Behavior of Temperature Dependence of χ Parameter in Random Copolymer Blends Showing an Immiscibility Window

Tsukasa SATO, Masato SUZUKI, Masao TOHYAMA, Masaki ENDO, Tomoo SHIOMI,[†] and Kiyokazu IMAI

Department of Materials Science and Technology, Nagaoka University of Technology, 1603–1 Kamitomioka, Nagaoka, Niigata 940–21, Japan

ABSTRACT: Previously miscibility for the blends of poly(vinyl chloride-*stat*-vinyl acetate) (VCVAc90, containing 90 wt% of VC) with poly(isobutyl methacrylate-*stat-n*-butyl methacrylate) (iBMAnBMA) was found to be like a so-called immiscibility window. In this work, the temperature dependence of the Flory–Huggins χ parameter was calculated for the VCVAc90/iBMAnBMA blends using the Flory-type equation-of-state theory extended to random copolymer systems. The equation-of-state parameters necessary for calculation of χ was determined using the experimental results of osmotic pressures and heats of mixing for solutions of these polymers in cyclohexanone (CHN). The temperature dependence of χ was a monotonically increasing function over all the copolymer compositions of iBMAnBMA copolymers, and there existed a range of copolymer compositions in which χ for the copolymer blends VCVAc90/iBMAnBMA was positive though χs for both homopolymer blends VCVAc90/PiBMA and VCVAc90/PnBMA (where VCVAc90 was regarded as a homopolymer) were negative. This corresponds qualitatively to miscibility behavior observed for the present copolymer blends. It was concluded that miscibility behavior in the present copolymer blends is one of two types of immiscibility windows classified previously by us.

KEY WORDS Immiscibility Window / Miscibility Window / Random Copolymer Blends / Interaction Parameter χ / Equation-of-State Theory /

Dependence of miscibility on copolymer composition for random copolymer blends has been investigated[1–8] theoretically and experimentally. In particular, so-called miscibility[1–5] and immiscibility[6,7] windows are typical miscibility behavior. The former window is that blends containing random copolymers are miscible in a certain range of the copolymer composition even though any binary combinations of their corresponding homopolymers are immiscible, while the latter window is the reverse case. This miscibility behavior can be explained on the basis of the copolymer composition dependence of the Flory–Huggins intermolecular interaction parameter χ which is expressed in terms of the intersegmental parameters χ_{ij} between the different constituent monomers.[2–4,7,9] Namely, the occurrence of the miscibility and immiscibility windows is based on a change of the sign of intermolecular χ with copolymer composition. Even though such situations are valid at certain temperatures, they may not be necessarily held at other temperatures because χ usually depends on temperature.

Equation-of-state theories such as the Flory–Patterson theory[10–13] and the Sanchez–Lacombe lattice fluid theory[14,15] have been developed to describe 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.[16] An integral equation theory has also been applied to polymer systems recently by Curro and Schweizer.[17,18] Of these equation-of-state approaches, the Flory–Patterson theory based on the principle of corresponding states has been applied to many polymer solutions[11,19–23] and polymer blends[24–28] because of its practical advantages and simple physical meaning. In this theory, thermodynamic

quantities for mixtures have been calculated using the characteristic parameters evaluated from experimental P–V–T relations for the pure components. As long as this evaluation technique is used, as shown previously by Fujisawa et al.,[29,30] all van der Waals-like equation-of-state theories based on the corresponding state principle give almost the same thermodynamic results for polymer solutions at a constant temperature and pressure.

According to the Flory–Patterson equation-of-state theory,[10–13] there are two kinds of temperature dependence of χ: a U-shaped curve in which χ is always positive and a monotonically increasing curve changing from negative to positive with increase in temperature. As described in our previous paper,[31] each window may be classified into further two types by change of such temperature-χ (T–χ) curves with copolymer composition. For immiscibility windows focused on in this work, there are two types of changes of the T–χ curve with copolymer composition: one is change from a monotonically increasing function of temperature to a U-shaped curve and again to a monotonically increasing function, and the other is a monotonically increasing function regardless of copolymer composition.

Previously we found that the blends of poly(vinyl chloride-*stat*-vinyl acetate) (VCVAc)/poly(isobutyl methacrylate-*stat-n*-butyl methacrylate) (iBMAnBMA) behave like an immiscibility window.[7] As shown in Figure 1, VCVAc with a copolymer composition of 90 wt% of VC (VCVAc90) was immiscible with iBMAnBMA in a certain range of copolymer composition at a certain temperature although any binary combination of the homopolymers, PiBMA, PnBMA, and VCVAc90, where VCVAc90 is regarded as a *homopolymer* to avoid com-
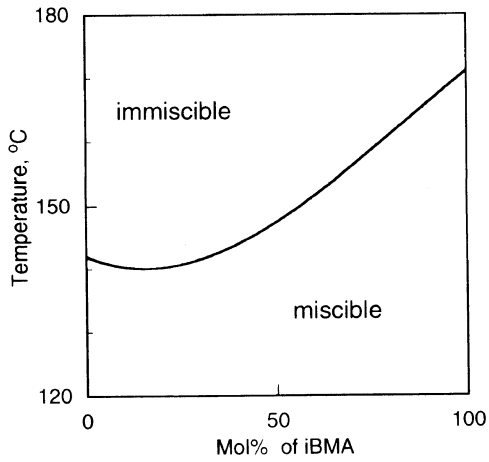

