Application of Equation-of-State Theory to Random Copolymer Systems. 2. Copolymer Blends

Tomoo Shiomi,* Toshimasa Eguchi, Hirofumi Ishimatsu, and Kiyokazu Imai*

Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan

Received July 3, 1989; Revised Manuscript Received April 10, 1990

ABSTRACT: The modified equation-of-state theory extended to random copolymer systems was applied to ternary solutions of two random copolymers in tetrahydrofuran and to random copolymer blends. Two random copolymers were poly(ethylene-*co*-vinyl acetate) (EtVAc) and poly(vinyl acetate-*co*-vinyl chloride) (VAcVC), whose blends are known to have a miscibility region with respect to the copolymer composition. First, the theory was applied to ternary solutions to reproduce well the dependence of the interaction parameter, χ, on copolymer composition. Next, the theory was applied to the random copolymer blends, and it was examined how the temperature dependence of χ changed with the copolymer composition. For the EtVAc copolymer/PVC homopolymer blends with a series of the copolymer compositions, the calculated temperature dependence of χ changed from a U-shaped curve to a monotonically increasing function and back to a U-shaped curve with changing copolymer composition. This calculated result shows that the EtVAc/PVC blends have a so-called miscibility window. The calculations of the temperature dependence of χ were carried out over all copolymer compositions for EtVAc/VAcVC copolymer blends. Consequently, the copolymer composition range in which the calculated χ increased monotonically from negative to positive with an increase in temperature corresponded to the miscibility region obtained experimentally by Shiomi et al.

Introduction

Recently, dependence of miscibility on the copolymer composition for random copolymer blends have been studied theoretically and experimentally.[1-7] So-called miscibility and immiscibility windows are typical miscibility behaviors though any clear evidence for the immiscibility window may not be found yet for real systems.[6,7] The former window is that two polymers are miscible with each other in a certain range of the copolymer composition even though any binary combinations of their corresponding homopolymers are immiscible, while the latter is the reversed case. These behaviors have been explained[3-5,8] by expressing the Flory–Huggins intermolecular interaction parameter, χ, in terms of the intersegmental χ parameters between the different constituent monomers; such miscibility and immiscibility windows may occur due to the intramolecular repulsive and attractive effects between the different monomers, respectively.[4]

According to Flory's equation-of-state theory,[9,10] we have two kinds of temperature dependences of χ shown in Figure 1: (A) one is a U-shaped curve and (B) the other is a monotonically increasing function. For infinite molecular weight polymer blends, two polymers are immiscible over all of the temperature range in the case of the curve A because χ is always positive, and in the case of B two polymers are miscible below a certain temperature at which χ is zero. For random copolymer blends with a miscibility or immiscibility region with respect to copolymer composition, alternativity of the curves A and B may depend on the copolymer composition. It may be reasonable[5,11] that so-called miscibility and immiscibility windows are defined by the changes of A → B → A and of B → A → B, respectively, with copolymer composition, and therefore any other case is not such windows even though the miscibility or immiscibility regions are observed at a certain temperature. The poly(ethylene-*co*-vinyl acetate) (EtVAc)/poly(vinyl acetate-*co*-vinyl chloride) (VAcVC) copolymer blends studied in the present paper have a miscibility region in certain ranges of the copolymer composition and of the temperature.[12] Therefore, it is very interesting to evaluate the copolymer composition dependence of the temperature–χ curve over all the copolymer compositions for the EtVAc/VAcVC blends.

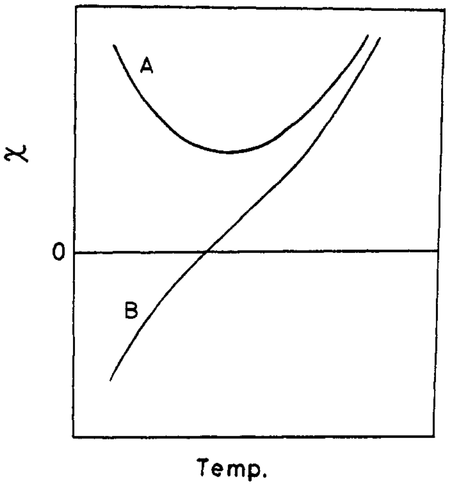

Figure 1. Schematic illustrations of the temperature dependence of χ.

