published.
5. A. Dondos and H. Benoît, *Makromol. Chem.* **133,** 119 (1970).
6. C. Strazielle and H. Benoît, *J. Chim. Phys.* **38,** 678 (1961).
7. M. Hert and C. Strazielle, *Eur. Polym. J.* **9,** 543 (1973).
8. K. Šolc, *Macromolecules* **6,** 378 (1973).
9. T. A. Orofino, *Polymer* **2,** 305 (1961).
10. J. Herz, M. Hert, and C. Strazielle, *Makromol. Chem.* **160,** 213 (1972).
11. M. Hert, C. Strazielle, and J. Herz, *C.R. Acad. Sci. (Paris) C* **276,** 394 (1973).
12. F. Candau and P. Rempp, *Makromol. Chem.* **122,** 15 (1969).
13. F. Candau, P. Rempp, and H. Benoît, *Macromolecules* **5,** 627 (1972).

DISCUSSION

Prof. G. Challa (*State University of Groningen, Groningen*): Did you investigate the preferential solvation of polystyrene as a function of temperature? If so, did you observe any transition at about 50°C due to the onset of a more vigorous vibration of phenyl sidegroups? Did you also study the influence of configuration by using isotactic instead of atactic polystyrene?

Dr. C. Strazielle: We have studied the temperature dependence (range 20–60°C) of the preferential solvation in the mixed solvent benzene-methanol (78:22) for different molecular weights of polystyrene. In the case of high molecular weights ($M_w \approx 320{,}000$) the coefficient λ remains constant, but for low molecular weights ($M_w \approx 20{,}000$) we can observe a decrease in λ with increasing temperature. No transition has been observed in the range about 50°C. In the system polystyrene-benzene-methanol the preferential solvation has been studied only with atactic polystyrene.

Dr. G. M. Kosanovich (*Hooker Research Center, Niagara Falls, New York*): What physical significance can be attributed to the intersection of the two-parameter curve λ *vs.* v_3 with the axis v_3, i.e., to the polymer concentration $v_3|_{\lambda=0}$? This could yield greater fundamental value to the prediction.

Dr. C. Strazielle: The relation $\lambda = 0.14 - 0.7\, v_3$ (for $u_{20} = 0.1$) is only a first approximation valid for small values of v_3. Now, if v_3 is increasing, the λ coefficient can take negative values; that means an inversion in preferential solvation phenomenon. A similar inversion, provoked however by a change in the mixed solvent composition rather than by an increase of polymer concentration, has been observed by Živný and Pouchlý [*J. Polymer Sci. A*2 **10**, 1467 (1972)]. This type of inversion is due to the molar volume difference of the two solvents.