Figure 1. Dependence of miscibility on copolymer composition for VCVAc90/iBMAnBMA blends at 50/50 wt% blend ratio.[7]

plicated treatment of two kinds of copolymer compositions, was miscible at this temperature. In this work, we evaluated temperature dependence of χ for these blends showing immiscibility window-like behavior using the Flory equation-of-state theory extended to random copolymer systems, and obtained a change of the $T-\chi$ curve with copolymer composition. On the basis of the results obtained here and simulated in our previous work,[31] relations between behavior of $T-\chi$ curves and immiscibility windows for the present copolymer blends are discussed. For this purpose, the equation-of-state parameters necessary for calculation of χ were determined from osmotic pressures and heats of mixing for the binary and ternary solutions of VCVAc90, PiBMA, and PnBMA in cyclohexanone (CHN).

THEORETICAL

The Flory-type equation-of-state theory[10,11] starts from a partition function for N r-mers with external degrees of freedom of $3cr$ per molecule and expresses thermodynamic functions using the characteristic parameters of volume v^*, pressure p^*, and temperature T^*, and their reduced parameters $\tilde{v}(=v/v^*)$ and $\tilde{T}(=T/T^*)$. In the modified Flory equation-of-state theory[32-34], thermodynamic functions including the interaction parameter χ for binary mixtures comprising N_1 r_1-mers and N_2 r_2-mers can be written as follows: The interaction parameter defined by

$$\chi = (\mu_1 - \mu_1^0)^R/RT\phi_2^2 = (\mu_1 - \mu_1^0)/RT\phi_2^2$$
$$- [\ln(1-\phi_2) + (1-r_1v_1^*/r_2v_2^*)\phi_2]/\phi_2^2 \quad (1)$$

is expressed with the residual chemical potential

$$(\mu_1 - \mu_1^0)^R$$
$$= r_1 RT\{3\theta_2^2 c_{12}\ln[(2\pi mkT)^{1/2}/h(gv^*)^{1/3}(\tilde{v}^{1/3}-1)]$$
$$+ 3c_1\ln(m_1/m)^{1/2} + (3/2)c(m-m_1)/m\}$$
$$+ p_1^*r_1v_1^*\tilde{T}_1\{\ln(v_1^*/v^*) + 3\ln[(\tilde{v}_1^{1/3}-1)/(\tilde{v}^{1/3}-1)]\}$$
$$+ 2p^*r_1v^*\tilde{T}(v^* - \sigma_1v_1^* - \sigma_2v_{12}^*)/v^*$$
$$+ (p^*r_1v^*/\tilde{v})[(\theta_1/\sigma_1) - 2(v^* - \sigma_1v_1^* - \sigma_2v_{12}^*)/v^*$$
$$- 2(\theta_1p_1^*v_1^{*2} + \theta_2p_{12}^*v_{12}^{*2})/(p^*v^{*2})] \quad (2)$$

where ϕ_i ($i=1, 2$), θ_i and σ_i are the fractions of the core

volume, site and segment, respectively. m is the mass of the segment, and c_{12} is deviation from additivity of external degrees of freedom. g is the geometric factor which has been taken as $(4\pi/3)2^{1/2}$. The heat of mixing at infinite dilution per gram of component 2 is

$$\Delta H_M(\infty) = (p_1^* V_{sp,2}^*/\tilde{v}_1)(v_1^*/v_2^*)(1+\alpha_1 T)[(s_2/s_1)$$
$$+ 2(v_{12}^*/v_1^*) - 2] + p_2^*v_{sp,2}^*[\alpha_1 T(T_1^*/T_2^*)/\tilde{v}_1 + 1/\tilde{v}_2]$$
$$- 2(p_{12}^*v_{sp,2}^*/v_1)(v_1^*/v_2^*)(v_{12}^*/v_1^*)^2(s_2/s_1)(1+\alpha_1 T)$$
$$- RTc_{12}(v_{sp,2}^*/v_2^*)(s_2/s_1)[(3/2)+\alpha_1 T/(\tilde{v}_1\tilde{T}_1)] \quad (3)$$

In the derivation of the above $(\mu_1 - \mu_1^0)^R$ and $\Delta H_M(\infty)$, the following combining rules for binary mixture are assumed: v^* and p^* for the mixture are expressed as

$$v^* = \sigma_1^2 v_1^* + 2\sigma_1\sigma_2 v_{12}^* + \sigma_2^2 v_2^* \quad (4)$$

$$v_{12}^* = [(v_1^{*1/3} + v_2^{*1/3})/2]^3 \quad (5)$$

$$p^* = [\sigma_1\theta_1 p_1^* v_1^{*2} + \sigma_2\theta_2 p_2^* v_2^{*2} + 2\sigma_1\theta_2 p_{12}^* v_{12}^{*2}]/v^{*2} \quad (6)$$

where p_{12}^* is related to the exchange enthalpy parameter X_{12} by

$$X_{12} = p_1^* + (v_2^*/v_1^*)(s_1/s_2)p_2^* - 2(v_{12}^*/v_1^*)p_{12}^* \quad (7)$$

The external degrees of freedom c for the mixture are assumed to be

$$c = \sigma_1 c_1 + \sigma_2 c_2 - \sigma_1\theta_2 c_{12} \quad (8)$$

The characteristic temperature T^* can be obtained from eq 8 using the following relation:

$$p^*v^* = cRT^* \quad (9)$$

Therefore, thermodynamic functions can be calculated using the characteristic parameters for component polymers and intermolecular parameters such as the surface ratio of segments s_2/s_1, exchange enthalpy parameter X_{12} and deviation from additivity of external degrees of freedom c_{12}.

