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A consideration on miscibility behaviour in random copolymer blends based on the equation-of-state theory

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So-called miscibility and immiscibility windows in random copolymer blends are terms that describe the variation in miscibility with copolymer composition, i.e. immiscible → miscible → immiscible and miscible → immiscible → miscible, respectively. The miscibility has been explained by the change of sign of the intermolecular interaction parameter χ expressed in terms of the intersegmental interaction parameters. For the former and the latter windows the sign of the intermolecular parameter χ changes with copolymer composition from positive → negative → positive and negative → positive → negative, respectively. However, the changing pattern of the sign of χ may depend on temperature because the Flory–Huggins interaction parameter χ depends on temperature. Flory's equation-of-state theory gives two kinds of temperature dependence of χ: (a) a U-shaped curve, which is always positive, and (b) a function increasing monotonically from negative to positive. In this report we discuss, on the basis of Flory's equation-of-state theory, how the pattern of the temperature dependence of χ changes with copolymer composition for copolymer blends. In consequence, even though the sign of χ changes with copolymer composition from positive → negative → positive in a limited temperature range, there were two types of dependences of temperature *versus* χ curve on copolymer composition: (1) (b) regardless of the copolymer composition as well as (2) (a) → (b) → (a) with copolymer composition predicted by theory. Also, for the blends in which χ changes from negative → positive → negative at a certain temperature, two types were obtained: (3) (b) regardless of the copolymer composition as well as (4) (b) → (a) → (b) with copolymer composition. U-shaped curves can be found only in types (2) and (4); namely in these two types there exists a copolymer composition range where the two polymers are immiscible regardless of temperature. Therefore, it was concluded that so-called miscibility and immiscibility windows should be defined by types (2) and (4), respectively, even though the miscibility change is observed to be immiscible → miscible → immiscible or miscible → immiscible → miscible with copolymer composition in a limited range of temperature.

(Keywords: copolymer blend; miscibility window; immiscibility window; interaction parameter; equation-of-state theory)

INTRODUCTION

Recently, miscibility in random copolymer blends has been studied theoretically and experimentally[1–6]. In particular, it has been reported that some polymer blends containing random copolymers are miscible in a certain range of copolymer composition even though any binary combination of the homopolymers of their constituent monomers is immiscible. Such miscibility has been called a miscibility window, and explained by extension of the Flory–Huggins interaction parameter χ to random copolymer systems as follows[3–5].

The intermolecular interaction parameter χ for blends of homopolymer 1 with random copolymer 2, C_yD_{1-y}, can be written as:

$$\chi = y\chi_{1C} + (1-y)\chi_{1D} - y(1-y)\chi_{CD} \tag{1}$$

where χ_{ij} are the intersegmental χ parameters and y is the copolymer composition expressed as a volume fraction. According to the Flory–Huggins theory[7], the critical value of χ for a mixture of r_1- and r_2-mers is:

$$\chi_{\text{crit}} = \frac{1}{2}(r_1^{-1/2} + r_2^{-1/2})^2 \tag{2}$$

where the size of the segment is taken to be of equal volume between r_1- and r_2-mers. In the limit of infinite molecular weights of both polymers, as is clear from equation (2), two polymers are miscible in the whole concentration range when $\chi < 0$. In equation (1), even though all the intersegmental χ_{ij} are positive, the intermolecular χ can be negative when the relation among χ_{ij} satisfies the equation[5,6]:

$$|\chi_{CD}| > (|\chi_{1C}|^{1/2} + |\chi_{1D}|^{1/2})^2 \tag{3}$$

Equation (3) means that the repulsive interaction between the segment monomers C and D in the copolymer C_yD_{1-y} is significantly large compared to the interactions between the segments belonging to different polymers. Therefore, this has been called a repulsive effect.

Furthermore, equation (1) suggests that an immiscibility region may exist in a certain range of copolymer composition even if all combinations of homopolymers corresponding to the constituent monomers are miscible. Namely, even though all the χ_{ij} are negative, the intermolecular χ parameter can be positive. Even in this case, equation (3) is satisfied. This immiscibility may be called an immiscibility window by analogy with the miscibility window. A few real systems[8,9] whose miscibil-

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ity changes with copolymer composition from miscible → immiscible → miscible have been found.

