Table II
Degrees of Deprotonation of Micellar and Random Coil Forms at Various Conversions

	butyl copolymer		pentyl copolymer	
θ	α_m	α_r	α_m	α_r
0.25	0.32	0.59	0.68	0.94
0.50	0.39	0.70	0.77	0.98
0.75	0.42	0.75	0.85	1.02

chains and the repulsive forces between the hydrophilic head groups.[13,14] The amphiphiles of a homologous series differ only in their hydrocarbon moieties. In contrast, because of the unequal extents of ionization over the ranges of their conformational transitions, the butyl and pentyl copolymers differ essentially also in their hydrophilic groups. To illustrate this point the degrees of ionization of these copolymers are compared at corresponding stages of their conversions in Table II. As can be seen, α_m is about twice as large for the pentyl as for the butyl copolymer. The larger repulsive forces between the residues of the pentyl copolymer arising from this difference in α_m oppose the larger attractive forces arising from its bigger hydrocarbon group. An unambiguous quantitative estimate of the relative magnitudes of these effects is not attainable at present. However, our experimental results are in accord with the effect of the repulsions exceeding that of the attractions.

It is quite possible that in the ionization range below that in which we observe the conformational transition the pentyl copolymer has larger micelles than those reported here. Some evidence for this comes from the fluorescence intensity at 520 nm of a dansylated pentyl copolymer, which was found to increase continuously with decreasing degree of ionization,[15] an indication of increasing contacts between hydrocarbon groups. The overall picture would then be that the pentyl copolymer starts out at low degrees of ionization with large micelles which gradually diminish in size with increasing ionization until a limiting size is reached at which point the micelles disintegrate with further ionization. The effect of the initial decrease in micelle size on the pH–α relation is not cooperative and therefore not pronounced enough to be deducible from the potentiometric titration data.

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(5) The negative infinity in the integral of eq 5 presents no computational problem. The integral is divided into two parts, one going from $-\infty$ to pH_0 (a pH value arbitrarily chosen from the low-α region of the titration curve), the other from pH_0 to pH. The first part can be evaluated in a number of ways. One method is to rewrite this part as $\int_0^{\alpha_0} (\alpha_r - \alpha_m)/h \, dh$, where h is the antilogarithm of the pH. The ratios α_r/h and α_m/h approach the respective intrinsic ionization constants of the r and m forms, as α_r and α_m approach zero, and thus the integrand remains finite.
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Thermodynamic Interactions in the Poly(vinyl methyl ether)–Polystyrene System

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ABSTRACT: The interaction parameters χ in the poly(vinyl methyl ether)–polystyrene (PVME–PS) system were obtained from osmotic pressure measurements for the concentrated solvent–polymer and solvent–polymer–polymer solutions. Toluene and ethylbenzene were used as solvents. The absolute values of χ thus obtained were extremely small. The modified Flory theory was applied to the present systems by extension to ternary systems. The theory reproduced well values of χ, excess volumes for binary and ternary systems with either toluene or ethylbenzene, and also heats of mixing to infinite dilution for the solvent–polymer binary systems. For the PVME–PS system, the theory gave extremely small χ values and negative excess volumes and also gave agreement with the experimental value of the heat of mixing.

Thermodynamic interactions in polymer–polymer systems have been studied experimentally and theoretically from the viewpoint of determination of polymer compatibility.[1,2] The Flory–Huggins interaction parameter χ has been experimentally evaluated mainly by gas–liquid chromatography and by vapor sorption, by using the expression extended to a ternary system by Scott[3] and Tompa.[4] In addition, recently this parameter has been determined from neutron scattering measurements[5,6] for polymer blends without a solvent and from light scattering measurements[7] for solvent–polymer–polymer ternary systems. The absolute values of χ obtained by the scattering methods appear to be very small compared with those obtained by the thermodynamic methods. Also, the

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polymer–polymer χ parameter obtained from the ternary systems may be dependent on solvent.

A theoretical interpretation of polymer compatibility has been made by the Flory[8,9] and Patterson[10] theories based on the free-volume concept and by the Sanchez lattice fluid theory.[11] These theories can explain the LCST (lower critical solution temperature) phenomenon occurring for usual compatible polymer blends.

In this paper, the polymer–polymer interaction parameter χ for the poly(vinyl methyl ether)–polystyrene (PVME–PS) system will be determined from osmotic pressures for concentrated solvent–polymer and solvent–polymer–polymer solutions. Toluene and ethylbenzene are used as solvents.