In the preceding paper,[13] we extended the modified equation-of-state theory[14-16] to random copolymer systems and applied it to the EtVAc and VAcVC solutions in THF. In this paper, we will first apply it to the solutions of EtVAc/VAcVC blend in THF, i.e., the ternary solutions. Next, we will evaluate the temperature dependence of χ for the EtVAc/VAcVC copolymer blends with various copolymer compositions according to the theory. In the theoretical calculations, the characteristic parameters and the intersegmental parameters determined in the preceding paper and in the above ternary systems will be used. Through these theoretical evaluations of the temperature dependence of χ, it will be clarified whether the miscibility behavior of the EtVAc/VAcVC blends is corresponding to a miscibility window defined as mentioned above or not.

Experimental Section

Polymer samples employed were the same as those used in the preceding paper.[13] Their molecular weights and copolymer compositions are shown in Table I of the preceding paper.

The interaction parameter, χ_{0p}, for the ternary solutions was

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Table I
Intersegmental Parameters Used for Calculations of the Interaction Parameters, χ

system (k/l)	s_l/s_k	X_{kl}, J/cm^3	c_{kl}
Et/VAc[a]	0.680	63.0	0.117
Et/VC	0.747	23.9	0.000 15
VAc/VC[a]	1.099	12.9	0.000 05

[a] Determined in the preceding paper.[13]

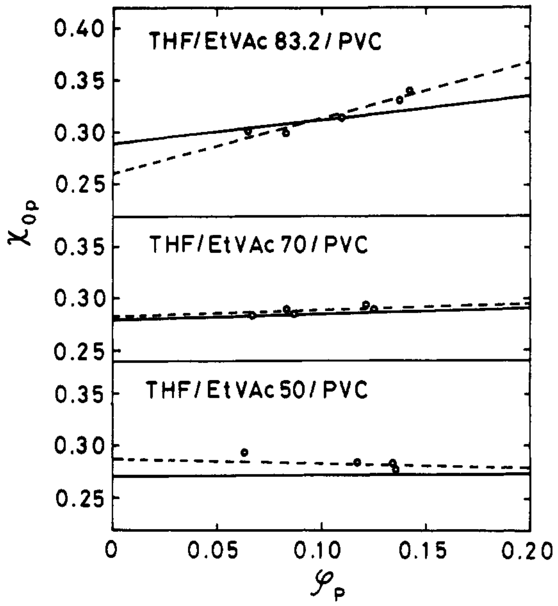

Figure 2. Dependence of χ_{0p} on the total polymer core volume fraction, ϕ_p, for the THF/EtVAc/PVC systems at 25 °C. The calculated curves are shown by the solid lines.

obtained from osmotic pressures, π, by using the equation

$$-\pi V_s/RT = (\mu_s - \mu_s{}^\circ)/RT = \ln (1 - \phi_p) + (1 - m_s v_{sp,s}{}^*/m_1 v_{sp,1}{}^*)\phi_1 + (1 - m_s v_{sp,s}{}^*/m_2 v_{sp,2}{}^*)\phi_2 + \chi_{0p}{}^2 \quad (1)$$

where V_s is the molar volume of the solvent, m_s, m_1, and m_2 are the masses of the solvent and polymers 1 and 2, respectively, $v_{sp,i}{}^*$ (i = s, 1, and 2) is the respective characteristic or core volume per gram, ϕ_1 and ϕ_2 are the core volume fractions of the polymers 1 and 2, respectively, and ϕ_p is the total polymer core volume fraction given by

$$\phi_p = \phi_1 + \phi_2 = 1 - \phi_s \quad (2)$$

These core volume fractions are given in the same way as eq 13 in the preceding paper. Excess volume ratios V^E/V° were determined from the respective specific volumes $v_{sp,i}$ by using

$$V^E/V^\circ = v_{sp}/(w_s v_{sp,s} + w_1 v_{sp,1} + w_2 v_{sp,2}) - 1 \quad (3)$$

where w_s, w_1, and w_2 are the weight fractions of the solvent and the polymers 1 and 2, respectively.