Although miscibility and immiscibility windows have been explained so far by equation (1), as mentioned above, equation (1) does not explicitly reveal the temperature dependence of χ. Even if equation (3) is valid at a certain temperature, it does not necessarily hold at another temperature because the interaction parameter depends on temperature.

According to the equation-of-state theory[10,11], χ is expressed as follows:

$$\chi = f(T) + X_{12}/g(T) \tag{4}$$

where both $f(T)$ and $g(T)$ are functions increasing monotonically with temperature and X_{12} is the intermolecular exchange enthalpy parameter. The first and second terms on the right-hand side express the contributions of the free-volume difference and enthalpic interactions, respectively. When X_{12} is positive, the temperature dependence of χ is a U-shaped curve and χ is positive at all temperatures; while χ increases monotonically from negative to positive values with an increase in temperature when X_{12} is negative. For so-called miscibility and immiscibility windows, therefore, the above two types of temperature dependences of χ should be taken into account as well as the change of the sign of χ at a certain temperature, i.e. equation (3). ten Brinke *et al.*[4] qualitatively discussed miscibility and immiscibility windows on the basis of the second term of equation (4).

In this paper, we will discuss the miscibility and immiscibility windows in random copolymer blends on the basis of the interaction parameter χ obtained by extending Flory's equation-of-state theory for homopolymer systems to random copolymer systems. In particular, we will show how the type of temperature dependence of χ changes with copolymer composition for copolymer blends for which equation (3) is valid at a certain temperature.

THEORETICAL

In this section, we extend Flory's equation-of-state theory[10] to the random copolymer system, the mixture of homopolymer 1 and random copolymer 2 (C_yD_{1-y}).

In the Flory theory, the principle of corresponding states is assumed; the reduced variables $\tilde{v}$, $\tilde{T}$ and $\tilde{p}$ of volume, temperature and pressure are given by:

$$\tilde{v} = v/v^* \tag{5}$$

$$\tilde{T} = T/T^* \tag{6}$$

$$\tilde{p} = p/p^* \tag{7}$$

where v^*, T^* and p^* are the reduction or characteristic parameters. T^* and p^* are defined by

$$T^* = s\eta/2v^*ck \tag{8}$$

$$p^* = s\eta/2v^{*2} \tag{9}$$

where s is the number of contact sites per segment, η is the parameter characterizing the intermolecular energy and c is the external degrees of freedom per segment. These characteristic parameters p^*, v^* and T^* satisfy the equation:

$$p^*v^* = ckT^* \tag{10}$$

For a mixture comprising N_1 r_1-mers of (homopolymer) 1 and N_2 r_2-mers of (copolymer) 2, C_yD_{1-y}, the total intermolecular energy E_0 may be expressed by the following equation under the assumption that the total energy is additive in the segmental contact sites:

$$E_0 = -(A_{11}\eta_{11} + A_{CC}\eta_{CC} + A_{DD}\eta_{DD} + A_{CD}\eta_{CD} + A_{1C}\eta_{1C} + A_{1D}\eta_{1D})/v \tag{11}$$

where $-\eta_{ij}/v$ is the intersegmental energy per i–j contact and A_{ij} is the number of i–j contacts. When random mixing of segments is assumed and when a method the same as Flory's[10] is used, then the energy E_0 can be rewritten as:

$$\begin{aligned} -E_0/(r_1N_1 + r_2N_2) &= \{\phi_1 p_1^* + \phi_2[yp_C^* + (1-y)p_D^* - y\theta_{2D}X_{CD}] \\ &\quad - \phi_1\theta_2[\theta_{2C}X_{1C} + \theta_{2D}X_{1D} \\ &\quad - \theta_{2C}\theta_{2D}(s_1/s_C)X_{CD}]\}v^*/\tilde{v} \end{aligned} \tag{12}$$