Recently, Hamada and co-workers[12-14] modified the combining rules for a binary system given by Flory[8] and showed that the modified theory reproduced well various thermodynamic properties for solvent–polymer systems. In this work we derive an expression for the interaction parameter χ_{1p} for a solvent–polymer–polymer ternary system, by extension of the modified combining rules to a ternary system, and apply it to the present systems. Then, we show that the theory can reproduce consistently thermodynamic properties of the solvent–polymer, solvent–polymer–polymer, and polymer–polymer systems. For this purpose, heats of mixing to infinite dilution for the solvent–polymer systems and excess volumes for the solvent–polymer and solvent–polymer–polymer systems were measured. The thermal expansivity and thermal pressure coefficient of toluene were also measured.

Theoretical Expression for a Ternary System

From the work of Prigogine[15] and Flory,[8] the reduced partition function for a system comprising N r-mers having $3c$ external degrees of freedom per segment can be written as[12-14]

$$Z = Z_{\text{comb}} q_{\text{int}}(T)^{Nr}[(2\pi mkT/h^2)^{1/2}(gv^*)^{1/3}]^{3Nrc}(\tilde{v}^{1/3} - 1)^{3Nrc} \exp(Nrc/\tilde{v}\tilde{T}) \quad (1)$$

where Z_{comb} and $q_{\text{int}}(T)^{Nr}$ are the factors related to the combinatorial entropy and to the internal degrees of freedom, respectively, g is the geometric factor, m and v^* are the mass and core volume per segment, respectively, and $\tilde{v}$ and $\tilde{T}$ are the reduced variables of volume and temperature, respectively. $\tilde{v}$ and $\tilde{T}$ are defined by the following equations, together with the reduced pressure $\tilde{p}$

$$\tilde{v} = v/v^* \quad (2)$$

$$\tilde{T} = T/T^* \quad (3)$$

$$\tilde{p} = p/p^* \quad (4)$$

where T^* and p^* are the characteristic parameters of temperature and pressure, respectively.

For a solvent (1)–polymer (2)–polymer (3) system, we assume that the segments of three components are of equal core volume, i.e., $v^*_1 = v^*_2 = v_3^* = v^*$, and that m, p^*, and c for the mixture are expressed by the following equations, respectively, by extension of the combining rules for a binary system[12-14]

$$m = \phi_1 m_1 + \phi_2 m_2 + \phi_3 m_3 \quad (5)$$

$$p^* = \phi_1\theta_1 p^*_1 + \phi_2\theta_2 p^*_2 + \phi_3\theta_3 p^*_3 + 2\phi_1\theta_2 p^*_{12} + 2\phi_1\theta_3 p^*_{13} + 2\phi_2\theta_3 p^*_{23} \quad (6)$$

$$c = \phi_1 c_1 + \phi_2 c_2 + \phi_3 c_3 - \phi_1\theta_2 c_{12} - \phi_1\theta_3 c_{12} - \phi_2\theta_3 c_{23} \quad (7)$$

where p^*_{ij} is the characteristic pressure related to the intermolecular energy between the segments i and j, c_{ij} is the parameter characterizing the deviation from additivity, and ϕ_i and θ_i are the core volume (or segment) and site fractions of component i (i = 1, 2, 3), respectively, given by

$$\phi_i = r_1 N_1/(r_1 N_1 + r_2 N_2 + r_3 N_3) \quad (8)$$

and

$$\theta_i = s_i r_i N_i/(s_1 r_1 N_1 + s_2 r_2 N_2 + s_3 r_3 N_3) \quad (9)$$

in which s_i is the number of contact sites per segment. The exchange enthalpy parameter X_{ij} defined by Flory[8] can be expressed as

$$X_{ij} = p^*_i + (s_i/s_j)p^*_j - 2p^*_{ij} \quad (10)$$

by using p^*_{ij} in eq 6. The characteristic temperature T^* for the mixture is related to c by

$$T^* = p^* v^*/cR \quad (11)$$

where R is the gas constant.

On the basis of eq 1 and of the above combining rules, the residual chemical potential (noncombinatorial part of chemical potential) of component 1, $(\mu_1 - \mu_1{}^0)^R$, can be derived as follows:

