Macromolecules **1990,** *23,* 229–233

Thermodynamics of Polymer Blends of Poly(vinyl methyl ether) and Polystyrene

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Revised Manuscript Received May 30, 1989

ABSTRACT: Heats of mixing, excess volumes, and a cloud point curve were experimentally obtained for the poly(vinyl methyl ether)/polystyrene blends. The heats of mixing for the blend obtained by application of Hess' law to heats of dissolution of the component polymers and their blends and to heats of mixing of polymer solutions were negative. The excess volumes also showed the negative values. Flory's equation-of-state theory with modified combining rules was applied to this blend system. For this purpose, densities, thermal expansion coefficients, and thermal pressure coefficients for poly(vinyl methyl ether) were also measured, from which the equation-of-state parameters were obtained. The exchange enthalpy parameter obtained so that the calculated values of the excess volume and heat of mixing can fit those experimental data was negative. The calculated dependences of the interaction parameter χ on the concentration as well as temperaure were in agreement with those obtained from the neutron scattering measurements by Stein and co-workers.

Introduction

Polymer blends are usually immiscible because the combinatorial entropy on mixing is too small, owing to high degrees of polymerization,[1] and in addition because enthalpy changes on mixing are often positive. However, since the 1970s, many polymer blends have been found to be miscible in the molecular level by small-angle neutron and X-ray scattering techniques.[2–4] This finding made it possible to investigate polymer blends from the thermodynamic point of view, and miscibility for polymer blends has been thermodynamically studied.[5–10]

Miscible polymer blend systems found so far may be classified as follows: (1) systems having a specific interaction between different polymer molecules, (2) systems consisting of oligomers, and (3) systems consisting of polymers that are similar to each other in the chemical structure. In addition, recently some random copolymer blends have been found to be miscible in a certain range of copolymer composition even though the combinations of their corresponding homopolymers are immiscible.[11–14] Type 1 is a typical miscible polymer blend, which has only an LCST, while in type 2 a UCST has been found. Types 2 and 3 may have both LCST and UCST according to the equation-of-state theory.[5,6,15,16] The initial studies on the real systems classified into type 1 were carried out for poly(vinyl methyl ether)/polystyrene blends by Nishi and Kwei.[17–19] For type 2, Allen et al.[20,21] and Higgins et al.[22] reported the phase diagrams for the oligomer blends of polyisobutylene/poly(dimethylsiloxane) and poly(ethylene glycol)/poly(propylene glycol). For type 3, Zacharius et al.[23] suggested that both UCST and LCST could be found in the blends of polystyrene/poly(*o*-chlorostyrene).

In this paper, we will present thermodynamics for the blends of the type 1, poly(vinyl methyl ether)/polystyrene (PVME/PS) system. We will report the experimental results of excess volumes, enthalpies on mixing, and a cloud point curve for this system.

Flory and co-workers[15,16] proposed the polymer solution theory based on the free-volume concept. This theory enabled us to describe LCST phenomena as well as UCST.[5,6,24] However, for such polymer solutions as poly(dimethylsiloxane) solutions,[25–27] the theory did not give very good quantitative agreement with experiments. Hamada and co-workers[28–30] modified or generalized the combining rules on mixing given by Flory et al.[15,16] This modified theory successfully reproduced thermodynamic quantities for various polymer solutions as well as poly(dimethylsiloxane) solutions without using the parameter Q_{12},[31] which was introduced to adjust only the χ parameter or chemical potential. We will apply this modified Flory's equation-of-state theory to the PVME/PS system.

Theoretical Background

According to the modified combining rules proposed by Hamada and co-workers,[28–30] the core volume, v^*, and external degrees of freedom, c, per segment for binary mixtures can be written as

$$v^* = \phi_1^2 v_1^* + 2\phi_1\phi_2 v_{12}^* + \phi_2^2 v_2^* \qquad (1)$$

where

$$v_{12}^* = [(v_1^{*1/3} + v_2^{*1/3})/2]^3 \quad \text{or} \quad v_{12}^* = (v_1^* + v_2^*)/2 \qquad (2)$$

and

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1\theta_2 c_{12} \qquad (3)$$

respectively, where ϕ_i and θ_i (i = 1, 2) are the segment and site fractions, respectively, of the component i, v_i^* is the core volume per segment of the component i, and c_{12} is the parameter characterizing the deviation from additivity. As another combing rule, random mixing was assumed in the same way as Flory's assumption. Using the partition function for N r-mers proposed by Flory et al., we can derive various thermodynamic functions under the above three combining rules.