Results

(1) Solutions of Copolymer Blend in THF. The experimental results of χ_{0p} for the solutions of the copolymer blend in THF are shown by the circles in Figures 2 and 3. In all the systems, the blend ratio is 1/1 by weight, and the measurement temperature is 25 °C. Figure 2 shows the results for the solutions containing the EtVAc copolymer/PVC homopolymer blend, and Figure 3, the results for the EtVAc/VAcVC solutions in THF. The result of V^E/V° for the THF/EtVAc70/PVC system is indicated by the triangle in Figure 2* of the preceding paper. (Hereafter, the figures, tables, and equations taken from the preceding paper[13] will be referred to by an asterisk.)

We will apply the modified Flory equation-of-state theory[14-16] to ternary solutions. The combining rules[17] for the ternary mixture of solvent (s)/polymer 1/polymer 2 can be given as follows by extension of the binary mixture

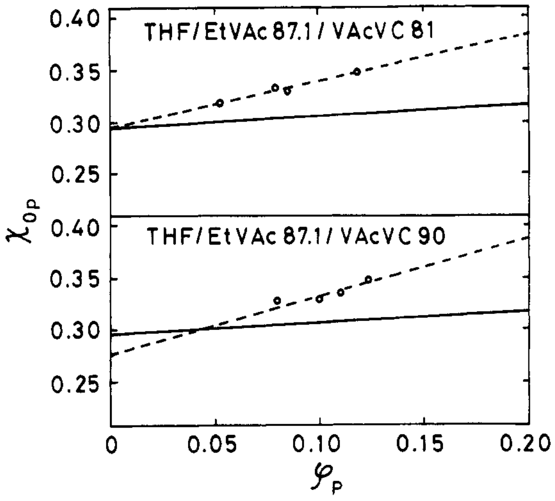

Figure 3. Dependence of χ_{0p} on the total polymer core volume fraction, ϕ_p, for the THF/EtVAc/VAcVC systems at 25 °C. The calculated curves are represented by the solid lines.

$$m = \sigma_s m_s + \sigma_1 m_1 + \sigma_2 m_2 \quad (4)$$

$$v^* = \sigma_s{}^2 v_s{}^* + \sigma_1{}^2 v_1{}^* + \sigma_2{}^2 v_2{}^* + 2(\sigma_s\sigma_1 v_{s1}{}^* + \sigma_1\sigma_2 v_{12}{}^* + \sigma_s\sigma_2 v_{s2}{}^*) \quad (5)$$

$$p^* = [\sigma_s\theta_s p_s{}^* v_s{}^{*2} + \sigma_1\theta_1 p_1{}^* v_1{}^{*2} + \sigma_2\theta_2 p_2{}^* v_2{}^{*2} + 2(\sigma_s\theta_1 p_{s1}{}^* v_{s1}{}^{*2} + \sigma_1\theta_2 p_{12}{}^* v_{12}{}^{*2} + \sigma_s\theta_2 p_{s2}{}^* v_{s2}{}^{*2})]/v^{*2} \quad (6)$$

$$X_{ij} = p_i{}^* + (v_j{}^*/v_i{}^*)(s_i/s_j)p_j{}^* - 2(v_{ij}{}^*/v_i{}^*)p_{ij}{}^* \quad (7)$$

$$v_{ij}{}^* = [(v_i{}^{*1/3} + v_j{}^{*1/3})/2]^2 \qquad (i,j) = (\mathrm{s},1), (1,2), (\mathrm{s},2) \quad (8)$$