$$(\mu_1 - \mu_1{}^0)^{\text{R}} = p^*_1 V^*_1 \tilde{T}_1\{\ln[(m_1/m)^{3/2}] - A\ln[(2\pi mkT/h^2)^{3/2}(gv^*)] - (3/2)(c/c_1)[(1 - \phi_1)m_1 - \phi_2 m_2 - \phi_3 m_3]/m + 3\ln[(\tilde{v}_1{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] - 3A\ln(\tilde{v}^{1/3} - 1) + (1/\tilde{v}_1\tilde{T}_1 - 1/\tilde{v}\tilde{T}) - A(1/\tilde{v}\tilde{T}) + (1/\tilde{v}\tilde{T}^2)(c/c_1)[p^*_1\tilde{T}_1 - 2\theta_1 p^*_1\tilde{T} - 2\theta_2 p^*_{12}\tilde{T} + (\theta_1/\phi_1)p^*\tilde{T} + ARTc_1/v^*]/p^*\} \quad (12)$$

where

$$A = [(\theta_1/\phi_1)(\phi_1\theta_2 c_{12} + \phi_2\theta_3 c_{23} + \phi_1\theta_3 c_{13}) - \theta_2 c_{12} - \theta_3 c_{13}]/c_1 \quad (13)$$

and $V_1{}^*$ is the molar core volume of component 1.

Using the Flory–Huggins expression of the combinatorial entropy[16] extended to a ternary system by Scott[3] and Tompa,[4] one can write the chemical potential as

$$(\mu_1 - \mu_1{}^0)/RT = \ln\phi_1 + (1 - V^*_1/V^*_2)\phi_2 + (1 - V^*_1/V^*_3)\phi_3 + \chi_{1\text{p}}\phi_{\text{p}}{}^2 \quad (14)$$

with

$$\chi_{1\text{p}} = (\mu_1 - \mu_1{}^0)^{\text{R}}/(RT\phi_{\text{p}}{}^2) \quad (15)$$

where V^*_2 and V^*_3 are the molar core volumes of component 2 and 3, respectively, and ϕ_{p} is the total polymer core-volume fraction given by

$$\phi_{\text{p}} = \phi_2 + \phi_3 \quad (16)$$

The above combining rules are available to binary systems of solvent (1)–polymer (2), solvent (1)–polymer (3), and polymer (2)–polymer (3). Therefore, the interaction parameters χ_{12}, χ_{13}, and χ_{23} for the binary systems are given by putting the fraction of the corresponding component at zero. The interaction parameter for the binary systems is then expressed by the same equation as that obtained by Fujisawa et al.[14]

Other thermodynamic functions such as enthalpy and excess volume can be also derived on the basis of eq 1 and 5–7. The expressions for binary systems are the same as those derived by Fujisawa et al.[14]

Experimental Section

Two samples of PS were used for measurements. A sample whose viscosity-average molecular weight was $M_{\text{v}} = 1.6 \times 10^5$ was obtained by fractionation of a polymer bulk polymerized at 160 °C without catalyst. Another sample with $M_{\text{v}} = 2.1 \times 10^5$, ob-

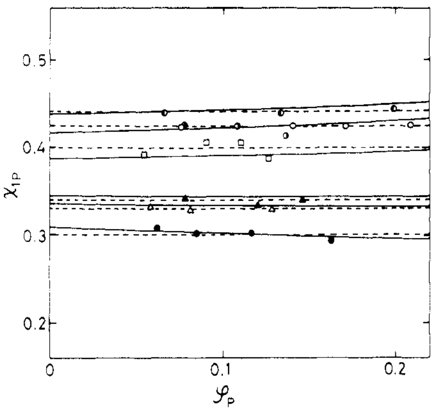

Figure 1. ϕ_p dependences of interaction parameters χ_{1p}, χ_{12}, and χ_{13} for toluene systems at 25 °C. The points were obtained from osmotic pressures by the use of eq 14: (○, ◑) toluene–PS system ((◑) determined from osmotic pressures measured by Higo et al.[20]); (□) toluene–PVME–PS system with ξ_3 = 0.726; (▲) toluene–PVME–PS system with ξ_3 = 0.338; (△) toluene–PVME–PS system with ξ_3 = 0.250; (●) toluene–PVME system; (◐) toluene–PS system at 40 °C. The broken lines were drawn through the points on the approximation that χ was independent of ϕ_p, as described in the text. The solid lines are the theoretical ones calculated by the use of eq 12 and 15.

tained by anionic polymerization, was a monodisperse polymer supplied by Prof. T. Fujimoto. PVME with $M_v = 7.4 \times 10^4$, which was found to be almost atactic from the NMR spectrum, was obtained by crude fractionation of a commercial polymer purchased from Tokyo Chemical Industry Co. Chromatoquality toluene was used without further purification, and reagent-grade ethylbenzene was free from thiophene with concentrated sulfuric acid and then distilled. In calorimetric measurements, each solvent was purified by shaking with mercury, followed by distillation.