In this work, for simplicity, it is assumed that the sizes of the core volume per segment for the pure components and their mixture are equal to one another instead of eq 1; i.e.

$$v^* = v_1^* = v_2^* \qquad (4)$$

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0024-9297/90/2223-0229$02.50/0

Then, the residual chemical potential, $(\mu_1 - \mu_1^\circ)^R$, of the component 1 defined by

$$\mu_1 - \mu_1^\circ = RT[\ln(1 - \phi_2) + (1 - r_1/r_2)\phi_2] + (\mu_1 - \mu_1^\circ)^R \tag{5}$$

can be expressed as

$$\begin{aligned}(\mu_1 - \mu_1^\circ)^R = {}& -{}^3/{}_2 r_1 p_1^* v^* \tilde{T}_1 \ln(m/m_1) + \\ & 3r_1 RTc_{12}\theta_2^2 \ln K - {}^3/{}_2[(m_1 - m_2)/m]p^* r_1 v^* \tilde{T}\phi_2 + \\ & 3p_1^* r_1 v^* \tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + 3r_1 RTc_{12}\theta_2^2 \times \\ & \ln(\tilde{v}^{1/3} - 1) + p_1^* r_1 v^*(1/\tilde{v}_1 - 1/\tilde{v}) + r_1 v^* X_{12}\theta_2^2/\tilde{v}\end{aligned} \tag{6}$$

with

$$K = (2\pi mkT/h^2)^{1/2}(gv^*e^3)^{1/3} \qquad m = \phi_1 m_1 + \phi_2 m_2 \tag{7}$$

where r_i is the number of segments in the molecule i, m_i is the mass per segment of the component i, and X_{12} is the exchange enthalpy parameter. $\tilde{p}$, $\tilde{v}$, and $\tilde{T}$ is the reduced parameters of pressure, volume, and temperature, respectively, defined using their reduction parameters p^*, v^*, and T^* as follows:

$$\tilde{p} = p/p^* \qquad \tilde{v} = v/v^* \qquad \tilde{T} = T/T^* \tag{8}$$

g, which is the geometric factor, is taken as $(4/3)2^{1/2}\pi$ under the assumption of the coordination number $z = 12$. The interaction parameter χ can be written from eq 5 as follows

$$\chi = (\mu_1 - \mu_1^\circ)^R/(RT\phi_2^2) \tag{9}$$

and at infinite dilution

$$\begin{aligned}\chi_1 = \lim_{\phi_2 \to 0} \chi = {}& 3p_1^* r_1 v^* \tilde{T}_1\{(m_2/m_1 - 1) \times \\ & [2(T_1^* p_2^*/T_2^* p_1^*) - (m_2/m_1 + 1) - 2(T_1^*/p_1^*)(s_2/s_1) \times \\ & (Rc_{12}/v^*)]/4 + \ln[K_1(\tilde{v}_1^{1/3} - 1)](s_2/s_1)^2(T_1^*/p_1^*) \times \\ & (Rc_{12}/v^*)\}/RT + (p_1^* r_1 v^*/\tilde{v}_1)(A^2\alpha_1 T/2 + Y_{12})/RT\end{aligned} \tag{10}$$

where

$$\begin{aligned}A = {}& (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (s_2/s_1)(X_{12}/p_1^*) + \\ & (T_1^*/p_1^*)(s_2/s_1)(Rc_{12}/v^*)\end{aligned} \tag{11}$$

$$Y_{12} = (s_2/s_1)^2(X_{12}/p_1^*) \tag{12}$$

in which s_2/s_1 is the surface ratio of the segment.

