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Application of Equation-of-State Theory to Random Copolymer Blends with Upper Critical Solution Temperature Type Miscibility

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ABSTRACT: The Flory interaction parameters χ for blends of random copolymers consisting of binary combinations of methyl methacrylate (MMA), *n*-butyl methacrylate (nBMA), and isobutyl methacrylate (iBMA) monomers were calculated using the Flory equation-of-state theory with modified combining rules extended to random copolymer systems. In order to determine the intersegmental or intermolecular parameters necessary for the calculation of χ for the blends, osmotic pressures, heats of mixing at infinite dilution, and excess volumes of mixing for solutions of the methacrylate random copolymers in cyclohexanone were measured, and the equation-of-state theory was applied to these solutions. Using the intersegmental parameters thereby determined, the theory gives U-shaped curves for the temperature dependence of χ for the blends. Namely, the theory shows that miscibility of these polymer blends is of the upper critical solution temperature type, which is consistent with the miscibility results obtained experimentally in our previous work. The interaction parameters χ calculated for PiBMA/PnBMA were much smaller than those for PMMA/PiBMA and PMMA/PnBMA. This result is also consistent with the experimental results of miscibility. The calculated χ parameters were compared with those evaluated using two other methods, i.e., from the dependence of miscibility on the copolymer composition of the random copolymer blends and from the osmotic pressures for the random copolymer solutions. It was found that the χ values obtained using all three methods were nearly the same.

Introduction

Equation-of-state theories such as the Flory−Patterson free volume theory[1−4] and the Sanchez-Lacombe lattice fluid theory[5,6] have been developed to describe successfully thermodynamic properties including miscibility behavior for polymer blends. For liquid−liquid phase equilibria, neither of the above two theories is superior to the other, as pointed out by Sanchez himself.[7] An integral equation theory has also been applied to polymer systems recently by Curro and Schweizer.[8,9] Of these equation-of-state approaches, the Flory−Patterson free volume theory based on the principle of corresponding states has been applied to many polymer solutions[2,10−14] and polymer blends[15−19] because of its practical advantages and simple physical meaning. In this theory, thermodynamic properties for mixtures are expressed in terms of free volume and interaction energy contributions, and in actual evaluations the equation-of-state parameters (or characteristic parameters) for the pure components, which are necessary for calculations of mixtures, have been estimated from experimental pressure−volume−temperature relations. As long as this evaluation technique is used, as shown previously by Fujisawa et al.,[20,21] all van der Waals-like equation-of-state theories based on the corresponding states principle give almost the same thermodynamic results for polymer solutions at a constant temperature and pressure.

According to the Flory−Patterson theory,[1−4] the Flory−Huggins interaction parameter χ is composed of enthalpic and free volume contributions. Occurrences of UCST (upper critical solution temperature) and LCST (lower critical solution temperature) can be explained by two kinds of temperature dependences of the χ parameter, as shown schematically in Figure 1. In systems where van der Waals interactions are dominant, the χ parameter is positive over all temperatures and its temperature dependence is U-shaped (curve c), which leads to occurrences of both UCST and LCST. In attractive interaction-dominant systems where only an LCST occurs, on the other hand, the χ parameter is represented by a monotonically increasing function which changes from negative to positive with temperature (curve c′). Since critical values of χ for high

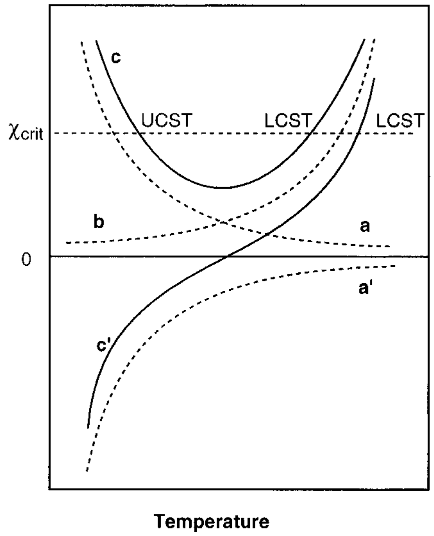

Figure 1. Schematic illustration of the temperature dependence of χ: (a and a′) the enthalpic interaction terms in van der Waals interaction dominant and attractive interaction dominant systems, respectively; (b) the free volume term; and (c and c′) χ = (a) + (b) and χ = (a′) + (b), respectively.

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molecular weight polymer blends are very small, reflecting the small combinatorial entropy on mixing, most miscible blends found so far are of the latter type, and UCST behavior following the former case is very rare. Only when the minimum of the U-shaped curve for χ is small enough to satisfy the critical condition, can a UCST appear. Such a very small value of χ may be realized when both the enthalpic interactions and free volume differences are very small. Therefore, polymer blends having UCST-type miscibility have been limited to blends containing random copolymers.[22,23] In some random copolymer blends, both the enthalpic interactions and free volume differences may be forced to be small by appropriate combinations of the constituent monomers. In a previous paper[24] we reported that homopolymer blends as well as copolymer blends composed of a series of different methacrylate monomers indicated UCST-type miscibility. In this case, since the constituent monomers have similar chemical structures, small χ values may be realized.

The Flory equation-of-state theory has been extended to apply to random copolymer systems and to describe successfully miscibility behavior peculiar to the random copolymer blends such as miscibility and immiscibility windows.[25−27] In this theory some combining rules for random copolymer systems are assumed. According to these combining rules, the characteristic and intermolecular parameters for random copolymer systems can be evaluated using the characteristic and intersegmental parameters for the constituent monomer segments. If these parameters for the monomer segments have been assembled, therefore, one can calculate thermodynamic properties for mixtures of various random copolymers composed of the corresponding monomers. In the present paper, this equation-of-state theory is applied to the above random copolymer and homopolymer blends consisting of the different methacrylate monomer units. In particular, its applicability to UCST-type blends is verified by calculations of the temperature dependence of χ. The calculated χ parameters between the different methacrylate polymers are compared with miscibility behavior observed for the same polymer pairs. Furthermore, the χ values evaluated using the equation-of-state theory are also compared with those obtained using two other methods, i.e., from the dependence of miscibility on the copolymer composition observed for the random copolymer blends[24] and from the χ parameters obtained by osmotic pressure measurements for the copolymer solutions in the solvent. For these purposes, osmotic pressures, heats of mixing at infinite dilution, and volume changes on mixing for solutions of poly(methyl methacrylate-*ran*-isobutyl methacrylate) (MMA·iBMA) and poly(isobutyl methacrylate-*ran*-*n*-butyl methacrylate) (iBMA·nBMA) in cyclohexanone (CHN) were measured, and the equation-of-state theory was applied to these random copolymer solution results to determine the intersegmental parameters.