Thermal expansivities α were determined from densities ρ measured dilatometrically at intervals of ca. 2 °C on the basis of the absolute value measured with pycnometers. Thermal pressure coefficients γ and osmotic pressures π were measured by the methods similar to those used by Flory and co-workers,[17,18] as described previously.[19] Heats of mixing to infinite dilution, $\Delta H^M(\infty)$, were observed by the electromotive force due to the heat occurring when polymer and solvent separated with mercury in a cell were mixed. Mixing was carried out by slowly shaking the calorimeter apparatus containing the cell inside. The calorimeter used was a Tian-Calvet microcalorimeter.[19] Excess volumes V^E/V^0 were determined from the densities of each component and their mixture by

$$V^E/V^0 = (1/\rho)/(w_1/\rho_1 + w_2/\rho_2 + w_3/\rho_3) - 1 \qquad (17)$$

where w_i is the weight fraction of component i (i = 1, 2, 3).

Results and Discussion

Thermodynamic Properties of Binary and Ternary Systems. Interaction Parameters. From the work of Scott[3] and Tompa[4], the interaction parameter χ_{1p} in eq 14 and 15 can be related to χ_{12}, χ_{13}, and χ_{23} by

$$\chi_{1p} = \chi_{12}\xi_2 + \chi_{13}\xi_3 - \chi_{23}\xi_2\xi_3 \qquad (18)$$

where ξ_i is the relative core-volume fraction of polymer i (i = 2, 3) given by

$$\xi_i = \xi_i/(\xi_2 + \xi_3) = \phi_i/\phi_p \qquad (19)$$

As is obvious from eq 14, these interaction parameters are all normalized to the size of molecule 1. In this paper, subscript 1 refers to the solvent (toluene or ethylbenzene), and subscripts 2 and 3 refer to PVME and PS, respectively. The values of χ_{12}, χ_{13}, and χ_{1p} determined from the osmotic pressures at 25 °C by using eq 14 are summarized in Table I. χ_{12} and χ_{13} are obtained by putting $\phi_3 = 0$ and $\phi_2 = 0$ in eq 14, respectively.

Table I
Osmotic Pressure π and Interaction Parameter χ_{1p} (χ_{12}, χ_{13}) at 25 °C[a]

w_p/w_1	ϕ_p	$\pi \times 10^3$, J cm^{-3}	χ_{1p} (χ_{12}, χ_{13})
Toluene–PS			
0.0959	0.0773	15.60	0.424
0.1888	0.1415	61.95	0.425
0.2385	0.1723	101.1	0.424
0.3046	0.2101	167.6	0.423
Toluene–PS (at 40 °C)			
0.0803	0.0663	10.10	0.439
0.1746	0.1336	50.29	0.438
0.2806	0.1987	129.8	0.445
Toluene–PVME			
0.0772	0.0627	21.50	0.309
0.1072	0.0851	41.37	0.301
0.1520	0.1165	79.21	0.303
0.2198	0.1637	163.7	0.294
Toluene–PVME–PS (w_3/w_2 = 0.332, ξ_3 = 0.250)			
0.0718	0.0587	16.70	0.333
0.1023	0.0816	33.26	0.329
*0.1704	0.1290	87.78	0.330
Toluene–PVME–PS (w_3/w_2 = 0.507, ξ_3 = 0.338)			
0.0984	0.0789	28.71	0.345
0.1434	0.1111	61.78	0.335
0.1971	0.1465	111.6	0.339
Toluene–PVME–PS (w_3/w_2 = 2.64, ξ_3 = 0.726)			
0.0663	0.0547	9.93	0.393
0.1160	0.0918	26.55	0.407
0.1436	0.1113	40.68	0.407
*0.1672	0.1272	62.44	0.388
Ethylbenzene–PVME			
0.0731	0.0597	17.00	0.312
0.1161	0.0916	41.15	0.307
0.2128	0.1560	125.0	0.314
0.2305	0.1668	150.7	0.305
Ethylbenzene–PVME–PS (w_3/w_2 = 0.333, ξ_3 = 0.251)			
*0.0776	0.0635	16.00	0.348
0.1235	0.0970	40.01	0.338
0.1921	0.1436	90.80	0.349
0.2013	0.1491	103.2	0.335
*0.2185	0.1597	116.5	0.343
Ethylbenzene–PVME–PS (w_3/w_2 = 3.00, ξ_3 = 0.751)			
0.0901	0.0729	15.00	0.401
0.1201	0.0949	24.71	0.409
*0.2076	0.1534	72.43	0.412
*0.2521	0.1804	102.1	0.419

[a] Polystyrene used for the systems marked with an asterisk was obtained by anionic polymerization. w_p/w_1 is the weight ratio of the total polymer to the solvent, and w_3/w_2 is the weight ratio of PS to PVME.