The heat of mixing per segment is

$$\begin{aligned}\Delta H^{\mathrm{M}}/\bar{r}N & \\ = {}& -RT[c/\tilde{v}\tilde{T} - \phi_1 c_1/\tilde{v}_1\tilde{T}_1 - \phi_2 c_2/\tilde{v}_2\tilde{T}_2] - {}^3/{}_2 RTc_{12}\phi_1\theta_2 \\ = {}& v^*[\phi_1 p_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + \phi_2 p_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + \\ & \phi_1\theta_2 X_{12}/\tilde{v}] - {}^3/{}_2 RTc_{12}\phi_1\theta_2\end{aligned} \tag{13}$$

where $\bar{r}N$ is the number of the total segments of N_1 r_1-mers and N_2 r_2-mers. The heat of mixing to infinite dilution, $\Delta H^{\mathrm{M}}(\infty)$, can be derived from eq 13 as follows:

$$\begin{aligned}\Delta H^{\mathrm{M}}(\infty) = {}& (v_{\mathrm{sp},2}^*/\tilde{v}_1)p_2^*[(T_1^*/T_2^*) - 1]\alpha_1 T + \\ & v_{\mathrm{sp},2}^* p_2^*(1/\tilde{v}_2 - 1/\tilde{v}_1) + (v_{\mathrm{sp},2}^*/\tilde{v}_1)(s_2/s_1)(1 + \alpha_1 T)X_{12} - \\ & (RTc_{12}v_{\mathrm{sp},2}^*/v^*)(s_2/s_1)[{}^9/{}_2 + 4\alpha_1 T]\end{aligned} \tag{14}$$

The ratio of the excess volume V^{E} to the sum V° of the volumes of the pure components is

$$V^{\mathrm{E}}/V^\circ = \tilde{v}/\tilde{v}_0 - 1 \tag{15}$$

where

$$\tilde{v}_0 = \phi_1\tilde{v}_1 + \phi_2\tilde{v}_2 \tag{16}$$

Table I
Equation-of-State Parameters for PVME and PS

temp, °C	v_{sp}^*, g/cm³	T^*, K	p^*, J/cm³
	PVME		
50	0.8085	6738	517
100	0.8173	7051	483
	PS[a]		
50	0.8132	7592	532
100	0.8205	7948	506

[a] Reference 33.

Experimental Section

Materials. A monodisperse PS whose molecular weight was $M_{\mathrm{w}} = 1.1 \times 10^5$ ($M_{\mathrm{w}}/M_{\mathrm{n}} < 1.06$) was purchased from the Pressure Chemical Co. A PVME polymer, which was found to be almost atactic from the NMR spectrum, was purchased from the Tokyo Chemical Industry Co. The viscosity-average molecular weights of PVME fractionated in the benzene/*n*-hexane system were 5.28×10^4, 7.4×10^4, and 1.0×10^5. The first one was used for measurements of excess volumes and cloud points, the second for densities, thermal expansion coefficients, and thermal pressure coefficients, and the last for heats of mixing.

Measurements. Densities and thermal expansion coefficients of PVME were measured by the weighing dilatometer method according to the procedure of Flory et al.[32] The relative volumes obtained at intervals of ca. 4 °C were converted to the absolute volumes based on the density at 25 °C, and from those volumes thermal expansion coefficients were determined.

Thermal pressure coefficients of PVME were measured by the method similar to that used by Flory et al.[32,33]

Densities of the blends were measured by the sink-and-float method at 50 °C. The liquids used for the measurement were 1,3-butanediol and diethylene glycol, and the densities of their mixtures were measured using a pycnometer with a 100-mL volume.

Heats of mixing for blends of PS and PVME were obtained by application of Hess' law[34-36] to the heats of mixing of the component polymers and their blend with toluene to infinite dilution (to ca. 0.8 wt % solution) and to the heat of mixing of polymer solution. The measurements were carried out with a Tian–Calvet microcalorimeter at 50 °C under agitation.