In the systems containing random copolymers,[35] the characteristic parameters for random copolymers and the intermolecular parameters can be obtained using the characteristic parameters for components of copolymers and the intersegmental parameters, s_B/s_A, X_{AB}, and c_{AB}. For the characteristic parameters of copolymer 2, $(A_x \cdot B_{1-x})$, the following combining rules are given on the assumption of random mixing of the segments:

$$v_2^* = x^2 v_A^* + 2x(1-x)v_{AB}^* + (1-x)^2 v_B^* \quad (10)$$

$$p_2^* = [x\theta_{2A}p_A^*v_A^{*2} + (1-x)\theta_{2B}p_B^*v_B^{*2} + 2x\theta_{2B}p_{AB}^*v_{AB}^{*2}]/v_2^{*2} \quad (11)$$

where

$$v_{AB}^* = [(v_A^{*1/3} + v_B^{*1/3})/2]^3 \quad (12)$$

and p_{AB}^* can be related to X_{AB} by

$$X_{AB} = p_A^* + (v_B^*/v_A^*)(s_A/s_B)p_B^* - 2(v_{AB}^*/v_A^*)p_{AB}^* \quad (13)$$

For the external degrees of freedom

$$c_2 = xc_A + (1-x)c_B - x\theta_{2B}c_{AB} \quad (14)$$

A copolymer effect, i.e., bonding effect between the segments, can be taken into account by the external degrees of freedom c_2. The characteristic temperature T_2^* can be given by eq 14 and the following equation:

$$p_2^* v_2^* = cRT_2^* \tag{15}$$

For the mixture of homopolymer 1 and copolymer 2, the intermolecular parameters p_{12}^* and c_{12} in eq 7 and 8, respectively, can be placed by

$$p_{12}^* = [\theta_{2A} p_{1A}^* v_{1A}^{*2} + \theta_{2B} p_{1B}^* v_{1B}^{*2}]/v_{12}^{*2} \tag{16}$$

$$c_{12} = \theta_{2A} c_{1A} + \theta_{2B} c_{1B} \tag{17}$$

and s_1/s_2 is expressed as

$$s_1/s_2 = s_1/[x s_A + (1-x) s_B] \tag{18}$$

EXPERIMENTAL

Materials

The molecular characteristics for the polymers used in this study are listed in Table I. Poly(isobutyl methacrylate) (PiBMA), poly(n-butyl methacrylate) (PnBMA) and poly(isobutyl methacrylate-$stat$-n-butyl methacrylate) (iBMAnBMA) were prepared by radical polymerization in bulk at 80°C using 1.3 wt% of AIBN as an initiator. The conversion was controlled within 20—30% to avoid copolymer composition drift. The resulting polymers were crudely fractionated using acetone/methanol system. A large second fraction was used for measurements. The polymers obtained were purified by reprecipitating from the acetone solution with a large excess of methanol, and then dried under vacuum. VCVAc copolymer containing 90 wt% of VC units (VCVAc90) was purchased from Scientific Polymer Products, Inc. (Ontario) and purified by precipitation from THF solution with a large excess volume of petroleum ether.

Measurements

The interaction parameters χ_p for ternary solutions containing two kinds of polymers were obtained from osmotic pressures π expressed as

$$-\pi V_s/RT = \ln(1-\phi_p) + (1 - m_s v_{sp,s}^*/m_1 v_{sp,1}^*)\phi_1$$
$$+ (1 - m_s v_{sp,s}^*/m_2 v_{sp,2}^*)\phi_2 + \chi_p \phi_p^2 \tag{19}$$

where V_i, m_1, and $v_{sp,i}^*$ are the molar volume, mass, and characteristic or core volume per gram, respectively, for component i ($i =$ s, 1 and 2 indicate the solvent and polymers 1 and 2, respectively) and ϕ_p is the total core volume fraction of polymers given by

$$\phi_p = \phi_1 + \phi_2 = 1 - \phi_s \tag{20}$$

The osmotic pressures were measured in a bath thermostatted at 25 ± 0.03°C by a high-pressure osmometer similar to that used by Eichinger and Flory.[36] Heat of mixing $\Delta H_M(\infty)$ at infinite dilution for glassy polymers was obtained by correcting the heat generated in the microcalorimeter for glass transition. 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, $\Delta H_M(\infty)$ can be expressed by[37]

$$\Delta H_M(\infty) = \Delta H_M^{app}(\infty) + \int \Delta C_p dT \tag{21}$$

where $\Delta H_M^{app}(\infty)$ is the heat generated on mixing in the microcalorimeter and $\int \Delta C_p dT$ is the heat of glass transition obtained from the temperature dependence of specific heats. The calorimeter used was a Tian–Calvet microcalorimeter. Specific heats were determined with a differential scanning calorimeter (DSC) (Seiko I & E Ltd., DSC 20 with SSC/580 thermal controller and data system) by calibration with sapphire.