Figure 1 shows the dependences of χ_{1p} on ϕ_p for the toluene solutions. The figure includes the results of χ_{12} and χ_{13} for the toluene–PVME and toluene–PS binary systems, respectively. The results for the toluene–PS system are in good agreement with those obtained from the osmotic pressures measured at 25 °C by Higo et al.[20] The χ parameters for the toluene–PS and toluene–PVME–PS systems are almost independent of ϕ_p at least in the present concentration range, while those for the toluene–PVME system slightly depend on it. For the toluene–PS system, Scholte[21] showed from the light scattering measurement that the concentration dependence of χ was small. Also, Bawn et al.[22] measured vapor sorption at PS volume fractions higher than ca. 0.45 and obtained the result that χ tended to decrease with increasing polymer concentration. Also, the ϕ_p dependence of χ in the high core-volume fraction range obtained by Gaecklé et al.[23] is smaller than that by Bawn et al. Thus, the ϕ_p

Table II
Interaction Parameters χ_{23} and χ_{23}/V^*_1 for PVME (2)-PS (3) System at 25 °C

χ_3	χ_{23}	χ_{23}/V^*_1
	From Toluene System	
0.250	0.0093	0.000 11
0.338	0.0115	0.000 13
0.726	−0.0437	−0.000 51
	From Ethylbenzene System[a]	
0.251	−0.024 to 0.027	−0.000 24 to 0.000 27
0.751	−0.060 to −0.028	−0.000 61 to −0.000 28

[a] Values from ϕ_p = 0.05 to 0.20, respectively.

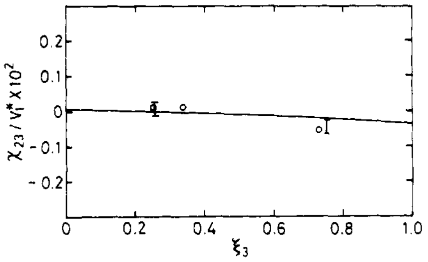

Figure 2. PVME-PS interaction parameters vs. $\xi_3 = (1 - \xi_2)$: (○) obtained from the toluene systems; (I) obtained from the ethylbenzene systems, where the bars present the range of χ_{23}/V^*_1 obtained at ϕ_p = 0.05–0.20. The solid line is theoretical.

dependence of χ for the toluene–PS system appears to be fairly small over the whole concentration range. For the toluene–PVME system, the ϕ_p dependence of χ is very small at least in the present range of ϕ_p. Therefore, we approximate the χ parameters to be independent of ϕ_p for all toluene solutions. Consequently, the values of χ_{12} and χ_{13} are estimated to be 0.301 and 0.424, respectively, at 25 °C, χ_{13} is 0.441 at 40 °C, and the value of χ_{1p} are 0.330, 0.340, and 0.399 for the ternary systems with ξ_3 = 0.250, 0.338, and 0.726, respectively, at 25 °C. These values are presented by the broken lines in Figure 1.

The PVME–PS interaction parameters χ_{23} obtained from the above values of χ_{1p}, χ_{12}, and χ_{13} by using eq 18 are presented in Table II. The values of χ_{23} are normalized to the size of the toluene molecule as described above. Table II also shows the values of χ_{23}/V^*_1. The quantity χ_{23}/V^*_1 is convenient for comparison among those obtained from ternary systems with different solvents since it is not influenced by the size of the solvent molecule. The open circles in Figure 2 show χ_{23}/V^*_1 plotted against ξ_3 $(=1 - \xi_2)$.

The values of χ_{12}, χ_{13}, and χ_{1p} for the ethylbenzene systems are shown in Table I and plotted against ϕ_p in Figure 3. The ϕ_p dependences of χ, shown by the broken lines, are expressed as χ_{12} = 0.311 for the ethylbenzene–PVME system, χ_{1p} = 0.341 for the ethylbenzene–PVME–PS system with ξ_3 = 0.251, $\chi_{1p} = 0.391 + 0.15\phi_p$ for the ethylbenzene–PVME–PS system with ξ_3 = 0.751, and $\chi_{13} = 0.408 + 0.05\phi_p + 0.8\phi_p^2$ for the ethylbenzene–PS system, where the expression for the ethylbenzene–PS system was determined from the data at 10 and 35 °C obtained by Höcker and Flory.[24] The χ parameters for the ethylbenzene–PS system and for the ethylbenzene–PVME–PS system with ξ_3 = 0.751 are dependent on ϕ_p. Therefore, χ_{23} obtained by using eq 18 varies with ϕ_p. The values of χ_{23} and χ_{23}/V^*_1 obtained in the osmotic pressure measurement range of ϕ_p are shown in Table II. In Figure 2, the ξ_3 dependence of χ_{23}/V^*_1 is presented by the bars.