$$c = \theta_s c_s + \sigma_1 c_1 + \sigma_2 c_2 - (\sigma_s\theta_1 c_{s1} + \sigma_1\theta_2 c_{12} + \sigma_s\theta_2 c_{s2}) \quad (9)$$

where the symbols are the same as those used in the preceding paper. When the polymers 1 and 2 are the copolymers 1 and 2, respectively, the respective characteristic parameters for the copolymer can be expressed in terms of those for the copolymer components using the same relations as given for the binary copolymer mixture in the preceding paper.[13] On the basis of these relations and the partition function proposed by Flory,[9] we can derive the interaction parameter χ_{0p} for the ternary mixture as

$$\chi_{0p} = (\mu_s - \mu_s{}^\circ)^R/(RT\phi_p{}^2) \quad (10)$$

with

$$(\mu_s - \mu_s{}^\circ)^R = r_s RT\{3A \ln [(2\pi mkT)^{1/2}/h(gv^*)^{1/3}(\tilde{v}^{1/3} - 1)] + 3c_s \ln (m_s/m)^{1/2} + (3/2)c(m - m_s)/m\} + p_s{}^* r_s v_s{}^* \tilde{T}_s\{\ln (v_s{}^*/v^*) + 3 \ln [(\tilde{v}_s{}^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]\} + 2p^* r_s v^* \tilde{T}(1 - W) + p_s{}^* r_s v_s{}^*/\tilde{v}_s + (p^* r_s v^*/\tilde{v})[(\theta_s/\sigma_s) - 2(1 - W) - 2Y] \quad (11)$$

where

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

$$W = (\sigma_s v_s{}^* + \sigma_1 v_{s1}{}^* + \sigma_2 v_{s2}{}^*)/v^* \quad (13)$$

$$Y = (\theta_s p_s{}^* v_s{}^{*2} + \theta_1 p_{s1}{}^* v_{s1}{}^{*2} + \theta_2 p_{s2}{}^* v_{s2}{}^{*2})/(p^* v^{*2}) \quad (14)$$

The excess volume ratio, V^E/V°, can be written as

$$V^E/V^\circ = v^*\tilde{v}/(\sigma_s v_s{}^*\tilde{v}_s + \sigma_1 v_1{}^*\tilde{v}_1 + \sigma_2 v_2{}^*\tilde{v}_2) - 1 \quad (15)$$

In the present paper, the subscripts s, 1, and 2 indicate

Table II
Intermolecular Parameters Used for Calculations of the Interaction Parameters, χ, for the Ternary Systems

system (i/j)[a]	s_j/s_i	X_{ij}, J/cm^3	c_{ij}
EtVAc83.2/PVC	1.020	2.52	0.000 07
EtVAc70/PVC	0.966	−0.01	0.000 08
EtVAc50/PVC	0.892	2.38	0.000 10
EtVAc87.1/VAcVC90	1.026	2.44	0.001 8
EtVAc87.1/VAcVC81	1.016	1.46	0.003 3

[a] The numerical values indicate the copolymer compositions expressed in weight percent.

the solvent (THF), EtVAc copolymers, and VAcVC copolymers (or PVC homopolymer), respectively.