Theoretical Section

Combining Rules and Thermodynamic Functions for Binary Polymer Blends. To calculate the interaction parameters χ for polymer blends using the equation-of-state theory[1−2] based on the principle of corresponding states, it is required to determine the characteristic or reduction parameters of volume (v^*), pressure (p^*), and temperature (T^*) for the component polymers 1 and 2, and their mixtures. According to the equation-of-state theory with modified combining rules,[18,19,28−30] the following combining rules are assumed for binary mixtures consisting of N_1 r_1-mers and N_2 r_2-mers on the basis of the one-fluid model. For the characteristic volume per segment

$$v^* = {\sigma_1}^2 v_1^* + 2\sigma_1\sigma_2 v_{12}^* + {\sigma_2}^2 v_2^* \tag{1}$$

where

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

For the characteristic pressure

$$p^* = [\sigma_1\theta_1 p_1^*(v_1^*)^2 + \sigma_2\theta_2 p_2^*(v_2^*)^2 + 2\sigma_1\theta_2 p_{12}^*(v_{12}^*)^2]/(v^*)^2 \tag{3}$$

Here, σ_i (i = 1 and 2) and θ_i are the segment and site fractions, respectively, given by

$$\sigma_1 = 1 - \sigma_2 = r_1N_1/(r_1N_1 + r_2N_2) \tag{4}$$

$$\theta_1 = 1 - \theta_2 = s_1r_1N_1/(s_1r_1N_1 + s_2r_2N_2) \tag{5}$$

where s_i is the number of contact sites or surface per segment. $p_{12}{}^*$ in eq 3 is related to the exchange enthalpy parameter X_{12}

$$X_{12} = p_1^* + (v_2^*/v_1^*)(s_1/s_2)p_2^* - 2(v_{12}^*/v_1^*)p_{12}^* \tag{6}$$

For the external degrees of freedom (c)

$$c = \sigma_1c_1 + \sigma_2c_2 - \sigma_1\theta_2c_{12} \tag{7}$$

where c_{12} is a parameter characterizing the deviation from additivity. Since the parameter c is related to the characteristic temperature by the following definition,

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

the characteristic temperature for the mixture is expressed by

$$1/T^* = (\sigma_1p_1^*v_1^*/T_1^* + \sigma_2p_2^*v_2^*/T_2^* - \sigma_1\theta_2Rc_{12})/(p^*v^*) \tag{9}$$

From both the partition function proposed by Flory et al.[1,2] and the above combining rules the interaction parameter χ and the heat of mixing $\Delta H^{\rm M}(\infty)$ at infinite dilution are derived as follows:

The interaction parameter χ can be written as

$$\chi = (\mu_1 - \mu_1^{\rm o})^{\rm R}/RT{\phi_2}^2 = (\mu_1 - \mu_1^{\rm o})/RT{\phi_2}^2 - [\ln(1 - \phi_2) + (1 - r_1v_1^*/r_2v_2^*)\phi_2]/{\phi_2}^2 \tag{10}$$

with the residual chemical potential

$$\begin{aligned}(\mu_1 - \mu_1^{\rm o})^{\rm R} = {} & r_1RT\{3{\theta_2}^2c_{12}\ln[(2\pi mkT)^{1/2}/h(gv^*)^{1/3}(\tilde{v}^{1/3} - 1)] + 3c_1\ln(m_1/m)^{1/2} + (3/2)c(m - m_1)/m\} + \\ & p_1^*r_1v_1^*\tilde{T}_1\{\ln(v_1^*/v^*) + 3\ln[({\tilde{v}_1}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]\} + \\ & 2p^*r_1v^*T(v^* - \sigma_1v_1^* - \sigma_2v_{12}^*)/v^* + \\ & (p^*r_1v^*/\tilde{v})[(\theta_1/\sigma_1) - 2(v^* - \sigma_1v_1^* - \sigma_2v_{12}^*)/v^* - 2(\theta_1p_1^*(v_1^*)^2 + \theta_2p_{12}^*(v_{12}^*)^2)/(p^*(v^*)^2)]\end{aligned} \tag{11}$$

where ϕ_i is the core volume fraction of component i given by

$$\phi_i = r_i N_i v_i^*/(r_1 N_1 v_1^* + r_2 N_2 v_2^*) \quad (12)$$

$\tilde{T}$ and $\tilde{v}$ are the reduced temperature and volume, respectively, defined by

$$\tilde{T} = T/T^* \quad (13)$$

$$\tilde{v} = v/v^* \quad (14)$$

and g is a geometric factor which has been taken as $(4\pi/3)2^{1/2}$.[28–30] The heat of mixing at infinite dilution per gram of component 2 is

$$\Delta H^{\mathrm{M}}(\infty) = (p_1^* v_{\mathrm{sp},2}^*/\tilde{v}_1)(v_1^*/v_2^*)(1 + \alpha_1 T)[(s_2/s_1) + 2(v_{12}^*/v_1^*) - 2] + p_2^* v_{\mathrm{sp},2}^*[\alpha_1 T(T_1^*/T_2^*)/\tilde{v}_1 + 1/\tilde{v}_2] - 2(\tilde{p}_{12}^* v_{\mathrm{sp},2}^*/v_1)(v_1^*/v_2^*)(v_{12}^*/v_1^*)^2(s_2/s_1)(1 + \alpha_1 T) - RTc_{12}(v_{\mathrm{sp},2}^*/v_2^*)(s_2/s_1)[(3/2) + \alpha_T/(\tilde{v}_1\tilde{T}_1)] \quad (15)$$

where $v_{\mathrm{sp},2}^*$ is the specific characteristic volume of component 2 and α_1 is the thermal expansion coefficient of component 1. The ratio of the excess volume (V^{E}) on mixing to the total volume (V^{o}) before mixing can be expressed as

$$V^{\mathrm{E}}/V^{\mathrm{o}} = \tilde{v}v^*/(\sigma_1\tilde{v}_1 v_1^* + \sigma_2\tilde{v}_2 v_2^*) - 1 \quad (16)$$

Combining Rules for Random Copolymer Systems. Following Shiomi et al.,[25,26] the characteristic parameters for random copolymers can be expressed in terms of those for the components of the copolymers and the intersegmental parameters s_B/s_A, X_{AB}, and c_{AB}. (In this paper, the subscripts A and B indicate the segments and the subscripts 1 and 2 the molecules.) The characteristic volume of copolymer 1 ($A_x\cdot B_{1-x}$) is given by

$$v_1^* = x^2 v_A^* + 2x(1 - x)v_{AB}^* + (1 - x)^2 v_B^* \quad (17)$$

where

$$v_{AB}^* = [(v_A^{*1/3} + v_B^{*1/3})/2]^3 \quad (18)$$

The characteristic pressure of copolymer 1 can be written as

$$p_1^* = [x\theta_{1A}p_A^* v_A^{*2} + (1 - x)\theta_{1B}p_B^* v_B^{*2} + 2x\theta_{1B}p_{AB}^* v_{AB}^{*2}]/v_1^{*2} \quad (19)$$

where the parameter $p_{AB}{}^*$ can be also related to X_{AB} as

$$X_{AB} = p_A^* + (v_B^*/v_A^*)(s_A/s_B)p_B^* - 2(v_{AB}^*/v_A^*)p_{AB}^* \quad (20)$$

The external degrees of freedom for copolymer 1 can be given by

$$c_1 = xc_A + (1 - x)c_B - x\theta_{1B}c_{AB} \quad (21)$$

The characteristic temperature for copolymer 1 is defined by

$$T_1^* = p_1^* v_1^*/c_1 R \quad (22)$$

Then

$$1/T_1^* = \{xp_A^*(v_A^*)^2/T_A^* + (1 - x)p_B^*(v_B^*)^2/T_B^* - x\theta_{1B}Rc_{AB}\}/(p_1^* v_1^*) \quad (23)$$

Table 1. Characteristics for Polymers Used in Experiments

sample[a]	$\bar{M}_w \times 10^{-5}$	triad tacticity, % mm	mr	rr
PiBMA	2.6	4	32	64
MMA·iBMA-83	2.0			
MMA·iBMA-51	2.4	5	31	64
MMA·iBMA-32	2.7			
iBMA·nBMA-50	1.5	6	36	58

[a] Numerals express copolymer composition of iBMA (wt %).