Cloud points for the PS/PVME mixture were obtained by observing a turbidity point, which was detected as a rapid decrease in the intensity of the transmitted He–Ne laser light using a photoelectric tube. The turbidity temperature was measured both on heating and cooling the sample at 0.2 °C/min, and the temperature averaged for both measurements was taken as a cloud point. The employed sample films with 2-mm thickness were prepared at molding temperatures slightly higher than the respective glass transition temperatures.

Results and Discussion

Thermodynamic Properties. The results of the density, ρ, thermal expansion coefficient, α, and thermal pressure coefficient, γ, for PVME were

$$\rho\ (\mathrm{g/cm^3}) = 1.0725 - 7.259 \times 10^{-4}t + 1.160 \times 10^{-7}t^2 \qquad 25\text{–}120\ ^\circ\mathrm{C}$$

$$\alpha\ (\mathrm{deg^{-1}}) = 6.77 \times 10^{-4} + 2.42 \times 10^{-7}t \qquad 25\text{–}120\ ^\circ\mathrm{C}$$

$$\gamma\ (\mathrm{bar/deg}) = 1.381 \times 10 - 5.136 \times 10^{-2}t + 4.66 \times 10^{-7}t^2 \qquad 20\text{–}120\ ^\circ\mathrm{C}$$

where t is the centigrade temperature. The respective equation-of-state parameters used for calculations of various thermodynamic quantities for mixtures can be

Table II
Heats of Mixing for the PVME/PS System at 50 °C[a]

concn							
w_{PS}[b]	ϕ_{PS}	ΔH_1, J/g	ΔH_2, J/g	ΔH_3, J/g	ΔH_4, J/g	ΔH^M, J/g	ΔH^M, J/mol
0.0	0.0	-1.82			-1.82	0.0	0
0.195	0.196			-0.31	-1.53	-0.98	-103
0.317	0.318			-0.31	-1.70	-1.05	-110
0.414	0.415			-0.47	-1.18	-1.91	-200
0.495	0.496			-0.53	-1.02	-2.30	-240
0.594	0.595			-0.56	-0.77	-2.77	-289
0.594	0.595			-0.56	-0.77	-2.77	-289
1.0	1.0		-3.78		-3.78	0.0	0

[a] ΔH^M (J/g) = $w_{PVME}\Delta H_1 + w_{PS}\Delta H_2 + \Delta H_3 - \Delta H_4$. [b] Weight fraction of PS.

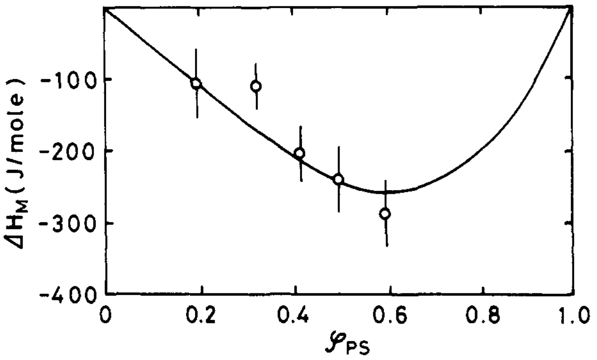

Figure 1. Heats of mixing for the PVME/PS system at 50 °C. The solid line is a calculated curve.

obtained from ρ or specific volume, v_{sp}, α and γ using the following reduced equations-of-state

$$\tilde{v}^{1/3} = 1 + \alpha/3(1 + \alpha T) \tag{17}$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{18}$$

$$p^* = \gamma T\tilde{v}^2 \tag{19}$$

Table I shows the values of the equation-of-state parameters obtained thus for PVME together with the values for PS obtained by Höcker et al.[33]

It is very difficult to measure directly heats of mixing for polymer/polymer systems. Therefore, such heats of mixing have been obtained indirectly using the following thermodynamic cycle according to Hess' law.[34-36]

$$\begin{tikzcd} \text{polymer 1} \arrow[d, "\Delta H_1"'] & + & \text{polymer 2} \arrow[d, "\Delta H_2"'] \arrow[r, "\Delta H^M"] & \text{1/2 mixture} \arrow[d, "\Delta H_4"'] \\ \text{solution 1} & + & \text{solution 2} \arrow[r, "\Delta H_3"] & \text{solution 1/2} \end{tikzcd}$$