As mentioned in the preceding paper,[13] in order to calculate thermodynamic quantities, we need the equation-of-state parameters for the component molecules and the intermolecular parameters X_{ij}, c_{ij}, and $s_{j/i}$. For the random copolymer system, these parameters can be obtained from those for the components of copolymers or the corresponding homopolymers. We already evaluated the equation-of-state parameters for THF, PEt, PVAc, and PVC and the parameters X_{kl}, c_{kl}, and s_l/s_k for THF/Et, THF/VAc, THF/VC, Et/VAc, and VAc/VC in the preceding paper.[13] The remaining parameters necessary for the calculations of thermodynamic quantities for the present copolymer systems are X_{kl}, c_{kl}, and s_l/s_k for Et/VC. $s_{\mathrm{VC}}/s_{\mathrm{Et}}$ can be obtained from Bondi's table.[18] We determine the values of $X_{\mathrm{Et/VC}}$ and $c_{\mathrm{Et/VC}}$ from the experimental values of $\chi_{0\mathrm{p}}$ and V^{E}/V° for the EtVAc70/PVC solutions in THF. When the values of X_{ij} and c_{ij} are used for EtVAc70/PVC shown in Table II together with the characteristic parameters for THF, EtVAc70, and PVC (shown in Table II*) and the intermolecular parameters X_{ij} and c_{ij} for THF/EtVAc70 and THF/PVC (shown in Table III*), the theory can reproduce very well the experimental $\chi_{0\mathrm{p}}$ and V^{E}/V° for the THF/EtVAc70/PVC system as shown in Figures 2 and 2*, respectively. From this value of $X_{\mathrm{EtVAc70/PVC}}$ and the values of $X_{\mathrm{Et/VAc}}$ and $X_{\mathrm{VAc/VC}}$ shown in Table III*, $X_{\mathrm{Et/VC}}$ was determined by using eqs 8*, 35*, and 31*. In the same way, $c_{\mathrm{Et/VC}}$ was also determined by using eq 42*. The values of $X_{\mathrm{Et/VC}}$ and $c_{\mathrm{Et/VC}}$ determined thus are shown in Table I together with $s_{\mathrm{Et}}/s_{\mathrm{VC}}$. Now we can obtain the intermolecular parameters X_{ij}, c_{ij}, and s_j/s_i over all the copolymer compositions according to the relations given in the preceding paper.[13] These values for the systems presented here are listed in Table II.

The solid lines in Figures 2 and 3 show the ϕ_{p} dependence of $\chi_{0\mathrm{p}}$ calculated by use of the parameters obtained above. The calculated results show satisfactory agreement with the experimental ones though the slope of the ϕ_{p}–$\chi_{0\mathrm{p}}$ curve somewhat deviates from the experimental one for the VAc-rich systems. This deviation may be caused by the surface ratio of THF/VAc as mentioned in the preceding paper.[13]

(2) χ Parameter for Copolymer Blends. The miscibility for the copolymer blends of EtVAc and VAcVC depends on their copolymer composition[12] as shown in Figure 4; namely, the miscibility region with respect to the copolymer composition exists. In this section, we will present the copolymer composition dependence of the temperature–χ_1 curve for these copolymer blends according to the equation-of-state theory extended to the random copolymer systems. The calculations of the interaction parameter, χ, were carried out at $\phi_2 \to 0$; i.e.

$$\chi_1 = \lim_{\phi_2 \to 0} \chi \tag{16}$$

to avoid complication of the concentration dependence of χ. In the calculations, the characteristic parameters for the corresponding homopolymers and the intersegmental parameters (Table I) obtained in the preceding section and paper[13] were used.