RESULTS AND DISCUSSION

Determination of Characteristic and Intersegmental Parameters

To calculate thermodynamic functions for mixtures using the equation-of-state theory, we need the characteristic and intermolecular parameters. For the systems containing random copolymers, as described in the theoretical section, the characteristic and intermolecular parameters can be evaluated from those for the copolymer components using eq 10—18. The values of these parameters for the copolymer components have been assumed to be equivalent to those for the corresponding homopolymers. To calculate χ parameters for the VCVAc90/iBMAnBMA blends, therefore, we need the characteristic parameters for VCVAc90, iBMA, and nBMA and the intermolecular or intersegmental parameters for VCVAc90/iBMA, VCVAc90/nBMA, and iBMA/nBMA. Since the characteristic parameters for these polymers and the intersegmental parameter for iBMA/nBMA were determined in our previous work,[35,38,39] as shown in Tables II and III, respectively, we have only to determine the intersegmental parameters for VCVAc90/iBMA and VCVAc90/nBMA. These parameters were determined from the experimental results of χ_p for the ternary solutions in CHN in the way described below. In the present work, copolymer VCVAc90 was dealt with as a

Table I. Characteristics of polymers

Sample	$\bar{M}_w \times 10^{-5}$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	Tacticity[b]/%		
			mm	mr	rr
VCVAc90[c]	0.26	2.1	—	—	—
PiBMA	3.0	1.7	4	32	64
iBMAnBMA50[d]	1.5	1.6	6	36	58
PnBMA	1.9	1.7	5	35	60

[a] Determined by GPC measurement, relative to the polystyrene standard. [b] Determined by ^{13}C NMR measurement in dimethyl sulfoxide (DMSO)-d_6. [c] Containing 90 wt% of VC units. [d] Containing 50 mol% of iBMA units.

Table II. Characteristic parameters of polymers and solvent obtained at 25°C

Component	v_{sp}^*	v^*	p^*	T^*
	cm^3 g^{-1}	cm^3 seg·mol^{-1}	J cm^{-3}	K
CHN[a]	0.8652	68.63	628	5534
PiBMA[b]	0.7979	62.29	584	6566
PnBMA[a]	0.8103	66.73	577	6947
VCVAc90[c]	0.6311	71.17	606	7774
iBMAnBMA50[d]	0.8041	64.44	583	5678

[a] Reference 38. [b] Reference 39. [c] Reference 35. [d]Calculated using the combining rules for random copolymers.

Table III. Intermolecular or intersegmental parameters

System (i/j)	s_j/s_i	$X_{ij}/\text{J cm}^{-3}$	c_{ij}
CHN/VCVAc90	0.700	−32.4	0.032
CHN/PiBMA[a]	1.050	18.0	−0.0024
CHN/PnBMA[b]	1.100	9.93	0.0011
VCVAc90/PiBMA	1.500	−23.0	0.015
VCVAc90/iBMAnBMA50[c]	1.535	−9.30	0.0052
VCVAc90/iBMAnBMA13[c]	1.562	−0.0468	0.00283
VCVAc90/PnBMA	1.571	−7.25	0.0010
PiBMA/PnBMA[b]	1.048	0.0001	0.010

[a] Reference 39. [b] Reference 38. [c] Calculated using the combining rules for random copolymers. Numeral values indicate copolymer compositions of iBMA in mol%.

Table IV. Osmotic pressures π and interaction parameters χ_p at 25°C[a]

w_p	ϕ_p	$\pi/\text{J cm}^{-3}$	χ_p
	Binary system		
	CHN/VCVAc90		
0.0600	0.0446	0.0238	0.044
0.0836	0.0625	0.0461	0.0497
0.104	0.0778	0.0709	0.0544
0.120	0.0906	0.0928	0.0731
0.144	0.109	0.139	0.0617
	Ternary system		
	CHN/VCVAc90/PiBMA		
0.0802	0.0676	0.0256	0.302
0.117	0.0989	0.0577	0.297
0.154	0.131	0.108	0.291
0.181	0.156	0.158	0.292
	CHN/VCVAc90/iBMAnBMA50		
0.0671	0.0496	0.0159	0.266
0.0684	0.0494	0.0198	0.251
0.104	0.0770	0.0427	0.238
0.114	0.0843	0.0530	0.229
0.131	0.0974	0.0681	0.243
0.151	0.113	0.102	0.217
0.182	0.138	0.154	0.218
	CHN/VCVAc90/PnBMA		
0.0786	0.0663	0.0230	0.317
0.125	0.106	0.0618	0.317
0.148	0.126	0.0909	0.314
0.187	0.161	0.163	0.301

[a] w_p and ϕ_p are the weight and core volume fractions of the polymer, respectively.