where X_{kl} is the exchange enthalpy parameter between the components k and l defined in the same way as Flory's, ϕ_1 and ϕ_2 are the segment fractions, θ_1 and θ_2 are the site fractions of the polymers 1 and 2 and θ_{2C} and θ_{2D} are the site fractions of the segment C and D in the copolymer 2. These fractions are defined by:

$$\phi_2 = 1 - \phi_1 = r_2N_2/(r_1N_1 + r_2N_2) \tag{13}$$

$$\theta_1 = 1 - \theta_2 = \phi_1 s_1/[\phi_1 s_1 + \phi_2 y s_C + \phi_2(1-y)s_D] \tag{14}$$

$$\theta_{2C} = 1 - \theta_{2D} = \theta_C/\theta_2 = ys_C/[ys_C + (1-y)s_D] \tag{15}$$

respectively.

Defining the characteristic pressure p_2^* of the copolymer 2 and the exchange enthalpy X_{12} between the polymers 1 and 2 as:

$$p_2^* = yp_C^* + (1-y)p_D^* - y\theta_{2D}X_{CD} \tag{16}$$

and

$$X_{12} = \theta_{2C}X_{1C} + \theta_{2D}X_{1D} - \theta_{2C}\theta_{2D}(s_1/s_C)X_{CD} \tag{17}$$

respectively, then equation (12) can be rewritten as:

$$-E_0/(r_1N_1 + r_2N_2) = (\phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2 X_{12})v^*/\tilde{v} \tag{18}$$

When the energy E_0 for the mixture is defined by:

$$-E_0/(r_1N_1 + r_2N_2) = p^*v^*/\tilde{v} \tag{19}$$

comparison of equation (19) with equation (18) gives:

$$p^* = \phi_1 p_1^* + \phi_2 p_2^* - \phi_1\theta_2 X_{12} \tag{20}$$

for the characteristic pressure p^* for the mixture.

The characteristic temperature T_2^* of copolymer 2 can be derived using equation (10) under the assumption of additivity for the external degrees of freedom, namely the equation:

$$c_2 = yc_C + (1-y)c_D \tag{21}$$

gives:

$$1/T_2^* = [y(p_C^*/T_C^*) + (1-y)(p_D^*/T_D^*)]/p_2^* \tag{22}$$

In the same way, T^* for the mixture can be expressed as follows:

$$1/T^* = [\phi_1(p_1^*/T_1^*) + \phi_2(p_2^*/T_2^*)]/p^* \tag{23}$$

As shown in equations (16), (17) and (22), it should be noted that p_2^* and T_2^* for the copolymer and X_{12} are independent of the polymer concentration, and also the expressions of p^* and T^* given by equations (20) and (23), respectively, for the mixture are the same as Flory's. Therefore, various thermodynamic quantities of mixing for random copolymer systems derived using the partition function proposed by Flory are completely the same as those for homopolymer systems if p_2^* and T_2^* are fixed. The enthalpy of mixing is:

$$\Delta H^{\mathrm{M}} = (r_1 N_1 + r_2 N_2) v^* (\phi_1 p_1^*/\tilde{v}_1 + \phi_2 p_2^*/\tilde{v}_2 - p^*/\tilde{v}) \tag{24}$$

and the excess volume V^{E} is:

$$V^{\mathrm{E}}/V^0 = \tilde{v}^{\mathrm{E}}/\tilde{v}_0 = (\tilde{v} - \tilde{v}_0)/\tilde{v}_0 \tag{25}$$

where V^0 is the unmixed volume and:

$$\tilde{v}_0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2 \tag{26}$$

The interaction parameter χ defined by the expression for the following chemical potential:

$$(\mu_1 - \mu_1^0)/RT = \ln(1 - \phi_2) + (1 - r_1/r_2)\phi_2 + \chi\phi_2^2 \tag{27}$$

can be written as:

$$\begin{aligned}\chi = {} & (p_1^* r_1 v^*/RT\phi_2^2)\{3\tilde{T}_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] \\ & + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} + r_1 v^* X_{12}\theta_2^2/(\tilde{v}RT\phi_2^2)\end{aligned} \tag{28}$$