The combining rules for copolymer 2 ($C_y\cdot D_{1-y}$) are given by the same expressions as those for copolymer 1.

For a mixture of copolymers 1 and 2, s_1/s_2 can be evaluated from

$$s_1/s_2 = [xs_A + (1 - x)s_B]/[ys_C + (1 - y)s_D] \quad (24)$$

c_{12} is assumed to be

$$c_{12} = x\theta_{2C}c_{AC} + x\theta_{2D}c_{AD} + (1 - x)\theta_{2C}c_{BC} + (1 - x)\theta_{2D}c_{BD} \quad (25)$$

where

$$\theta_{1A} = 1 - \theta_{1B} = xs_A/\{xs_A + (1 - x)s_B\} \quad (26)$$

$$\theta_{2C} = 1 - \theta_{2D} = ys_C/\{ys_C + (1 - y)s_D\} \quad (27)$$

X_{12} can be expressed by the same equation as eq 6 with p_{12}^* given by

$$p_{12}^* = [x\theta_{2C}p_{AC}^* v(^*_{AC})^2 + (1 - x)\theta_{2C}p_{BC}^*(v_{BC}^*)^2 + x\theta_{2D}p_{AD}^*(v_{AD}^*)^2 + (1 - x)\theta_{2D}p_{BD}^*(v_{BD}^*)^2]/(v_{12}^*)^2 \quad (28)$$

Using the characteristic parameters and the intermolecular and intersegmental parameters given by eqs 17–28, various thermodynamic quantities for the mixture containing random copolymers can be calculated by use of eqs 10–16. In this study, the values of the characteristic parameters for the components of the copolymers are assumed to be equal to those for the corresponding homopolymers. The values of s_B/s_A, X_{AB}, and c_{AB} for the copolymer components will be determined from the thermodynamic quantities for the copolymer solutions in CHN.

Experimental Section

Materials. Poly(isobutyl methacrylate) (PiBMA), MMA·iBMA, and iBMA·nBMA were prepared by radical polymerization in bulk at 80 °C using 1.3 wt % of AIBN as an initiator. The conversion was controlled to be 20–30% to avoid copolymer composition drift. The resulting polymers were crudely fractionated using the acetone/methanol system. A large second fraction was used for measurements. The polymers obtained were purified by reprecipitating from acetone solution with a large excess of methanol and then dried under vacuum. Molecular weights were determined by gel permeation chromatography (GPC) relative to a polystyrene standard. The polydispersities were in the range of 1.4–1.7. Copolymer compositions and tacticities were determined by ^{1}H-NMR in $CDCl_3$ and ^{13}C-NMR in DMSO-d_6, respectively, using a JEOL-GMX270 apparatus. The polymers used for tacticity determination were converted into methyl esters, prior to the NMR measurements. The structural characteristics of the polymers used in this study are listed in Table 1.

Measurements. Specific volumes (v_{sp}) for PiBMA were measured by dilatometry in the temperature range from 90 to 170 °C at intervals of ca. 3 °C. The thermal expansion coefficients α for PiBMA were determined from the slope of temperature–v_{sp} curve. The interaction parameters χ for the polymer solutions were obtained from measured osmotic pressures π using

$$-\pi V_1/RT = \ln(1-\phi_2) + (1 - m_1 v^*_{sp,1}/m_2 v^*_{sp,2})\phi_2 + \chi\phi_2^{\,2} \tag{29}$$

where V_i and m_i are the molar volume and the mass, respectively, for component i ($i = 1$ and 2, indicating the solvent and polymer, respectively). The osmotic pressures were measured in a bath thermostated at 25 ± 0.03 °C by use of a high-pressure osmometer[12] similar to that used by Eichinger and Flory.[31] The heats of mixing at infinite dilution [$\Delta H^{M}(\infty)$] were measured by the electromotive force due to the heat occurring on mixing the polymer and solvent initially separated by mercury in a cell. Mixing was carried out by slowly shaking the calorimeter apparatus containing the cell inside. The calorimeter used was a Tian-Calvet microcalorimeter.[12] Since the polymers employed here are in the glassy state at the measurement temperature, the values of $\Delta H^{M}(\infty)$ measured by the calorimeter were corrected to the values in the liquid states by use of the specific heats in the glassy and rubbery states. The specific heats were determined by a differential scanning calorimeter (DSC) (Seiko I&E Ltd., DSC 20 with SSC/580 thermal controller and data system). The excess volumes on mixing (V^{E}/V^{o}) were determined from the densities ρ of each component and their mixtures by

$$V^{E}/V^{o} = (1/\rho)/(w_1\rho_1 + w_2\rho_2) - 1 \tag{30}$$

where w_i is the weight fraction of the component i.

Results and Discussion

In order to evaluate thermodynamic quantities for polymer blends, as mentioned in theoretical section, we need the characteristic parameters, v_{sp}*, T*, and p*, for the respective polymers. In addition to those, the intermolecular parameters, s_j/s_i, X_{ij}, and c_{ij}, are also required. These parameters for random copolymer systems can be evaluated from the characteristic and intersegmental parameters for the components of copolymers using the combining rules, eqs 17–28. The characteristic parameters for the copolymer components have been assumed to be identical with those for the corresponding homopolymers. The intersegmental parameters are also assumed to be equal to the intermolecular parameters for the corresponding homopolymer/homopolymer pairs. In a previous work,[26] the intersegmental parameters were determined using ternary solutions containing two kinds of homopolymers. In this study, the characteristic parameters for the homopolymers (i.e., the components of the random copolymers) are evaluated using Flory's method, and the intersegmental parameters are determined from the random copolymer solutions in CHN.

In this section, we first show the experimental results of thermodynamic properties for the solutions of the methacrylate random copolymer in CHN and apply the equation-of-state theory to these solutions, to determine the intersegmental parameters for the random copolymer systems. Prior to that, the characteristic parameters for the homopolymers are determined. Next, using the characteristic and intersegmental parameters determined thus, we describe the results of the χ parameters calculated for various polymer blends containing the random copolymer composed of different methacrylate monomer units. Finally, the polymer/polymer χ parameters obtained using three different methods are compared with one another.