homopolymer because only the effect of the copolymer composition dependence of iBMAnBMA was focused on. Thermodynamic treatment of VCVAc as a *copolymer* had been described in our previous papers.[35,40]

Experimental χ_p for the solutions in CHN obtained from the osmotic pressures at 25°C by use of eq 19 are summarized in Table IV and plotted against the core volume fraction of polymer in Figure 2. Here, the ratio of the two polymers in the ternary solutions is 1/1 by weight. The heat of mixing $\Delta H_M(\infty)$ at infinite dilution for the VCVAc90 solution in CHN was obtained at 31°C by correction for the heat of glass transition using eq 21, on the approximation that the same amount of heat as liberated in glass-to-rubber transition was generated on mixing the glassy polymer with the solvent. Figure 3 shows a specific heat curve for VCVAc90 obtained by DSC measurement. The heat of glass transition $\int \Delta C_p dT$ was evaluated from the area surrounded by two dot-dashed lines and the specific heat curve. $\Delta H_M(\infty)$ is shown
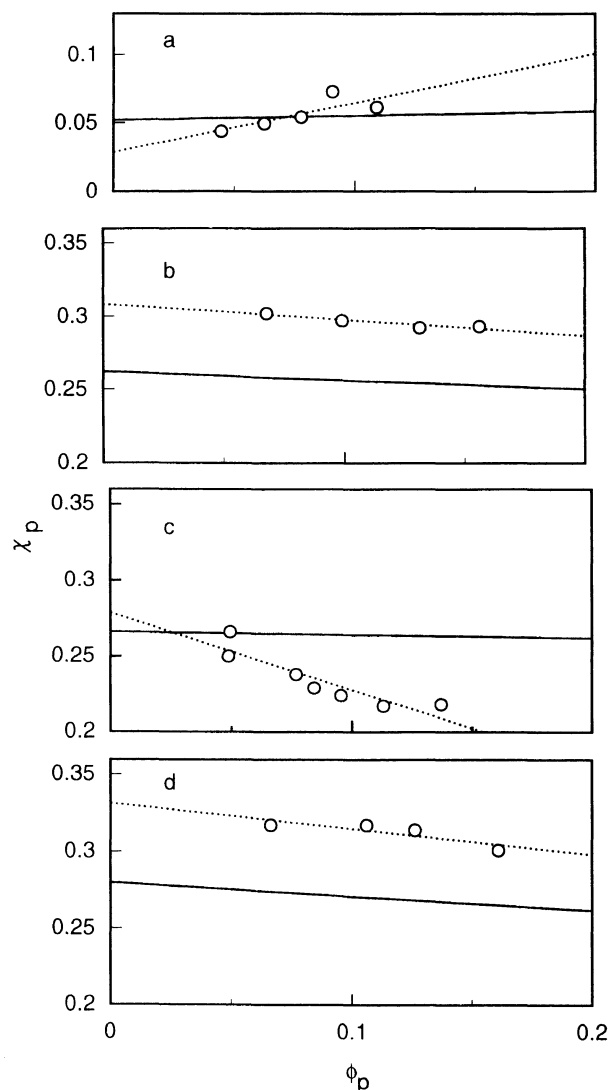

Figure 2. Dependence of χ_p on core volume fraction ϕ_p for polymer solutions in CHN at 25°C: (a) VCVAc90; (b) VCVAc90/PiBMA; (c) VCVAc90/iBMAnBMA50; (d) VCVAc90/PnBMA. The dotted lines are experimental ones, and the solid lines were calculated using the equation-of-state theory, see the text.
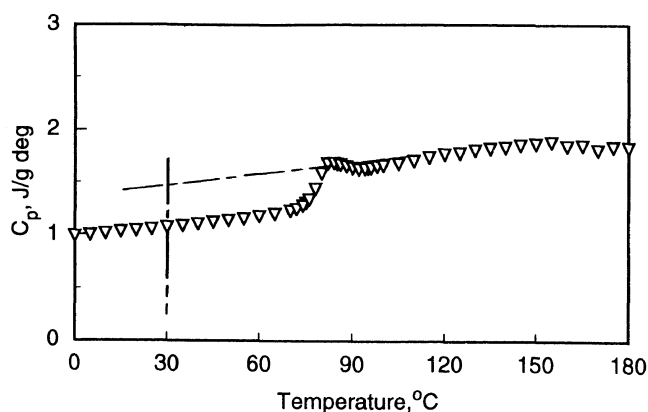

Figure 3. Temperature dependence of the specific heat for VCVAc90.

in Table V together with $\Delta H_M^{app}(\infty)$ and $\int \Delta C_p dT$.

First the intermolecular parameters for CHN/VCVAc90 were determined so that the theoretical χ and $\Delta H_M(\infty)$ could fit the above experimental results. X_{ij} and c_{ij} thus determined for CHN/VCVAc90 are shown in

Table V. Heat of mixing at infinite dilution at 31°C

System	$\Delta H_M^{app}(\infty)^a$	$\int \Delta C_p dT^b$	$\Delta H_M(\infty)$, J g^{-1}	
	J g^{-1}	J g^{-1}	Exptl^c	Calcd^d
CHN/VCVAc90	-37.2	20.7	-16.5	-16.5

^{a} Measured at 31°C with a Tian-Calvet microcalorimeter. ^{b} Determined from specific heats. ^{c} Obtained by $\Delta H_M^{app}(\infty) + \int \Delta C_p dT$. ^{d} Calculated using the equation-of-state theory.