At infinite dilution:

$$\begin{aligned}\chi_1 = {} & \lim_{\phi_2 \to 0} \chi \\ = {} & (p_1^* r_1 v^*/\tilde{v}_1 RT)\alpha_1 T A^2/2 + (p_1^* r_1 v^*/\tilde{v}_1 RT) Y_{12}\end{aligned} \tag{29}$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (s_2/s_1) X_{12}/p_1^* \tag{30}$$

$$Y_{12} = (s_2/s_1)^2 X_{12}/p_1^* \tag{31}$$

For simplicity, assuming that the numbers of contact sites per segment are the same among the components, i.e.:

$$s_1 = s_{\mathrm{C}} = s_{\mathrm{D}} \tag{32}$$

we obtain:

$$s_1 = s_2 \tag{33}$$

and

$$\theta_2 = 1 - \theta_1 = \phi_2 \tag{34}$$

$$\theta_{2\mathrm{D}} = 1 - \theta_{2\mathrm{C}} = 1 - y \tag{35}$$

Then, A and Y_{12} can be rewritten as:

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - X_{12}/p_1^* \tag{36}$$

$$\begin{aligned} = {} & \{y(1 - T_1^*/T_{\mathrm{C}}^*)p_{\mathrm{C}}^* - X_{1\mathrm{C}}] \\ & + (1 - y)[(1 - T_1^*/T_{\mathrm{D}}^*)p_{\mathrm{D}}^* - X_{1\mathrm{D}}]\}/p_1^*\end{aligned} \tag{37}$$

and

$$Y_{12} = X_{12}/p_1^* \tag{38}$$

with

$$X_{12} = yX_{1\mathrm{C}} + (1 - y)X_{1\mathrm{D}} - y(1 - y)X_{\mathrm{CD}} \tag{39}$$

In this case, X_{12} is a quadratic equation for the copolymer composition y at a given temperature.

RESULTS AND DISCUSSION

In this section we present the results of the temperature dependence of χ simulated using equation (29), i.e. the expression of χ_1 at $\phi_2 = 0$. Therefore, the shape of the phase diagram is rather different from that drawn using the concentration-dependent χ expressed in equation (28), and also the value of χ and its temperature dependence obtained here are somewhat different from those of χ at $\phi_1 = 0$ because the expression for χ in equation (28) is not symmetrical about the concentration. However, trends of temperature dependence of χ_1 simulated here would be useful for the purpose of this study. Furthermore, in calculations we use the expression of χ_1 with equations (36)–(39) which are for $s_1 = s_{\mathrm{C}} = s_{\mathrm{D}}$.

The results of the temperature dependence of $\chi_1/(r_1 v^*)$ calculated using the characteristic parameters shown in *Table 1* and using the exchange enthalpy parameters given in the respective figure legends are shown in parts (a) of *Figures 1–4*. The values of these parameters used in the calculation were arbitrarily given, though they are usual for polymers. In these figures, the broken and chain curves indicate the interactional and free-volume contributions, which correspond to the first and second terms on the right-hand side of equation (29), respectively, and the full curve is $\chi_1/(r_1 v^*)$, which is the sum of the above two contributions. Parts (b) in these figures show the copolymer composition dependence of the exchange enthalpy parameter obtained by use of equation (39). Parts (c) show the schematic illustrations of relation between the temperature at $\chi_1 = 0$ and the copolymer composition. The critical temperature should be obtained by the critical conditions $(\partial\mu_1/\partial\phi_2) = (\partial^2\mu_1/\partial\phi_2^2) = 0$. Since the concentration dependence of χ may be very small in the vicinity of $\chi = 0$[11–13], the critical temperature may be very close to the temperature at $\chi_1 = 0$. Therefore, parts (c) would show a good approximation to the relation between the critical temperature and the copolymer composition.