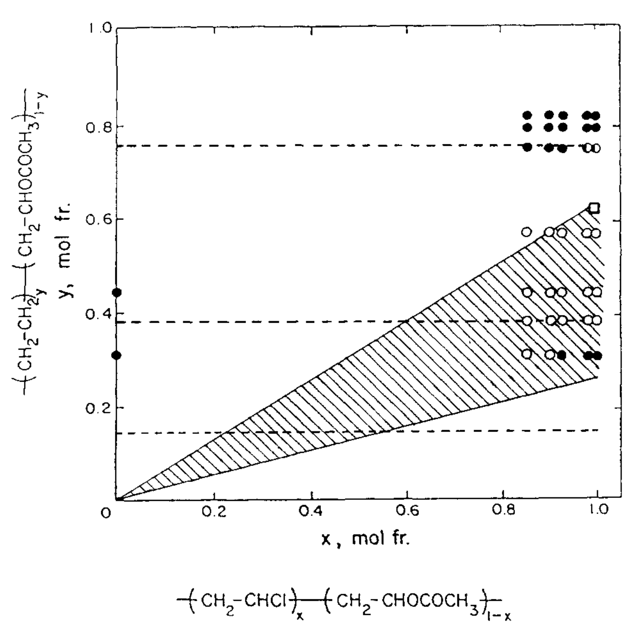

Figure 4. Summary of the calculated results for the temperature dependence of χ_1 for the EtVAc/VAcVC copolymer blends. The shadowy region shows the copolymer compositions where the temperature–χ_1 curve is a monotonically increasing function, and the other region corresponds to the copolymer composition range in which the temperature–χ_1 relation is a U-shaped curve. The symbols indicate the experimental results[12] for miscibility at 100–160 °C: the open and filled ones show miscible and immiscible results, respectively. The calculated temperature dependences of χ_1 for the copolymer blends corresponding to $x = 1$ and to the broken lines were illustrated; the line along $x = 1$ corresponds to Figure 5, and the upper, middle, and lower broken lines correspond to Figures 6–8, respectively.

Figure 5 shows the calculated result of the temperature dependence of χ for the EtVAc copolymer/PVC homopolymer blends with various VAc contents of EtVAc copolymer. As shown in this figure, the calculated temperature dependence of χ_1 changes from a U-shaped curve to a monotonically increasing function and again to a U-shaped curve with the copolymer composition. The U-shaped curves are always positive regardless of temperature, and the monotonically increasing curves change from negative to positive with an increase in temperature. Namely, the calculated result shows that the miscibility region may exist in a certain range of the copolymer composition below a temperature even for the EtVAc/PVC blends with infinite molecular weights. The experimental result[12] of the miscibility for these blends, which are along $x = 1$ in Figure 4, shows that the miscibility changes from immiscible to miscible and again to immiscible with the copolymer composition. The calculated result of χ_1 represents well this trend of the miscibility behavior for the EtVAc/PVC copolymer blends.

The calculations of the temperature dependence of χ_1 were carried out over all copolymer compositions. We will illustrate the results for three representative blends along the broken lines in Figure 4; (1) one corresponds to the miscibility behavior to be immiscible over all the copolymer compositions of VAcVC, (2) another corresponds to the miscibility change of immiscible → miscible with an increase in the VC content of VAcVC, and (3) the other is for the miscibility behavior of immiscible → miscible → immiscible. Figure 6 shows the result for the blends (1) of the EtVAc copolymer with a 0.76 mol fraction of Et

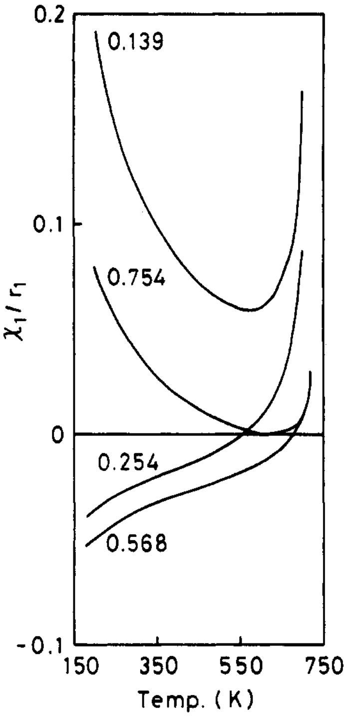

Figure 5. Temperature dependence of χ_1 for the blends of a series of EtVAc and the PVC homopolymer. The numerical values in the figure indicate the copolymer composition (mole fraction of Et) of EtVAc.