Table III. Here, the surface ratio s_j/s_i was obtained from the van der Waals radius and surface obtained from the Bondi's table.[41] The calculated χ_p and $\Delta H_M(\infty)$ are shown by the solid curve in Figure 2a and in Table V, respectively. Next the intermolecular or intersegmental parameters, X_{ij} and c_{ij}, for VCVAc90/PiBMA and VCVAc90/PnBMA were determined using the results for the ternary solutions. The interaction parameter χ_p for ternary systems can be expressed as follows using the residual chemical potential:[40]

$$\chi_p = (\mu_s - \mu_s^0)^R / RT\phi_p^2 \tag{22}$$

$$(\mu_s - \mu_s^0)^R = r_s RT\{3A \ln[(2\pi mkT)^{1/2}/h(gv^*)^{1/3}(\tilde{v}^{1/3} - 1)]$$
$$+ 3c_s \ln(m_s/m)^{1/2} + (3/2)c(m - m_s)/m\}$$
$$+ p_s^* r_s v_s^* \tilde{T}_s\{\ln(v_s^*/v^*) + 3\ln[\tilde{v}_s^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]\}$$
$$+ 2p^* r_s v^* \tilde{T}(1 - W) + p_s^* r_s v_s^*/\tilde{v}_s$$
$$+ (p^* r_s v^*/\tilde{v})[(\theta_s/\sigma_s) - 2(1 - W) - 2Y] \tag{23}$$

where

$$A = [\sigma_s(1 - \theta_s)\theta_1 c_{s1} + \sigma_s(1 - \theta_s)\theta_2 c_{s2} - \sigma_1\theta_s\theta_2 c_{12}]/\sigma_s \tag{24}$$

$$W = (\sigma_s v_s^* + \sigma_1 v_{s1}^* + \sigma_2 v_{s2}^*)/v^* \tag{25}$$

$$Y = (\theta_s p_s^* v_s^{*2} + \theta_1 p_{s1}^* v_{s1}^{*2} + \theta_2 p_{s2}^* v_{s2}^{*2})/(p^* v^{*2}) \tag{26}$$

Here, the combining rules for ternary systems are given by extension of those for the binary mixture as

$$v^* = \sigma_s^2 v_s^* + \sigma_1^2 v_1^* + \sigma_2^2 v_2^* + 2(\sigma_s\sigma_1 v_{s1}^* + \sigma_1\sigma_2 v_{12}^* + \sigma_s\sigma_2 v_{s2}^*) \tag{27}$$

$$p^* = [\sigma_s\theta_s p_s^* v_s^{*2} + \sigma_1\theta_1 p_1^* v_1^{*2} + \sigma_2\theta_2 p_2^* v_2^{*2}$$
$$+ 2(\sigma_s\theta_1 p_{s1}^* v_{s1}^{*2} + \sigma_1\theta_2 p_{12}^* v_{12}^{*2} + \sigma_s\theta_2 p_{s2}^* v_{s2}^{*2})]/v^{*2} \tag{28}$$

where v_{ij}^* and p_{ij}^* are given by the same expressions as eq 5 and 7, respectively.

$$c = \sigma_s c_s + \sigma_1 c_1 + \sigma_2 c_2 - (\sigma_s\theta_1 c_{s1} + \sigma_1\theta_2 c_{12} + \sigma_s\theta_2 c_{s2}) \tag{29}$$

$$p^* v^* = cRT^* \tag{30}$$

X_{ij} and c_{ij} for VCVAc90/PiBMA and VCVAc90/PnBMA were determined so that the above theoretical χ_p could fit the experimental ones as well as possible for the three ternary solutions (Figures 2b, c, and d), using the intermolecular parameters obtained previously[38,39] for CHN/PiBMA, CHN/PnBMA and PiBMA/PnBMA and determined above for CHN/VCVAc90. Here, the surface ratio $s_{iBMA}/s_{VCVAc90}$ and $s_{nBMA}/s_{VCVAc90}$, were obtained by $(s_{iBMA}/s_{CHN})/(s_{VCVAc90}/s_{CHN})$ and $(s_{nBMA}/s_{CHN})/(s_{VCVAc90}/s_{CHN})$. When calculated χ_p for the two ternary solutions containing homopolymers PiBMA and PnBMA, respectively, are fitted to experiments completely, the calculated ones for solutions of VCVAc90/iBMAnBMA-
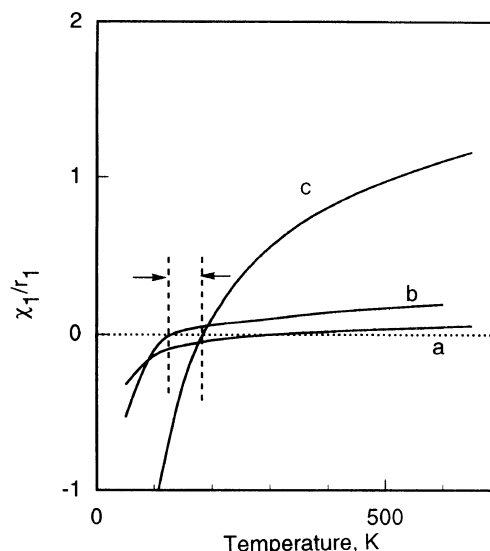

Figure 4. The temperature dependence of χ_1/r_1 for VCVAc90/iB-MAnBMA blends. Copolymer compositions of iBMA are (a) 0 mol%, (b) 13 mol%, and (c) 100 mol%, respectively.