Table 2. Characteristic Parameters for Homopolymers and Solvent at 25 °C

sample	v^*_{sp}, cm^3/g	v*, cm^3/segment mol	T*, K	p*, J/cm^3
PMMA[a]	0.7314	75.26	8271	609
PiBMA	0.7979	62.29	6566	584
PnBMA[a]	0.8103	66.73	6947	577
CHN[a]	0.8652	68.63	5534	628

[a] Determined in a previous work.[33]

Table 3. Osmotic Pressures (π) and Interaction Parameters (χ) at 25 °C[a]

w_2	ϕ_2	π, J/cm^3	χ
	CHN/MMA·iBMA-32		
0.1049	0.0910	0.0179	0.446
0.2297	0.1628	0.0854	0.453
0.2757	0.2455	0.1928	0.468
	CHN/MMA·iBMA-51		
0.0686	0.0601	0.00902	0.424
0.1041	0.0912	0.0221	0.427
0.1857	0.1650	0.0840	0.436
0.2428	0.2180	0.1625	0.445
	CHN/MMA·iBMA-83		
0.1369	0.1209	0.0381	0.438
0.1919	0.1751	0.0875	0.450
0.2394	0.2196	0.1538	0.452
	CHN/PiBMA		
0.0819	0.0760	0.0130	0.439
0.1361	0.1268	0.0436	0.438
0.2540	0.2389	0.1928	0.439
	CHN/iBMA·nBMA-50		
0.103	0.0963	0.1857	0.456
0.132	0.123	0.0352	0.453
0.188	0.177	0.0933	0.446
0.195	0.184	0.0976	0.453
0.216	0.204	0.138	0.444

[a] w_2 and ϕ_2 are the weight and core volume fractions of polymer, respectively.

Determination of Characteristic Parameters for Homopolymers. The characteristic parameters for the homopolymers and solvent were evaluated using Flory's method.[1,2] Namely, they were determined from the specific volume (v_{sp}), thermal expansion coefficient (α) and thermal pressure coefficient (γ), using the following equations:

$$\tilde{v}^{1/3} - 1 = (\alpha T/3)/(1 + \alpha T) \tag{31}$$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{32}$$

$$p^* = \gamma T \tilde{v}^2 \tag{33}$$

$$v^*_{sp} = v_{sp}/\tilde{v} \tag{34}$$

The characteristic parameters v^*_{sp} and T* for PiBMA were determined from the following results of v_{sp} and α measured at 90–170 °C in the present study:

$$v_{sp} = 0.9280 + 6.308 \times 10^{-4}t + 2.626 \times 10^{-7}t^2 \tag{35}$$

$$\alpha = 6.308 \times 10^{-4} + 5.252 \times 10^{-7}t \tag{36}$$

where t is the centigrade temperature. In the evaluation of the characteristic parameters, the values of v^*_{sp} and T* obtained in the above temperature range were extrapolated to 25 °C because PiBMA at 25 °C is in the glassy state. The characteristic pressure p* for PiBMA was determined from γ estimated according to the group contribution method proposed by Manzini and Crescenzi.[32] The characteristic parameters for PMMA and

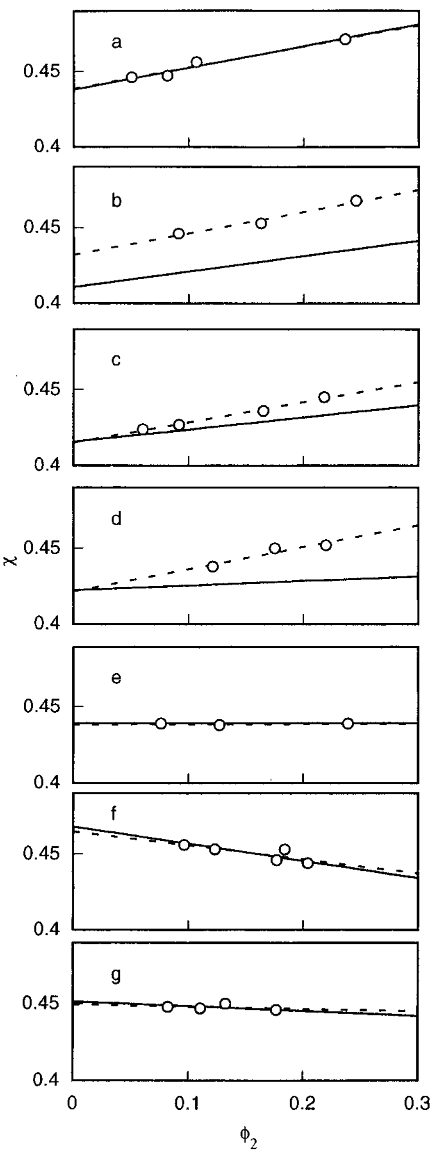

Figure 2. Dependence of interaction parameter χ on the core volume fraction ϕ_2 of polymer in CHN at 25 °C. The points were obtained from osmotic pressures: (a) PMMA, (b) MMA·iBMA-32, (c) MMA·iBMA-51, (d) MMA·iBMA-83, (e) PiBMA, (f) iBMA·nBMA-50, and (g) PnBMA. The solid curves were calculated by the equation-of-state theory; see the text.

PnBMA were obtained using the same method as in the previous work.[33]

The characteristic volume per segment of the component has been evaluated using the combination of the following equations:[28−30]

$$3cr = 2r + 1 \tag{37}$$

$$p^*rv^* = (p^*Mv^*_{\mathrm{sp}}) = rcRT \tag{38}$$

where eq 37 is the external degrees of freedom derived for flexible r-mers by Prigogine[34] and M is the molecular weight of r-mer.

These parameters are listed in Table 2.

Dependence of Thermodynamic Properties on Copolymer Composition for MMA·iBMA and iBMA·nBMA Solutions in CHN. (1) Experimental results. The experimental results of χ for the copolymer solutions in CHN determined from osmotic pressures at 25 °C by use of eq 29 are summarized in Table 3. In Figure 2 is shown the dependence of χ on the core volume fraction of polymer, together with the results for the solutions of the homopolymers PMMA and PnBMA obtained in the previous work.[33] The dashed lines in Figure 2 are experimental ones which are given by the following equations:

(a) $\chi = 0.4385 + 0.1390\phi_2$

for PMMA solutions[33]

(b) $\chi = 0.4318 + 0.1434\phi_2$

for MMA·iBMA-32 solutions

(c) $\chi = 0.4153 + 0.1322\phi_2$

for MMA·iBMA-51 solutions

(d) $\chi = 0.4218 + 0.1447\phi_2$

for MMA·iBMA-83 solutions

(e) $\chi = 0.4384 + 0.001470\phi_2$

for PiBMA solutions

(f) $\chi = 0.4647 - 0.09133\phi_2$

for iBMA·nBMA-50 solutions

(g) $\chi = 0.4497 - 0.01550\phi_2$

for PnBMA solutions[33]

The parameters χ_1 defined as

$$\chi_1 = \lim_{\phi_2 \to 0} \chi \tag{39}$$

are plotted against the copolymer composition in Figure 3.