As shown in Figure 2, the values of χ_{23}/V^*_1 obtained from either toluene or ethylbenzene systems appear to decrease slightly with increasing PS composition though the experimental evidence for this tendency is very weak, and their absolute values are very small. Although χ_{23} and χ_{23}/V^*_1 determined here are not obtained by extrapolation to $\phi_p = 1$, it is interesting to compare them with some results obtained by other measurement techniques. Kwei et al.[25] obtained −0.78 to −0.17 for χ_{23} (normalized to the size of benzene molecule) at 35.00 to 64.94 wt % of PS at 30 °C, respectively, from vapor sorption measurement. Su and Patterson[26] determined χ_{23} by gas–liquid chromatography using many probe molecules. In the case of the toluene probe, it was evaluated to be 0.11 and 0.07 at 0.45 and 0.625 weight fractions of PS, respectively, at 40 °C. Our absolute values are the smallest among them and are closer to those of Su and Patterson, while the composition dependence of χ_{23} obtained by us is similar to two other results. Jelenič et al.[5] showed from neutron scattering measurements for the PVME–PS system without a solvent that χ was negative and that the absolute values divided by reduction volume of one lattice site were very small, i.e., the order of 10^{-4}. Hadziioannou and Stein[6] obtained similar results from neutron scattering. Our results are very close to the above scattering results.

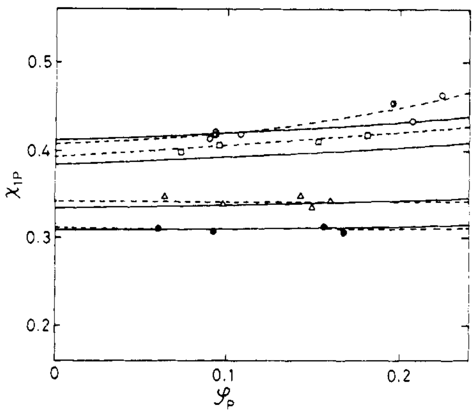

Figure 3. ϕ_p dependences of interaction parameters χ_{1p}, χ_{12}, and χ_{13} for ethylbenzene systems at 25 °C. The points were obtained from osmotic pressures by the use of eq 14: (○) ethylbenzene–PS system at 10 °C and (◑) at 35 °C, obtained by Höcker and Flory;[24] (□) ethylbenzene–PVME–PS system with ξ_3 = 0.751; (△) ethylbenzene–PVME–PS system with ξ_3 = 0.251; (●) ethylbenzene–PVME system. The broken lines were drawn through the points as described in the text. The solid lines are the theoretical ones calculated by the use of eq 12 and 15.

Heats of Mixing to Infinite Dilution and Excess Volumes. Heats of mixing to infinite dilution $\Delta H^M(\infty)$ for the PVME binary systems at 25 °C are shown in Table V. The value for the toluene–PS system, corrected for glass transition, was obtained by Morimoto.[27]

The results of excess volume V^E/V^0 for the binary and ternary systems at 25 °C are shown in Figures 5 and 6. The values for the ethylbenzene–PS system were cited from the work of Höcker and Flory.[24] The values for all the toluene systems are negative, while for the ethylbenzene systems they vary from negative to positive with increasing composition of PVME.

Application of Theory to Binary and Ternary Systems. Equation-of-state parameters of pure components are required in order to calculate thermodynamic quantities of mixtures according to the theory based on the combining rules eq 5–7. The reduced and reduction parameters can be obtained by using the following equation of state and related equations at p = 0,[8] derived from the partition function eq 1:

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \qquad (20)$$

$$\tilde{v}^{1/3} = 1 + \alpha T/3(1 + \alpha T) \qquad (21)$$

$$p^* = \gamma T \tilde{v}^2 \qquad (22)$$

Table III
Equation-of-State Parameters

t, °C	$\tilde{v}$	v^*_{sp}, cm^3 g^{-1}	T^*, K	p^*, J cm^{-3}
		Toluene		
25	1.2502	0.9275	5197	547
40	1.2709	0.9268	5182	545
		Ethylbenzene[a]		
25	1.2515	0.9262	5176	551
		Poly(vinyl methyl ether)[b]		
25	1.1775	0.8054	6622	519
50	1.1939	0.8085	6741	516
		Polystyrene[c]		
25	1.1528	0.8098	7420	547
40	1.1599	0.8188	7526	537
50	1.1647	0.8132	7592	532

[a] Reference 24. [b] Reference 30. [c] Höcker, H.; Blake, G. J.; Flory, P. J. *Trans. Faraday Soc.* **1971**, *67*, 2251.