As examples of the calculated results in *Figures 1* and *2* show, there are two types of dependences of the temperature–χ_1 curve on copolymer composition for the copolymer blends whose miscibility changes from immiscible → miscible → immiscible with copolymer composition in a certain temperature range around T_{ob}. In the example shown in *Figure 1*, the temperature dependence of χ_1 changes from a U-shaped → monotonically increasing → U-shaped function with copolymer composition. Since the pattern of the temperature dependence of χ_1 depends on the sign of the exchange enthalpy parameter X_{12} between polymers 1 and 2, this can be predicted by equation (29) with equation (39). As is obvious from equation (39), derived on the assumption of equation (32), X_{12} is changed from positive → negative → positive with copolymer composition y on the following condition:

$$|X_{\mathrm{CD}}| > (|X_{1\mathrm{C}}|^{1/2} + |X_{1\mathrm{D}}|^{1/2})^2 \tag{40}$$

Table 1 Characteristic parameters used in simulation of temperature dependence of χ_1 for blends of homopolymer 1 with random copolymer 2 ($C_y D_{1-y}$)

	T^* (K)			p^* (J cm^{-3})		
Figure number	1	C	D	1	C	D
1–3	5500	7500	4000	450	650	350
4	7500	5500	4000	650	450	350

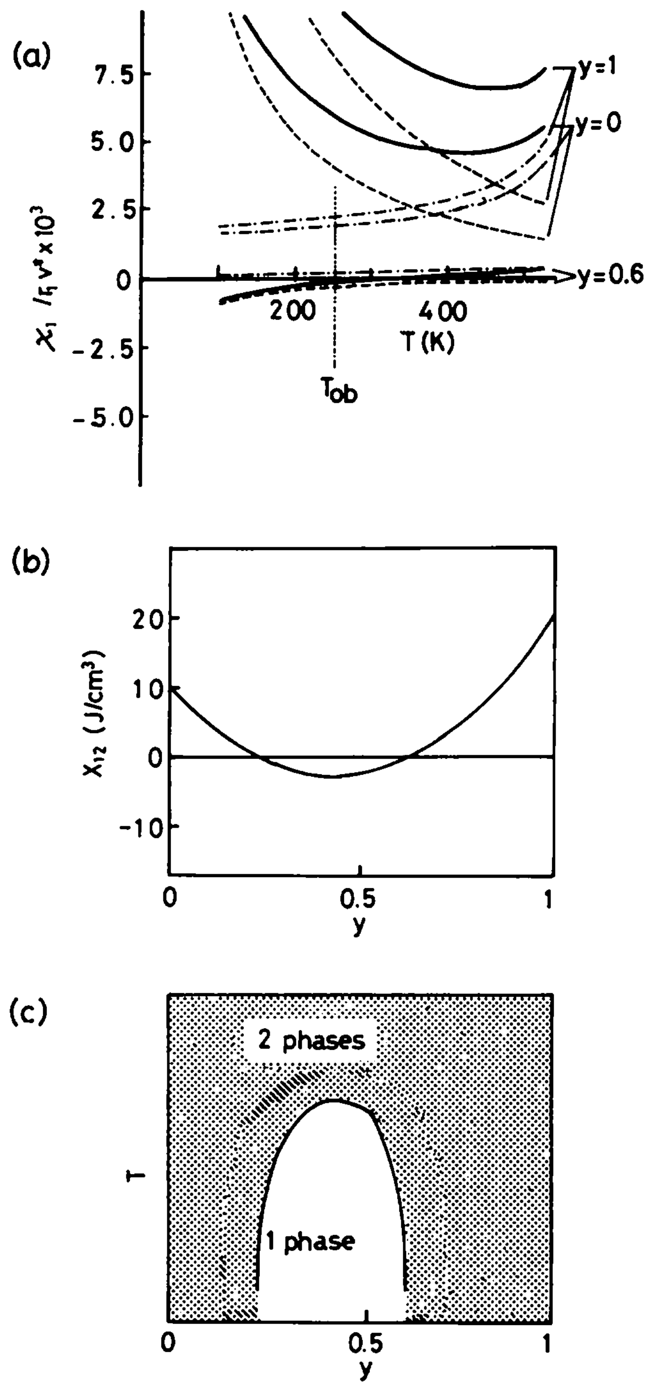

Figure 1 (a) Temperature dependence of χ_1 at copolymer composition y, (b) dependence of the exchange enthalpy parameter X_{12} on the copolymer composition and (c) schematic illustration of miscibility in the copolymer composition–temperature plane for the blend of homopolymer 1 with random copolymer 2 (C_yD_{1-y}). The calculations of χ_1 and X_{12} were carried out using $X_{1C} = 20$ J cm^{-3}, $X_{1D} = 10$ J cm^{-3} and $X_{CD} = 70$ J cm^{-3} together with the characteristic parameters shown in *Table 1*