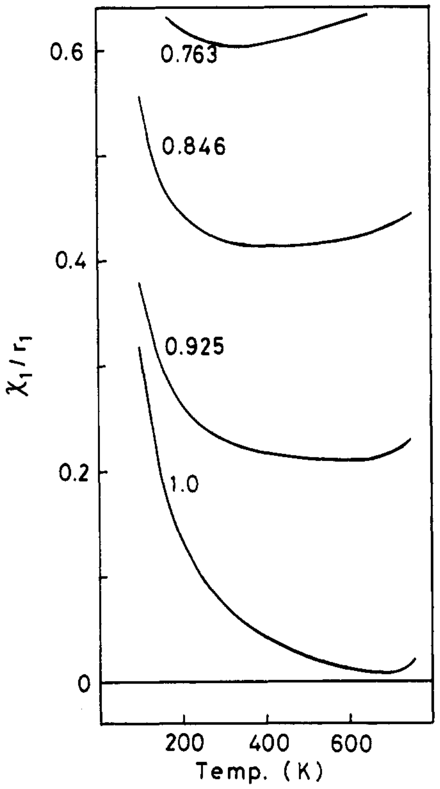

Figure 6. Temperature dependence of χ_1 for the blends, which correspond to the upper broken line in Figure 4, of the EtVAc copolymer with a 0.76 mol fraction of Et and the VAcVC copolymer with the copolymer composition (mole fraction) of VC indicated by the numerical values.

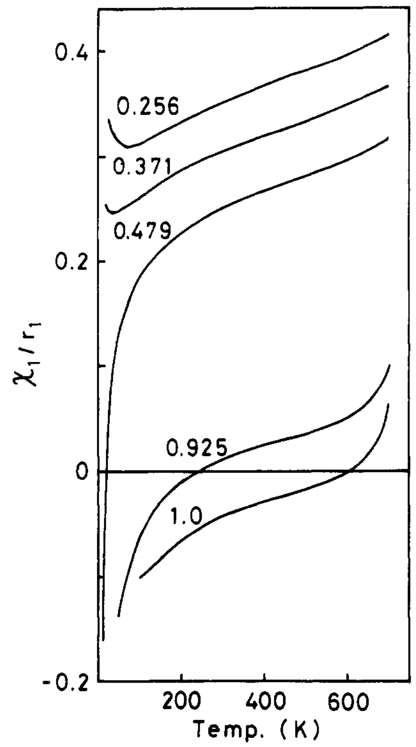

Figure 7. Temperature dependence of χ_1 for the blends, which correspond to the middle broken line in Figure 4, of the EtVAc copolymer with a 0.383 mol fraction of Et and the VAcVC copolymer with the copolymer composition (mole fraction) of VC indicated by the numerical values.

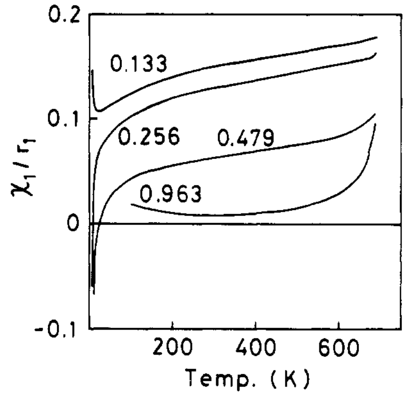

Figure 8. Temperature dependence of χ_1 for the blends, which correspond to the lower broken line in Figure 4, of the EtVAc copolymer with a 0.139 mol fraction of Et and the VAcVC copolymer with the copolymer composition (mole fraction) of VC indicated by the numerical values.

content and the VAcVC copolymer with a series of copolymer compositions. For this copolymer composition of EtVAc, as shown in Figure 6, the temperature dependence of χ_1 is U-shaped regardless of the copolymer composition of VAcVC. This means that the blends with infinite molecular weights are immiscible at any copolymer composition of VAcVC and at any temperature. Figure 7 shows the calculated results for the blends (2) of the EtVAc copolymer with a 0.383 mol fraction of Et and a series of the VAcVC copolymers. In this case, the calculated temperature–χ_1 curve changes from a U-shaped curve to a monotonically increasing curve as the VC content of the VAcVC copolymer increases. In Figure 8 are shown the result for the blends (3) containing EtVAc with a 0.139 mol fraction of Et content. In this copolymer composition of EtVAc, the temperature dependence of χ_1 changes from a U-shaped curve to a monotonically increasing function and again to a U-shaped curve with the copolymer composition of the VAcVC copolymer.