From the above cycle, we can obtain heats of mixing, ΔH^M, for polymer 1/polymer 2 systems from

$$\Delta H^M = \Delta H_1 + \Delta H_2 + \Delta H_3 - \Delta H_4 \tag{20}$$

In Table II are shown the experimental results of ΔH_i in the respective steps for the present system. The value for the pure PS, which is in the glassy state at 50 °C, was corrected to the value in the liquid state by using the following equations for the specific heats

glassy state

$$c_p \text{ (J/K mol)} = 7.7551 \times 10^5 T^{-2} + 0.53447T - 41.58$$

liquid state

$$c_p \text{ (J/K g)} = 0.59800 + 3.3013 \times 10^{-3} T$$

where these equations in the glassy and liquid states were obtained experimentally by Wunderlich[37] and Karasz,[38] respectively. The glass transition temperature T_g was taken to be 371.6 K. The heats of mixing, ΔH^M, expressed in joules per total segment per mole listed in the last column were converted from joules per total polymer weight in the 7th column to the value per segment using

$$\Delta H^M \text{ (J/mol)} = \Delta H/[(m_1 + m_2)(w_1 v_{sp,1}^*/v^* + w_2 v_{sp,2}^*/v^*)] \tag{21}$$

where $\Delta H/(m_1 + m_2)$ is the heat of mixing per gram. The values of ΔH^M (J/mol) are also plotted against ϕ_{PS} in Figure 1. As shown in Figure 1 and Table II, ΔH^M was negative as expected from the theory for an LCST-type system.

Table III
Densities and Excess Volume Ratios for the PVME/PS Mixture at 50 °C

w_{PS}	ϕ_{PS}	ρ, g/cm^3	$V^E/V^\circ \times 10^3$
0.295	0.296	1.0479	-1.7
0.314	0.315	1.0440	-1.9
0.495	0.496	1.0490	-2.8
0.588	0.589	1.0507	-2.7

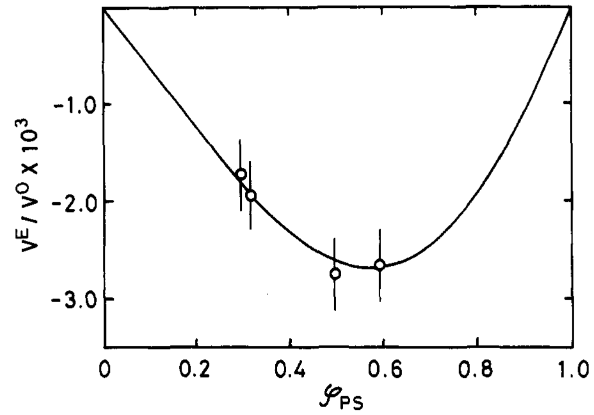

Figure 2. Excess volume ratios for the PVME/PS system at 50 °C. The solid line is a calculated curve.

The result of the excess volume is shown in Table III and Figure 2. Also, the cloud points are plotted against ϕ_{PS} in Figure 3.

Application of Equation-of-State Theory. As described in Theoretical Background, various thermodynamic properties can be theoretically obtained by the use of the equation-of-state parameters, X_{12}, and c_{12}. When X_{12} and c_{12} are determined so that both ΔH^M and V^E/V° calculated from eq 13 and 15, respectively, can fit the respective experimental data, we obtain X_{12} = -9.0 J/cm^3 and c_{12} = 0.020. In these calculations, the equation-of-state parameters at 50 °C and s_2/s_1 = 0.88 evaluated from Bondi's table[39] were used, and the core volume per