The heats of mixing at infinite dilution [$\Delta H^{\mathrm{M}}(\infty)$] were obtained by correcting $\Delta H^{\mathrm{M}}{}_{\mathrm{app}}(\infty)$ measured with the Tian-Calvet microcalorimeter for the glass transition heats $\int\Delta C_p\,\mathrm{d}T$. The dissolution process of the glassy polymer in the solvent can be separated into two steps: transition from the glassy state to the rubbery state and then dissolution of the rubbery polymer in the solvent. Therefore, $\Delta H^{\mathrm{M}}(\infty)$ can be expressed as[35]

$$\Delta H^{\mathrm{M}}(\infty) = \Delta H^{\mathrm{M}}{}_{\mathrm{app}}(\infty) + \int\Delta C_p\,\mathrm{d}T \tag{40}$$

The values of $\int\Delta C_p\,\mathrm{d}T$ were evaluated from the area surrounded by two dotted−dashed lines and the specific heat curve shown in Figure 4. Here, it was approximated that the same amount of the glass transition heat as measured with DSC was generated on mixing the glassy polymer with the solvent, since the samples used for both calorimetric measurements had the same thermal history. The values of $\Delta H^{\mathrm{M}}_{\mathrm{app}}(\infty)$, $\int\Delta C_p\,\mathrm{d}T$, and $\Delta H^{\mathrm{M}}(\infty)$ are shown in Table 4, and the results of $\Delta H^{\mathrm{M}}(\infty)$ are plotted against the copolymer composition in Figure 5. The excess volumes on mixing (V^{E}/V°) for MMA·iBMA solutions are shown in Figure 6.

As shown in Figures 3 and 5, the dependences of both χ_1 and $\Delta H^{\mathrm{M}}(\infty)$ on the copolymer composition for the MMA·iBMA system are upward concave curves, while those for the iBMA·nBMA system are downward concave curves. These suggest that the interaction between

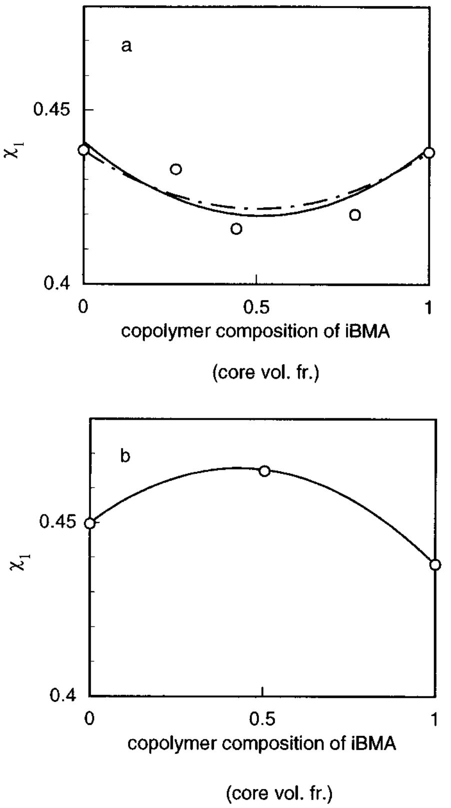

Figure 3. Dependence of χ_1 on the copolymer composition of iBMA: (a) CHN/MMA·iBMA system and (b) CHN/iBMA·nBMA system. The solid and dashed curves were calculated by the equation-of-state theory and eq 42, respectively. The solid curve in b indicates both calculated results, which were almost the same. In the calculations for a and b by use of eq 42, 0.060 and −0.00138 per molar core volume of CHN were used for $\chi_{\mathrm{MMA/iBMA}}$ and $\chi_{\mathrm{iBMA/nBMA}}$, respectively.

MMA and iBMA is repulsive while that between iBMA and nBMA is attractive.

(2) Application of Equation-of-State Theory and Determination of Intersegmental Parameters. We first apply the equation-of-state theory to the homopolymer solutions in CHN. In the calculations the intermolecular parameters of s_j/s_i, X_{ij}, and c_{ij} between the different components are necessary in addition to the characteristic parameters determined above for PMMA, PiBMA, PnBMA, and CHN. In the previous work[33] the intermolecular parameters for CHN/PMMA and CHN/PnBMA were determined as shown in Table 5. Therefore, we determine those for CHN/PiBMA here. The surface ratios s_j/s_i, in many cases, have been determined from the molecular models represented by a cylinder for polymers and a sphere for solvents[28] or from the van der Waals radius and surface obtained from Bondi's table.[36] The surface ratio s_j/s_i mainly affects the trend of χ with concentration.[12,25] In our previous work,[33] the slope of the χ vs concentration curve calculated for CHN/PMMA and CHN/PnBMA did not reproduce well the experimental one generated by use of the surface area obtained from Bondi's table. In this work, therefore, $s_{\mathrm{iBMA}}/s_{\mathrm{CHN}}$ was arbitrarily chosen to reproduce the slope of the ϕ_2−χ curve in Figure 2e, using the values of $X_{\mathrm{CHN/iBMA}}$ and $c_{\mathrm{CHN/iBMA}}$ shown in Table 5. Then, the theory gives good reproducibility of $\Delta H^{\mathrm{M}}(\infty)$, shown in Table 4, as well as χ, though the calculated $V^{\mathrm{E}}/V^{\mathrm{o}}$ deviates somewhat from the experimental one as compared between the curve a and the symbol (●) for the PiBMA solutions and between the curve a and the symbol (○) for the PMMA solutions in Figure 6.

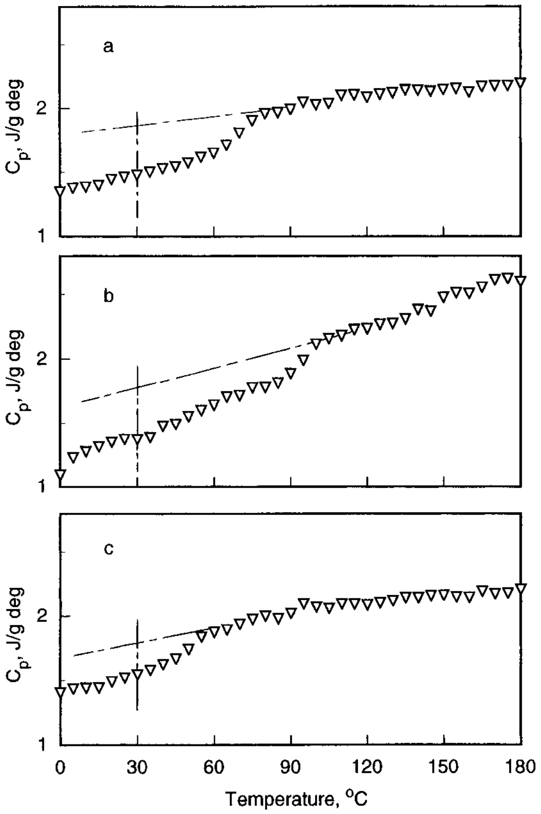

Figure 4. Specific heats measured by DSC for the polymers: (a) PiBMA, (b) MMA·iBMA-51, and (c) iBMA·nBMA-50. The regions surrounded by DSC thermograms and two dotted−dashed lines correspond to $\int \Delta C_p \, \mathrm{d}T$.