The results of the temperature dependence of χ_1 calculated over all the copolymer compositions are summarized in Figure 4. The shadowy region is corresponding to monotonically increasing curves and the other to U-shaped curves.

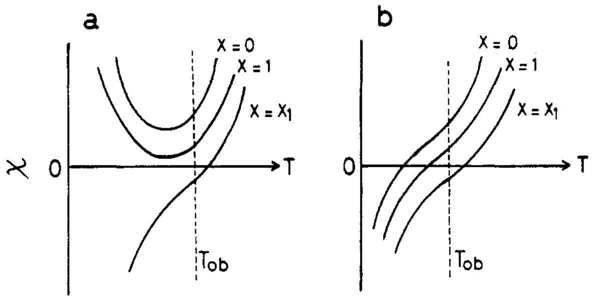

Figure 9. Schematic illustrations of the temperature dependence of χ for the copolymer blends, whose miscibility changes from immiscible to miscible to immiscible with the copolymer composition x at the temperature T_{ob}.

Discussion

So-called miscibility and immiscibility windows have been interpreted by the traditional Flory–Huggins theory extended to multicomponent systems.[3-5,8] According to that, the intermolecular χ parameter for the homopolymer A and the copolymer C_yD_{1-y} is given by

$$\chi = y\chi_{AC} + (1-y)\chi_{AD} - y(1-y)\chi_{CD} \tag{17}$$

where χ_{kl} is the intersegmental χ parameter between the monomer segments k and l. The condition for the miscibility window (as well as immiscibility window) is[4-6,12]

$$|\chi_{CD}| > (|\chi_{AC}|^{1/2} + |\chi_{AD}|^{1/2})^2 \tag{18}$$

Even if a miscibility region (or immiscibility region) is experimentally observed at a certain temperature, i.e., even if the condition 18 holds at a certain temperature, there are two types of dependences of the temperature–χ curve on the copolymer composition.[11] Figure 9 shows the schematic illustrations of two such types, a and b, in which the miscibility region exists: (a) U-shaped curve → monotonically increasing function → U-shaped curve with copolymer composition, and (b) monotonically increasing functions regardless of the copolymer composition. In both types, the sign of χ_1 changes from positive to negative to positive at a certain temperature T_{ob} with the copolymer composition, which means that the miscibility for both types changes from immiscible to miscible to immiscible at T_{ob}. In type a, however, a copolymer composition range in which the blend is immiscible over all temperature exists, while in type b the blend is miscible below a certain temperature regardless of the copolymer composition. A so-called miscibility window should be defined by type a.[11] For the EtVAc/PVC blends, as shown in Figure 4, the miscibility behavior obtained experimentally is in the temperature range of 100–160 °C;[12] the miscibility behavior below 100 °C is not experimentally unknown. As shown in Figure 5, on the other hand, the calculated results of the temperature dependence of χ_1 show that these blends are type a, described above. This suggests that the EtVAc/PVC blends may have a so-called miscibility window.

As shown in Figure 4, the calculated results for the EtVAc/VAcVC copolymer blends showed that the intermolecular parameters χ_1 increase monotonically from negative to positive with temperature in the shadowy copolymer composition range and that the temperature–χ_1 curves are U-shaped in the other range. This means that the blends can be miscible below a certain temperature regardless of the copolymer composition in the shadowy region. Comparison between the shadowy region and the experimental miscibility region shows that the theory extended to the random copolymer blends gives qualitative agreement with experiments for the copolymer composition dependence of miscibility.

Acknowledgment. We thank Kuraray Co. and Bayer Ltd. for supplying EtVAc copolymers and Shin-Etsu Chemical Co. for gifts of PVC homopolymers. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture (Subject No. 61550654) and by the Ogasawara Foundation for the Promotion of Science and Engineering.

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Registry No. EtVAc (copolymer), 24937-78-8; PVC, 9002-86-2; THF, 109-99-9; VAcVC90, 9003-22-9.