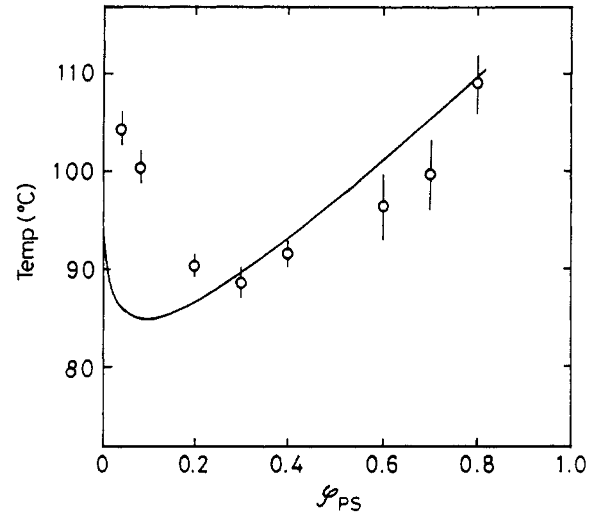

Figure 3. Cloud point curve for the PVME/PS system: M_V(PVME) = 5.28 × 10^4; M_W(PS) = 1.1 × 10^5. The solid line is a calculated binodal curve.

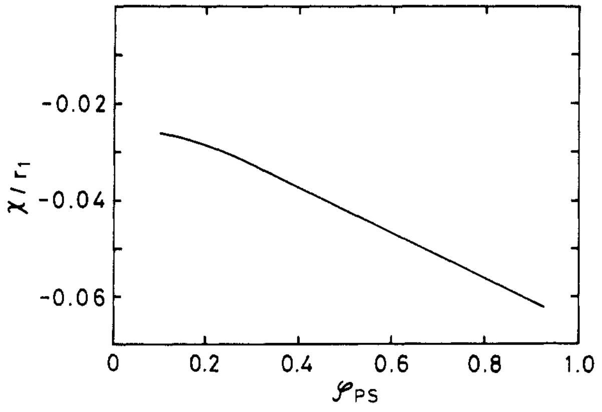

Figure 4. Calculated concentration dependence of the interaction parameter per segment at 50 °C.

segment was assumed to be equal to the core volume of styrene monomer. Here, the subscripts 1 and 2 indicate PVME and PS, respectively. As shown in Figures 1 and 2, the calculated curves of ΔH^M and V^E/V° can reproduce well the concentration dependences.

The negative value of X_{12} obtained here means that a specific interaction is dominant in this system, as suggested in the FT-IR studies by Garcia.[40] Strictly speaking, the Flory-type equation-of-state theory may be valid for only dispersion force-dominant systems. The specific interactions cannot be expressed by the van der Waals type interaction and also may induce some orientation of molecules or segments, which leads to nonrandom mixing. The theoretical treatment accounting for this effect was first carried out by Guggenheim.[41] Very recently, Balazs and Sanchez[42] incorporated the specific interaction term into the lattice fluid theory and discussed the contribution of this term to the phase diagram. Since the specific interaction in the present system is not so strong, the Flory-type equation-of-state theory may be applicable to this system.

The binodal curve calculated using the above values of X_{12} and c_{12} together with the equation-of-state parameters at 100 °C is shown in Figure 3. In the present theoretical treatment, we used only the parameters X_{12} and c_{12} determined from the experimental ΔH^M and V^E/V° but did not use the completely adjustable parameter Q_{12}, which was introduced to adjust only free energy and therefore does not contribute to any thermodynamic functions except the free energy. Taking into account this, the modified equation-of-state theory gives satisfactory agreement with the experimental results for the binodal curve as well as ΔH^M and V^E though the calculated binodal curve somewhat deviates from the experimental cloud point curve. If the Q_{12} parameter was used in the present system, the calculated binodal curve could be more adjusted to the experimental one.