Table 4. Heats of Mixing at Infinite Dilution

system	$\Delta H^{\mathrm{M}}_{\mathrm{app}}(\infty)$,[a] J/g	$\int \Delta C_p \, \mathrm{d}T$,[b] J/g	$\Delta H^{\mathrm{M}}(\infty)$, J/g exptl[c]	calculated[d]
CHN/PMMA[e]	−13.6	30.5	16.9	16.5
CHN/MMA·iBMA-51	−10.8	25.3	14.5	14.6
CHN/PiBMA	−5.2	18.4	13.2	13.5
CHN/iBMA·nBMA-50	5.9	8.1	14.0	11.5
CHN/PnBMA[e]	7.7	0.5	8.2	8.2

[a] Measured at 30 °C with a Tian−Calvet calorimeter. [b] Determined from specific heats. [c] Obtained by $\Delta H^{\mathrm{M}}_{\mathrm{app}}(\infty) + \int \Delta C_p \, \mathrm{d}T$. [d] Values at 25 °C. [e] Obtained in a previous work.[33]

Applying the theory to the MMA·iBMA and iBMA·nBMA copolymer solutions, we have only to determine the intersegmental parameters for MMA/iBMA and iBMA/nBMA, because both the characteristic parameters for the random copolymers and the intermolecular parameters between the copolymer and solvent can be evaluated according to the combining rules eqs 17−28. The surface ratios $s_{\mathrm{iBMA}}/s_{\mathrm{MMA}}$ and $s_{\mathrm{nBMA}}/s_{\mathrm{iBMA}}$ can be obtained from $(s_{\mathrm{iBMA}}/s_{\mathrm{CHN}})/(s_{\mathrm{MMA}}/s_{\mathrm{CHN}})$ and $(s_{\mathrm{nBMA}}/s_{\mathrm{CHN}})/(s_{\mathrm{iBMA}}/s_{\mathrm{CHN}})$, respectively. X_{AB} and c_{AB} were determined to reproduce the experimental results of χ and $\Delta H^{\mathrm{M}}(\infty)$ as well as possible. The values of these intersegmental parameters determined thus are listed in the lower part of Table 5, together with those for MMA/nBMA evaluated in the previous work.[33] As shown by the solid curves in Figures 3 and 5, the equation-of-state theory reproduces well the dependences of χ and $\Delta H^{\mathrm{M}}(\infty)$ on the copolymer composition, in particular, upward and downward concave curves for the MMA·iBMA and iBMA·nBMA solutions, respectively. It should be noted here that X_{ij} is positive even for iBMA/nBMA with downward concave curves. As shown in Figure 6, although the calculated values of $V^{\mathrm{E}}/V^{\mathrm{o}}$ deviate from the

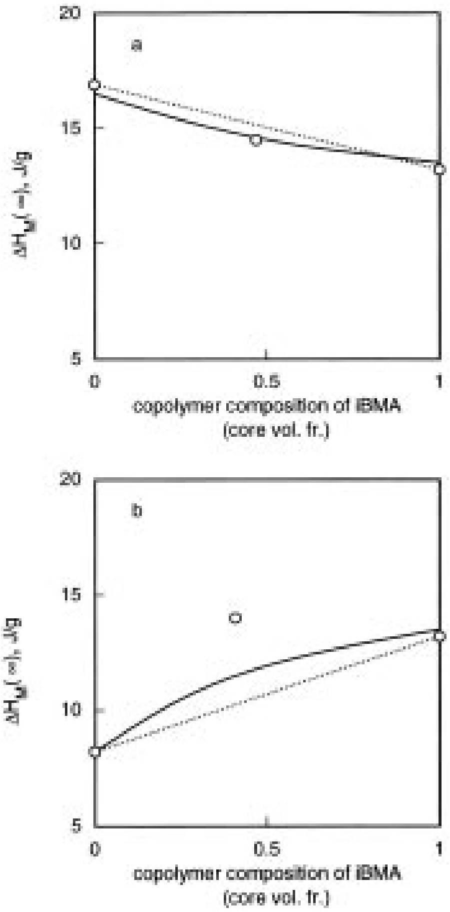

Figure 5. Copolymer composition dependence of heats of mixing at infinite dilution at 30 °C: (a) MMA•iBMA and (b) iBMA•nBMA. The solid curves were calculated by the equation-of-state theory at 25 °C; see the text.

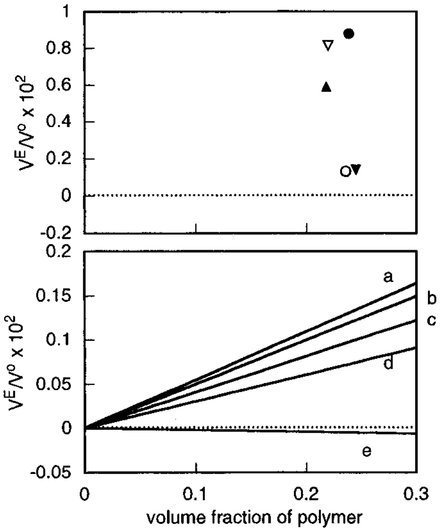

Figure 6. Excess volumes on mixing at 30 °C. The solid lines are theoretical at 25 °C. (● and a) PiBMA, (▽ and b) MMAiBMA-83, (▲ and c) MMA•iBMA-51, (▼ and d) MMA•iBMA-32, (○ and e) PMMA.

experimental ones in magnitude, their deviations are less than 10^{-2} and their copolymer composition dependence shows the same tendency as experiments. The combining rules used here for the random copolymer solutions successfully reproduce as a whole the dependences of the thermodynamic quantities on the copolymer composition.

Table 5. Intermolecular or Intersegmental Parameters

system (*i*/*j*)	s_j/s_i	X_{ij}, J/cm^3	c_{ij}
CHN/PMMA[a]	1.000	26.45	−0.0062
CHN/PiBMA	1.050	18.00	−0.0024
CHN/PnBMA[a]	1.100	9.93	0.0011
MMA/iBMA	1.050	11.50	−0.0001
iBMA/nBMA	1.048	0.0001	0.01
MMA/nBMA[a]	1.100	6.00	−0.001

[a] Determined in a previous work.[33]

Here, we note the dependences of the characteristic parameters on the copolymer composition for the random copolymers. Figure 7 shows the copolymer composition dependences of the characteristic parameters v^*_{sp}, p^*, and the reciprocal of T^*, respectively, for MMA•nBMA, MMA•iBMA, and iBMA•nBMA random copolymers, used in the above calculations for the copolymer solutions. From the original combining rules given by Flory,[1] the composition dependences of v^*_{sp} and $1/T^*$ are linear because the core volume size of the segments is taken to be equal for the constituent components and because the external degrees of freedom are additive, respectively. With our modified combining rules, on the other hand, both v^*_{sp} and $1/T^*$ are not linear with respect to the composition generally. p^* deviates from additivity in both our and Flory's combining rules because of the X_{AB} term. As shown in Figure 7-1, v^*_{sp} deviates downward from linearity. This tendency was shown experimentally[37] and theoretically[29] for poly(dimethylsiloxane) solutions. Figure 7-2 shows the dependence of p^* on the copolymer composition expressed in terms of the core volume fraction. According to the Flory combining rules, p^* deviates downward from additivity for positive X_{AB} and upward for negative X_{AB}, while with our modified combining rules the direction of the deviation depends on the core volume difference of the segment as well as the sign of X_{AB}. p^* values for the copolymers MMA•nBMA and iBMA•nBMA deviate upward in spite of a positive X_{AB} value. If the positive X_{AB} is larger, p^* could deviate downward slightly. The relation between $1/T^*$ and the composition also depends on the core volume difference as well as c_{AB}. The curves of $1/T^*$ for the copolymers MMA•nBMA and iBMA•nBMA deviate downward, as shown in Figure 7-3. These copolymer composition dependences of the characteristic parameters must be verified by experiment.