Table IV
Parameters Used for Calculations of Thermodynamic Quantities for Mixtures

system (i–j)	s_j/s_i	X_{ij}, J cm^{-3}	c_{ij}
toluene (1)–PVME (2)	1.08	-5.0	0.0124
toluene (1)–PS (3)	0.92	1.2	0.0102
ethylbenzene (1)–PVME (2)	1.07	7.0	0.0014
ethylbenzene (1)–PS (3)	0.91	3.8	0.0062
PVME (2)–PS (3)	0.85	-9.8	0.0084

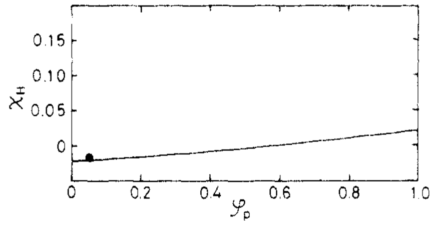

Figure 4. Calculated curve of χ_H for the ethylbenzene–PS system at 25 °C ((●) experimental value[29]).

Table V
Comparison between Calculated and Observed Values of $\Delta H^M(\infty)$ at 25 °C

	$\Delta H^M(\infty)$, J g^{-1}	
system	obsd	calcd
toluene–PVME	-7.1	-7.4
toluene–PS	-2.5[a]	-2.5
ethylbenzene–PVME	5.0	4.9
ethylbenzene–PS		-0.1

[a] Reference 27.

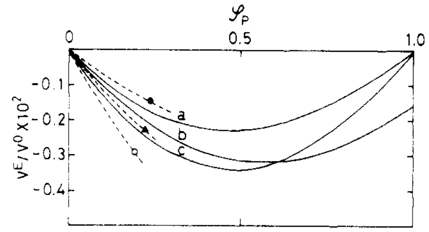

Figure 5. Comparison between the calculated and observed excess volumes for toluene systems at 25 °C: (● and a) toluene–PVME system; (▲ and b) toluene–PVME–PS system with $\xi_3 = 0.338$; (○ and c) toluene–PS system.

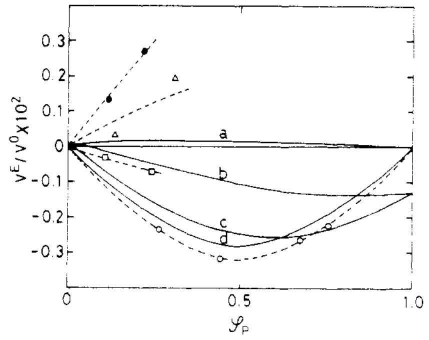

Figure 6. Comparison between the calculated and observed excess volumes for ethylbenzene systems at 25 °C: (● and a) ethylbenzene–PVME system; (△ and b) ethylbenzene–PVME–PS system with $\xi_3 = 0.251$; (□ and c) ethylbenzene–PVME–PS system with $\xi_3 = 0.751$; (○ and d) ethylbenzene–PS system (the experimental values for this system were observed by Höcker and Flory[24]).

The values of the reduced and reduction parameters for each component are summarized in Table III. The values for toluene were estimated from the following results:

$$\rho\ (\mathrm{g/cm^3}) = 0.8834 - (0.08089 \times 10^{-2})t - (0.01511 \times 10^{-4})t^2 + (0.00580 \times 10^{-6})t^3 \qquad (t = 20\text{–}60\ ^\circ\mathrm{C})$$

$$\alpha\ (1/\mathrm{deg}) = 0.913 \times 10^{-3} + 0.441 \times 10^{-5}t - (0.171 \times 10^{-7})t^2 \qquad (t = 20\text{–}60\ ^\circ\mathrm{C})$$

$$\gamma\ (\mathrm{bar/deg}) = 13.57 - (8.00 \times 10^{-2})t + (2.56 \times 10^{-4})t^2 \qquad (t = 20\text{–}60\ ^\circ\mathrm{C})$$

In all calculations of the thermodynamic quantities for the mixtures, the core volume of segment was assumed to be that of styrene monomer. The contact-site ratio per segment s_j/s_i was estimated from the surface area of groups given by Bondi.[28]