50 deviate towards larger values. Therefore, X_{ij} and c_{ij} were chosen so that deviations of χ_p from experiments for these three ternary solutions could be smallest as a whole. The values of the intersegmental parameters determined thus are listed in Table III, and the theoretical curves of χ_p are shown by the solid lines in Figure 2.

Temperature Dependence of χ for Copolymer Blends

Using the characteristic and intersegmental parameters obtained above for VCVAc90, iBMA, and nBMA, we can calculate χ for VCVAc90/iBMAnBMA copolymer blends. The calculation of the parameter χ was carried out at $\phi_2 \to 0$ to avoid complication of the concentration dependence of χ. Calculated temperature–$\chi_1/r_1(\chi_1 = \lim_{\phi_2 \to 0} \chi)$ curves were monotonically increasing functions regardless of the copolymer composition of the iBMAnBMA copolymer. Namely the blends of VCVAc-90 with the copolymer iBMAnBMA have LCST. In Figure 4 is shown the temperature dependence of χ_1/r_1 for the homopolymer blends of VCVAc90/PiBMA and VCVAc90/PnBMA and copolymer blend of VCVAc-90/iBMAnBMA13 containing 13 mol% iBMA units. It should be noted that there is a temperature range, between two dashed lines in Figure 4, in which χ_1/r_1 is positive for the copolymer blend while negative for both homopolymer blends. This means that in this temperature range the copolymer blend VCVAc90/iBMAnBMA13 is immiscible though both homopolymer blends VCVAc90/PiBMA and VCVAc90/PnBMA are miscible. In other words, the copolymer blends change from miscible to immiscible and again to miscible with copolymer composition in this temperature range. The trend of this miscibility behavior corresponds to the experimental one shown in Figure 1. Even in use of X_{ij} and c_{ij} obtained so that the theoretical χ_p for the ternary solutions containing homopolymers PiBMA and PnBMA, respectively, could fit the experimental one completely, the same behavior was obtained although the copolymer composition range in which the im-
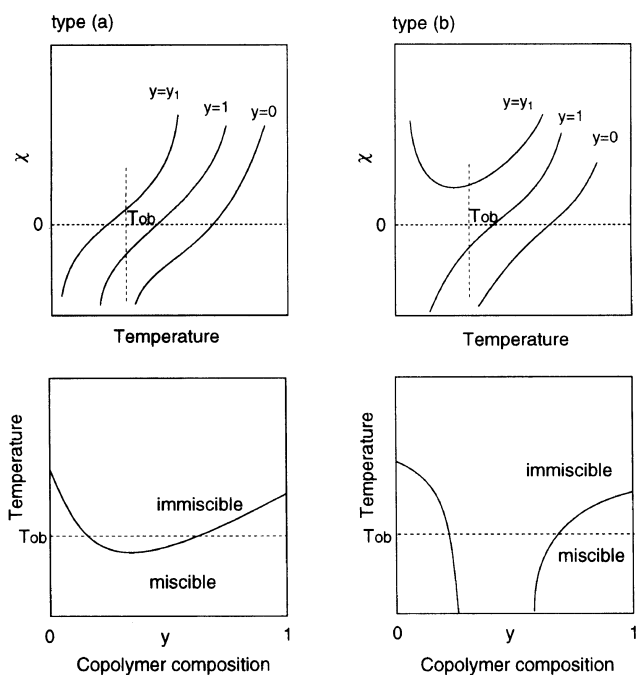
REFERENCES

Figure 5. Schematic illustrations of the temperature dependence of χ (upper) and the corresponding miscibility behavior (lower) for copolymer blends showing immiscibility windows around a temperature T_{ob}. y indicates the fraction of copolymer composition.

miscibility window appeared shifted. In both calculated results no quantitative agreement was obtained on the boundary temperature of miscibility. One reason 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.[29] In the present study, the values of the characteristic parameters at 25°C were used.

As discussed in the previous paper,[31] there are two changes in the T–χ curves with copolymer composition for the miscibility behavior like an immiscibility window. In type (a) shown in Figure 5, the T–χ curves are monotonically increasing functions regardless of copolymer composition. This means that blends are miscible below a certain temperature for any copolymer composition even though the miscibility behavior is like an immiscibility window at a certain temperature T_{ob}. In type (b) the T–χ curves change from a monotonically increasing function to a U-shaped curve and again to a monotonically increasing function with the copolymer composition. In this case, as shown in the lower figure of Figure 5(b), the blends are immiscible over all temperatures in the copolymer composition range corresponding to U-shaped T–χ curves. Thus, miscibility behavior of the immiscibility window can be classified into two types. The immiscibility window for the present copolymer blends of VCVAc90/iBMAnBMA is concluded to be type (a) from both results of the miscibility observation in Figure 1[7] and the T–χ curve behavior obtained in the present work.