Calculation of χ Parameters for Copolymer Blends. In this subsection, we calculate the temperature dependence of χ for the polymer blends containing the random copolymers consisting of different methacrylate monomer units using the characteristic parameters and the intersegmental parameters determined in the preceding subsection. To avoid complication of the concentration dependence of χ, the calculations were carried out at $\phi_2 \to 0$.

Figures 8−11 show the calculated results of the temperature dependences of χ_1/r_1 for the blends of the random copolymer/homopolymer systems MMA•iBMA/PiBMA, MMA•nBMA/PnBMA, MMA•iBMA/PnBMA, and MMA•nBMA/PiBMA, respectively, with various copolymer compositions. As shown in these figures, the temperature−χ_1/r_1 curves calculated for the respective blends display a U-shaped curve for all the copolymer compositions, although the temperature dependence of χ_1/r_1 is slight in the high temperature range. A U-shaped curve of χ suggests an occurrence of UCST, as shown in Figure 1. Namely, the theory shows that these

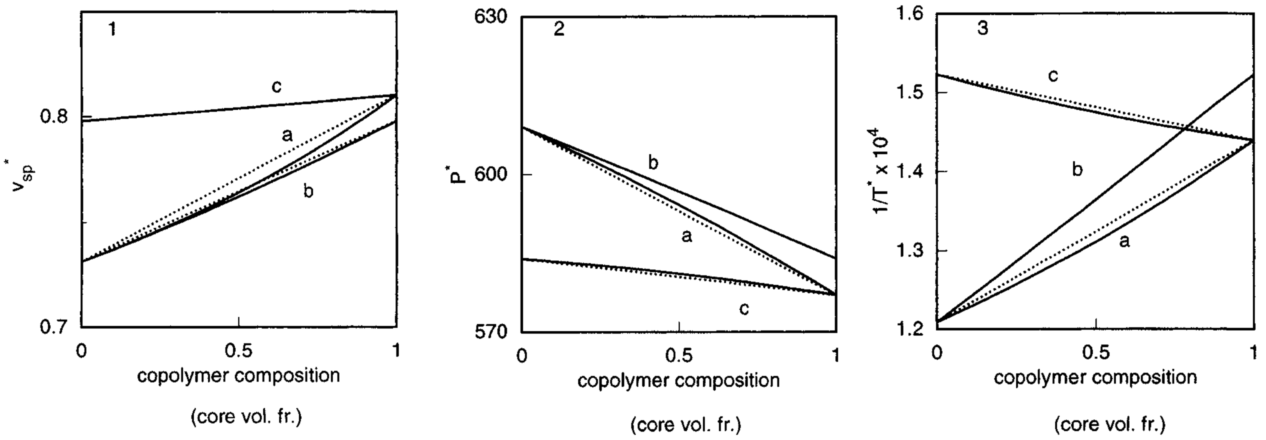

Figure 7. Dependence of the characteristic parameters on the copolymer composition expressed with the core volume fraction ϕ_B for the random copolymer (A·B): (a) MMA·nBMA, (b) MMA·iBMA, and (c) iBMA·nBMA; (1) specific characteristic voluem, (2) characteristic pressure, and (3) reciprocal characteristic temperature. The solid curves were calculated according to the combining rules, and the dotted lines represent a linear relation.

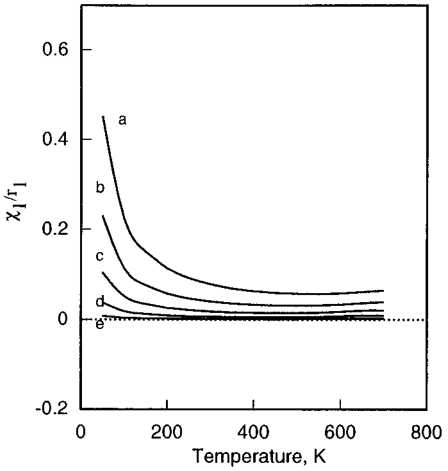

Figure 8. Temperature dependence of χ_1/r_1 calculated for MMA·iBMA/PiBMA blends with a variety of copolymer composition of iBMA: (a) 0 wt %, (b) 20 wt %, (c) 40 wt %, (d) 60 wt %, and (e) 80 wt %.

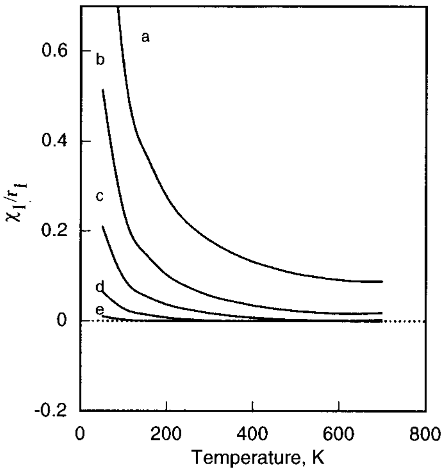

Figure 9. Temperature dependence of χ_1/r_1 calculated for MMA·nBMA/PnBMA blends with a variety of copolymer composition of nBMA: (a) 0 wt %, (b) 20 wt %, (c) 40 wt %, (d) 60 wt %, (e) 80 wt %.

polymer blends have UCST-type miscibility, as observed experimentally in the previous work.^{24} The slight temperature dependence of χ_1/r_1 in the high temperature range may be due to a small difference in the free volume because, as shown in Figure 1, the free volume term is dominant in that temperature range.

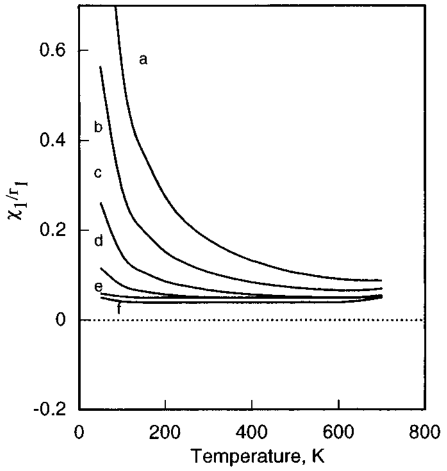

Figure 10. Temperature dependence of χ_1/r_1 calculated for MMA·iBMA/PnBMA blends with a variety of copolymer composition of iBMA: (a) 0 wt %, (b) 20 wt %, (c) 40 wt %, (d) 60 wt %, (e) 80 wt %, and (f) 100 wt %.

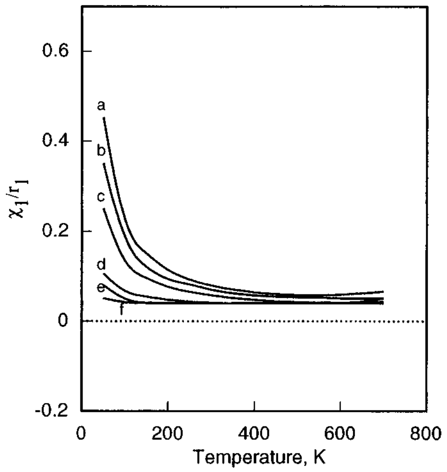

Figure 11. Temperature dependence of χ_1/r_1 calculated for MMA·nBMA/PiBMA blends with variety of copolymer composition of nBMA: (a) 0 wt %, (b) 20 wt %, (c) 40 wt %, (d) 60 wt %, (e) 80 wt %, and (f) 100 wt %.