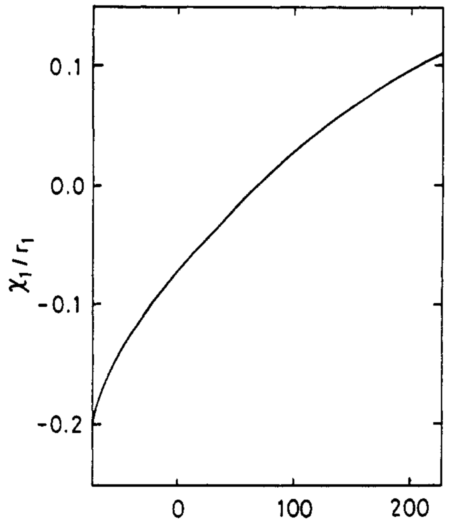

Figure 5. Calculated temperature dependence of the interaction parameter per segment.

Figure 4 shows the concentration dependence of the interaction parameter χ per segment, χ/r_1, at 100 °C. The calculated concentration dependence that χ decreases with increasing concentration of PS is in agreement with the results obtained by other measurement techniques for the present system, vapor sorption,[18] gas-liquid chromatography,[43] osmotic pressure,[10] and neutron-scattering[44,45] measurements. Particularly, our calculated values are in good agreement with those obtained from the neutron-scattering measurements by Shibayama et al.[45]

Figure 5 shows the temperature dependence of χ/r_1 extrapolated to $\phi_{PS} = 0$, χ_1/r_1, calculated using eq 10. χ_1/r_1 increases monotonically from a negative to a positive value. This tendency can be expected from the theory with a negative value of X_{12}, i.e., for specific interaction-dominant systems. In this case, the theory predicts that only an LCST but not a UCST exists for the present system.

Conclusion

In this system, both enthalpy changes and excess volumes measured near the LCST were negative. In application of equation-of-state theory to the system, the exchange enthalpy parameter, X_{12}, was negative, which suggests that a specific interaction is dominant in this system and that only an LCST exists at least theoretically.

Registry No. PS, 9003-53-6; PVME, 9003-09-2.

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Fluorescence Studies of Aqueous Solutions of Poly(*N*-isopropylacrylamide) below and above Their LCST

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ABSTRACT: Pyrene-labeled poly(*N*-isopropylacrylamides) (PNIPAM/Py) have been prepared by reaction of a copolymer of *N*-isopropylacrylamide and *N*-(acryloxy)succinimide with [4-(1-pyrenyl)butyl]amine. The fluorescence spectra of the labeled polymers in methanol are typical of isolated random-coil polymers. The emission of PNIPAM/Py in aqueous solutions at room temperature is characterized by a strong excimer emission attributed to ground-state pyrene aggregates. At polymer concentrations lower than 1 ppm there is evidence for the formation of single polymer micelles, when the level of labeling is high enough. At higher concentration both inter- and intrapolymeric aggregation takes place. Heating the polymer solutions above their lower critical solution temperature (LCST) results in the disruption of the pyrene aggregates, as evidenced by an increase of the pyrene monomer emission at the expense of the excimer emission. Results are interpreted in terms of interactions between polymer chains and between the polymer and water, which involve hydrogen bonding and hydrophobic interactions. The labeled polymers were also added as polymeric probes to solutions of poly(*N*-isopropylacrylamide). They become incorporated in the polymer-rich phase above the LCST.

Introduction

Polymers prepared from acrylamides exhibit unusual solution properties. The simplest analogue, polyacrylamide, is a water-soluble polymer. Poly(*N*-methylacrylamide) and poly(methacrylamide) are also water soluble, but poly(*N*-*n*-butylacrylamide) and poly(*N*-*tert*-butylacrylamide) are not. Other analogues are soluble in cold water but separate from solution upon heating. Aqueous solutions of poly(*N*-isopropylacrylamide) (PNIPAM) possess this interesting property. They exhibit a lower critical solution temperature (LCST) at 31–32 °C. This thermoreversible phase-separation property of PNIPAM was reported first by Heskins and Guillet.[1] Since then ingenious applications of this behavior of the PNIPAM aqueous solutions have been described. For instance, membranes consisting of PNIPAM or its copolymers with selected *N*-alkylacrylamides possess thermoselective permeability toward a large range of water-soluble permeants.[2] They are such that, as the temperature of the water increases, the flux of permeants through the membrane decreases. Recently Okahata and his co-

0024-9297/90/2223-0233$02.50/0