In the range of copolymer composition in which the temperature dependence of χ_1 is U-shaped, two polymers with infinite molecular weight are immiscible regardless of temperature, while two polymers are miscible below a certain temperature at the copolymer composition where χ_1 is a monotonically increasing function. The schematic illustration of miscibility corresponding to these behaviours of the temperature dependence of χ_1 is shown in *Figure 1c*. As shown in *Figure 2a*, even though the temperature dependence of χ_1 is a monotonically increasing function over all the copolymer compositions, the sign of χ_1 can change from positive → negative → positive with copolymer composition (namely miscibility changes from immiscible → miscible → immiscible) in a limited temperature range around T_{ob}. In this case, however, the sign of χ_1 is negative below a certain temperature regardless of the copolymer composition, namely two polymers are miscible below that temperature regardless of the copolymer composition (*Figure 2c*).

Figures 3 and *4* show the cases in which the dependence of miscibility behaviour on copolymer composition is like a so-called immiscibility window in a certain temperature range. In both cases, miscibility changes from miscible → immiscible → miscible with copolymer composition in the vicinity of T_{ob}. In the case of *Figure 3*, two polymers

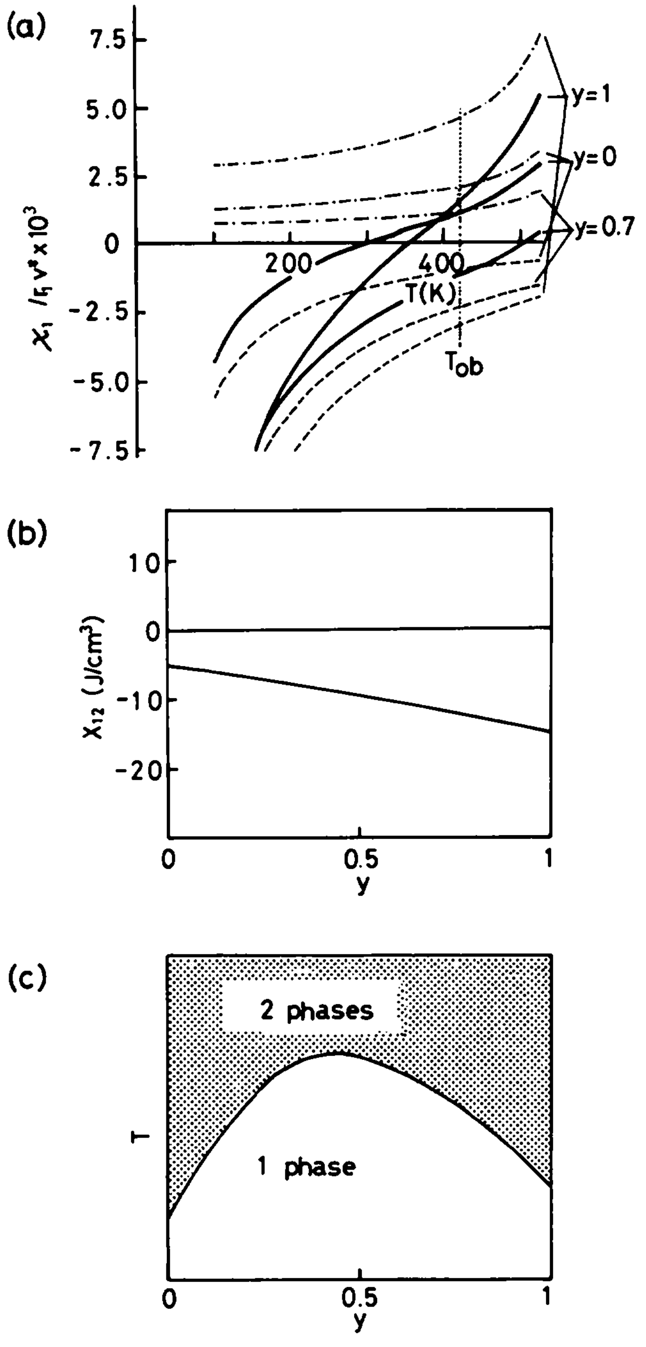

Figure 2 The calculations of χ_1 and X_{12} were carried out using $X_{1C} = 15$ J cm^{-3}, $X_{1D} = 5$ J cm^{-3} and $X_{CD} = -2$ J cm^{-3}. See the legend of *Figure 1*