First, the thermodynamic quantities for the solvent–polymer binary systems were calculated by the use of the values of X_{ij} and c_{ij} shown in Table IV. The results for χ_{12} and χ_{13} are presented by the solid lines in Figures 1 (for the toluene systems) and 3 (for the ethylbenzene systems). The calculation for the toluene–PS system at 40 °C was carried out by the use of the equation-of-state parameters at 40 °C. The calculated values of $\Delta H^M(\infty)$ for three solvent–polymer systems and of χ_H (the enthalpic part of χ) for the ethylbenzene–PS system are compared with the experimental ones in Table V and Figure 4, respectively. Also, the calculated excess volumes for the toluene systems and ethylbenzene systems are presented by the solid lines in Figures 5 and 6, respectively. As seen in these figures and table, the theory reproduces well the experimental values of χ, $\Delta H^M(\infty)$, χ_H, and V^E/V^0 for the solvent–polymer binary systems.

Next, thermodynamic quantities for the ternary systems were calculated by the use of the values of X_{23} and c_{23} shown in Table IV, in addition to the above values of X_{12}, X_{13}, c_{12}, and c_{13}. Here, it should be noted that the same values of X_{23} and c_{23} are used for both the toluene and ethylbenzene systems since these parameters should not be affected by the type of solvent. The calculated curves of χ_{1p}, presented by the solid lines in Figures 1 and 3, are in satisfactory agreement with the experimental values. The results of V^E/V^0 are shown by the solid lines in Figures 5 and 6. The values at $\phi_p = 1$ presents V^E/V^0 for the PVME–PS system without a solvent. As seen in Figure 6, the calculated values for the ethylbenzene systems deviate from the experimental ones for the PVME-rich systems, though the tendency of V^E/V^0 varying from positive to negative with increasing PS composition is predicted well by the theory. Thus, the theory reproduces successfully the experimental values of χ_{1p} and V^E/V^0 by the use of the values of X_{23} and c_{23} common to the toluene and ethylbenzene systems. It is noted that X_{23} used here is negative as predicted for the usual compatible polymer

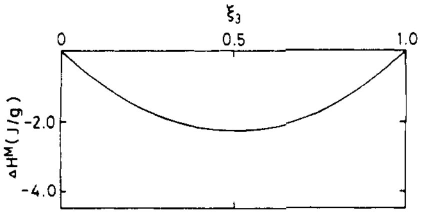

Figure 7. Calculated curve of heat of mixing, ΔH^M, for the PVME-PS system at 50 °C.

blends for which LCST occurs.[1,2,10]

For the PVME-PS system, the thermodynamic quantities were calculated by using the values of X_{23} and c_{23} employed for the ternary systems. The curve of the heat of mixing ΔH^M calculated by the use of the equation-of-state parameters at 50 °C is shown in Figure 7. The calculated value of $\Delta H^M = -2.24$ J g^{-1} at $\xi_3 = 0.5$ is in good agreement with $\Delta H^M = -1.8$ J g^{-1} at $\xi_3 = 0.496$ and 50 °C measured by Hamada et al.[30] The theory also gave the negative values of V^E/V^0 as shown by the values at $\phi_p = 1$ in Figures 5 and 6. The experimental results of V^E/V^0 obtained for this system by Kwei et al.[25] and by Hamada et al.[30] also gave negative values. In Figure 2 is shown the calculated curve of the PVME-PS χ parameter by the solid line. The χ parameter derived directly on the basis of eq 1 for the binary system is per polymer (2) molecule. Therefore, the theoretical values of χ were obtained by dividing the above χ value by V^*_2 so as to equal χ_{23}/V^*_1. The calculated value of χ_{23}/V^*_1 varies from positive to negative with increasing PS composition, and its absolute value is extremely small. The theoretical curve cannot be directly compared with the values observed here, because the former does not include the effect of the solvent in principle while the latter may include it. These theoretical values may not be so different from those for the polymer blend without a solvent, since the theory reproduces the experimental values of ΔH^M and V^E/V^0 for the PVME-PS system and various thermodynamic properties for two ternary systems and also since the theoretical values are very close to the experimental ones obtained for this system by Hadziioannou et al.[6] and Jelenič et al.[5] As described above, this theory is expected to predict the χ parameter for polymer-polymer systems without a solvent, by elimination of the influence of solvent from the χ parameter obtained for solvent-polymer-polymer systems. To confirm this, further investigations of other polymer blends and their ternary systems and also over the whole range of ϕ_p will be desired.

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Registry No. PVME (homopolymer), 9003-09-2; PS (homopolymer), 9003-53-6; toluene, 108-88-3; ethylbenzene, 100-41-4.

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