1. R. Vuković, F. E. Karasz, and W. J. Macknight, *Polymer*, **24**, 529 (1983).
2. R. P. Kambour, J. T. Bendler, and R. C. Bopp, *Macromolecules*, **16**, 753 (1983).
3. G. ten Brinke, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **16**, 1827 (1983).
4. D. R. Paul and J. W. Barlow, *Polymer*, **25**, 487 (1984).
5. T. Shiomi, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **19**, 2274, 2644 (1986).
6. A. C. Fernandes, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **32**, 5481 (1986).
7. T. Shiomi, M. Suzuki, M. Tohyama, and K. Imai, *Macromolecules*, **22**, 3578 (1989).
8. T. Sato, M. Endo, T. Shiomi, and K. Imai, *Polymer*, **37**, 2131 (1996).
9. R. Simha and H. Branson, *J. Chem. Phys.*, **12**, 253 (1944).
10. P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
11. P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).
12. D. Patterson and A. Robard, *Macromolecules*, **11**, 690 (1978).
13. D. Patterson, *Polym. Eng. Sci.*, **22**, 64 (1982) .
14. I. C. Sanchez and R. H. Lacombe, *J. Phys. Chem.*, **80**, 2352 (1976).
15. R. H. Lacombe and I. C. Sanchez, *J. Phys. Chem.*, **80**, 2568 (1976).
16. I. C. Sanchez, in "Polymer Compatibility and Incompatibility," K. Solč, Ed., MMI Press, Harwood Academic, New York, 1981, p 59.
17. K. S. Schweizer and J. G. Curro, *Phys. Rev. Lett.*, **60**, 809 (1988).
18. J. G. Curro, A. Yethiraj, K. S. Schweizer, J. D. McCoy, and K. G. Honnell, *Macromolecules*, **26**, 2655 (1993).
19. P. J. Flory and H. Shih, *Macromolecules*, **5**, 761 (1972).
20. K. Sugamiya, N. Kuwahara, and M. Kaneko, *Macromolecules*, **7**, 66 (1974).
21. T. Shiomi, Z. Izumi, F. Hamada, and A. Nakajima, *Macromolecules*, **13**, 1149 (1980).
22. T. Shiomi, Y. Kohra, F. Hamada, and A. Nakajima, *Macromolecules*, **13**, 1154 (1980).
23. D. J. Walsh and G. T. Dee, *Polymer*, **29**, 656 (1988).
24. G. ten Brinke, A. Eshuis, E. Roerdink, and G. Challa, *Macromolecules*, **14**, 867 (1981).
25. S. Cimmino, E. Martuscelli, and C. Silvestre, *Polymer*, **30**, 393 (1989).
26. D. J. Walsh, G. T. Dee, J. L. Halary, J. M. Ubiche, M. Millequant, J. Lesec, and L. Monnerie, *Macromolecules*, **22**, 3395 (1989).
27. T. Shiomi, F. Hamada, T. Nasako, K. Yoneda, K. Imai, and A. Nakajima, *Macromolecules*, **23**, 229 (1990).
28. T. Shiomi, F. Hamada, M. Mihoichi, T. Nasako, and A. Nakajima, *Polymer*, **31**, 448 (1990).
29. K. Fujisawa, T. Shiomi, F. Hamada, and A. Nakajima, *Polym. J.*, **13**, 993 (1981).
30. K. Fujisawa, T. Shiomi, F. Hamada, A. Nakajima, and J. Lee, *Polym. J.*, **13**, 1003 (1981).
31. T. Shiomi and K. Imai, *Polymer*, **32**, 73 (1991).
32. F. Hamada, T. Shiomi, K. Fujisawa, and A. Nakajima, *Macromolecules*, **13**, 729 (1980).
33. T. Shiomi, K. Fujisawa, F. Hamada, and A. Nakajima, *J. Chem. Soc., Faraday Trans. 2*, **76**, 895 (1980).
34. K. Fujisawa, T. Shiomi, F. Hamada, and A. Nakajima, *Polym. Bull.*, **3**, 261 (1980).
35. T. Shiomi, H. Ishimatsu, T. Eguchi, and K. Imai, *Macromolecules*, **23**, 4970 (1990).
36. B. E. Eichinger and P. J. Flory, *Trans, Faraday Soc.*, **64**, 2035 (1968).
37. G. V. Schulz, K. V. Guenner, and H. Gerrens, *Z. Phys. Chem. (F)*, **4**, 192 (1955).
38. T. Shiomi, M. Tohyama, M. Endo, T. Sato, and K. Imai, *J. Polym. Sci., Polym. Phys.*, **34**, 2599 (1996).
39. T. Sato, M. Tohyama, M. Suzuki, T. Shiomi, and K. Imai, *Macromolecules*, **29**, 8231 (1996).
40. T. Shiomi, T. Eguchi, H. Ishimatsu, and K. Imai, *Macromolecules*, **23**, 4978 (1990).
41. A. Bondi, *J. Phys. Chem.*, **87**, 1833 (1965).