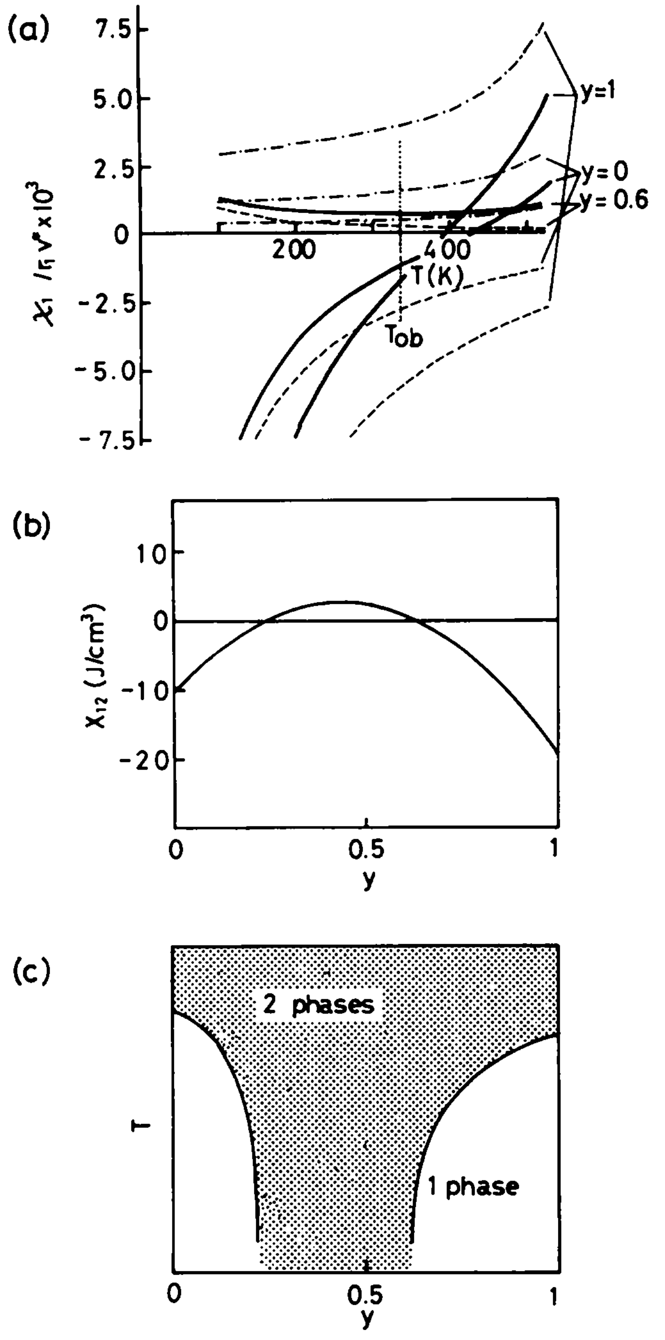

Figure 3 The calculations of χ_1 and X_{12} were carried out using $X_{1C} = -20$ J cm^{-3}, $X_{1D} = -10$ J cm^{-3} and $X_{CD} = -70$ J cm^{-3}. See the legend of *Figure 1*