The minimum of the U-shaped curve decreases with decreasing copolymer composition of MMA for MMA·iBMA/PnBMA and MMA·nBMA/PiBMA as well as MMA·iBMA/PiBMA and MMA·nBMA/PnBMA. As shown in Figure 12, on the other hand, the behavior of χ_1/r_1 for the iBMA·nBMA/MMA·iBMA-32 system does

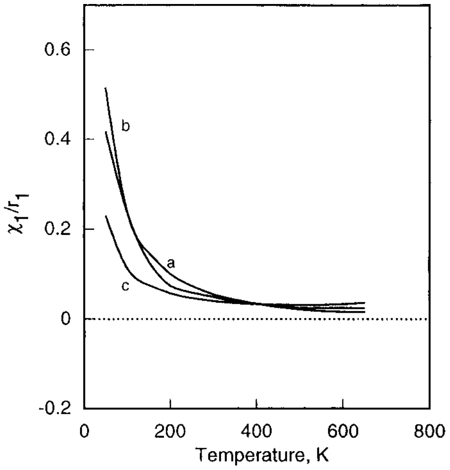

Figure 12. Temperature dependence of χ_1/r_1 calculated for iBMA·nBMA/MMA·iBMA-32 blends with variety of copolymer composition of iBMA: (a) 0 wt %, (b) 50 wt %, (c) 100 wt %.

not vary much with the copolymer composition of nBMA. These two contrasting results suggest that the interaction between iBMA and nBMA is very weak. According to the equation-of-state theory, the interaction parameter χ is composed of two terms consisting of a free volume difference and an enthalpic interaction. The free volume and the enthalpy are related to the characteristic temperature T^* and the characteristic pressure p^*, respectively. As shown in Table 2, the differences between PiBMA and PnBMA in both T^* and p^* are small, compared with those between PMMA and PiBMA and between PMMA and PnBMA. This leads to a small contribution of both terms to χ, namely to a very small value of χ between PiBMA and PnBMA.

Such a weak interaction for PiBMA/PnBMA is supported by its miscibility behavior reported in the previous paper.[24] The homopolymer blend of PiBMA/PnBMA at 50/50 wt/wt was not observed to be immiscible at least up to about 230 °C, while PMMA/PnBMA and PMMA/PiBMA were immiscible up to 150 and 190 °C, respectively. Namely, this miscibility behavior corresponds qualitatively to the interaction parameters χ calculated above. However, those values of χ_1/r_1 obtained from the equation-of-state theory do not become smaller than the critical values (0.001−0.002) given by

$$\chi_{crit}/r_1 = [r_1^{-1/2} + (r_2 v_2^*/v_1^*)^{-1/2}]^2/2 \qquad (41)$$

at the above experimental miscible−immiscible boundary temperatures. This may be due to the poor reproducibility of temperature dependence in the Flory-type equation-of-state, as seen by the fact that the characteristic parameters, i.e., reduction parameters, which should be independent of temperature depend on temperature.[20] In the present study the values of the characteristic parameters at 25 °C were used.

Comparison of χ Parameters Obtained Using Different Methods. Table 6 shows the χ values per MMA monomer evaluated at 25 °C using three different methods. The equation-of-state theory expresses χ in terms of the concentration dependence, as shown in Figure 13. Therefore, the values calculated at 50/50 wt blend ratio were shown in column I of Table 6. In another method the χ values were estimated from χ_1 in the CHN solutions using the following equation[38−40] for the solvent/random copolymer system ($1/C_y{\cdot}D_{1-y}$):

$$\chi_1 = y\chi_{1C} + (1-y)\chi_{1D} - y(1-y)\chi_{CD} \qquad (42)$$

The dashed and solid curves in a and b of Figure 3, respectively, were drawn according to eq 42, to fit the experimental results. The χ_{CD} values obtained using the experimental values of $\chi_{1/C}$ and $\chi_{1/D}$ for the homopolymer solutions were converted to those per MMA monomer because eq 42 was applied to the CHN solutions. The values determined thus are shown in column II together with that for PMMA/PnBMA evaluated in the previous work.[33] Column III shows the values of χ, which were extrapolated to 25 °C, obtained from the dependence of miscibility on the copolymer composition at 140−200 °C.[24] As compared in Table 6, the χ values obtained using the three methods are not so different from one another for each system. The value obtained for PiBMA/PnBMA using method II is negative, reflecting the downward concave curve of the copolymer composition dependence of χ shown in Figure 3b. On the other hand, χ calculated from the equation-of-state theory is positive for PiBMA/PnBMA in spite of the fact that the theory gives a downward concave curve for χ_1 with the CHN solutions. The χ values obtained from miscibility, i.e., using method III, are also positive for PiBMA/PnBMA. Since the interaction between PiBMA and PnBMA is very small in magnitude, it cannot be concluded at the present stage whether it is positive or negative.

Table 6. χ Parameters per Core Volume of MMA Monomer at 25 °C

system	I[a]	II[b]	III[c]
PMMA/PnBMA	0.129	0.0713	0.0812
PMMA/PiBMA	0.0746	0.0665	0.0682
PiBMA/PnBMA	0.0342	−0.00151	0.00186

[a] Calculated by use of the equation-of-state theory at 50/50 wt blend ratio. [b] Estimated from the dependence of χ_1 on the copolymer composition for the CHN solutions measured by osmometry. [c] Estimated from the dependence of miscibility on the copolymer composition.[24]

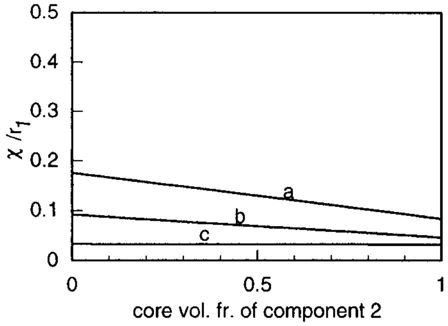

Figure 13. Concentration dependence of χ/r_1 at 25 °C calculated by use of the equation-of-state theory for polymer 1/polymer 2: (a) PMMA/PnBMA, (b) PMMA/PiBMA, and (c) PiBMA/PnBMA.

Conclusion

The Flory-type equation-of-state theory extended to random copolymer systems was applied to the blends of homopolymers and of random copolymers consisting of methacrylate monomers. Using the technique employed here for determination of the characteristic and the intermolecular parameters for random copolymer systems, the equation-of-state theory gives a U-shaped curve for the temperature dependence χ, namely UCST-type miscibility, for the methacrylate polymer blends. The correlation among the χ values evaluated for three kinds of methacrylate polymer pairs is consistent with their miscibility behavior. Furthermore, the magnitudes of χ evaluated using the equation-of-state theory are nearly the same as those obtained using two other methods. As shown in our previous papers,[26,27] the theory can express specific miscibility behavior such as miscibility windows. Therefore, accumulation of the characteristic and intersegmental parameters for various polymer systems will be useful for prediction of thermodynamic properties including miscibility for random copolymer blends.

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