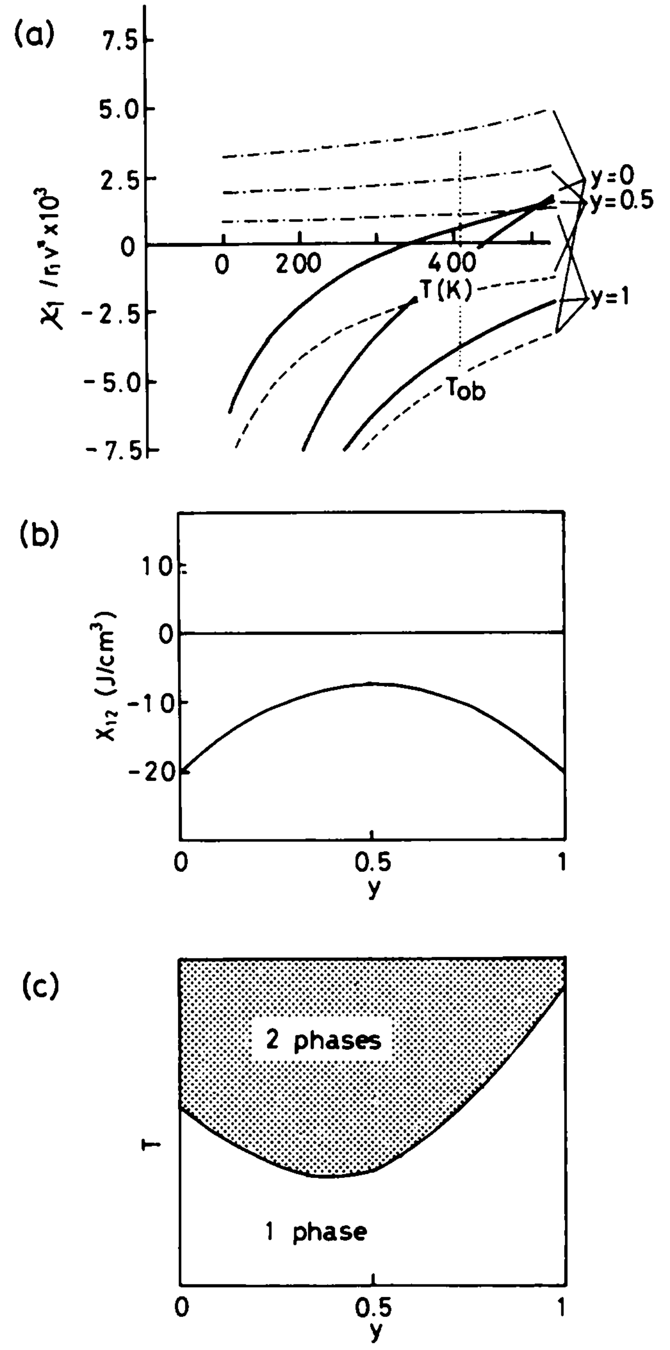

Figure 4 The calculations of χ_1 and X_{12} were carried out using $X_{1C} = -20$ J cm^{-3}, $X_{1D} = -20$ J cm^{-3} and $X_{CD} = -50$ J cm^{-3}. See the legend of *Figure 1*

are immiscible over all the temperatures in the copolymer composition range corresponding to the positive intermolecular exchange enthalpy parameter X_{12} shown in *Figure 3b*. In this case, equation (40) is satisfied. In the case shown in *Figure 4*, on the other hand, two polymers are miscible over all copolymer compositions below a certain temperature. These dependences of miscibility on copolymer composition are qualitatively shown in *Figures 3c* and *4c*, respectively.

As mentioned above, there are two types of dependences of temperature–χ curve on copolymer composition for both miscibility behaviours like miscibility and immiscibility windows observed in a certain temperature range. In addition to those, for the blends comprising polymers with finite molecular weights, *apparent* miscibility and immiscibility windows may obey some other types besides those discussed here because $\chi_{\rm crit}$ is not zero. The miscibility and immiscibility windows may be defined by the cases shown in *Figures 1* and *3*, respectively, or by equation (40) on the assumption of $s_1 = s_C = s_D$, because in these cases an immiscibility region with respect to copolymer composition exists regardless of temperature. Therefore, for the dependence of miscibility on copolymer composition obtained experimentally in a limited temperature range, whether it is a so-called miscibility (or immiscibility) window or not should be concluded by the type of temperature dependence of χ.

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