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UCST and LCST behaviour in polymer blends containing poly(methyl methacrylate-stat-styrene)

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Miscibility behaviour was investigated for the blends of homopolymer A with the random copolymer consisting of two components B and C, where the A homopolymer is miscible with homopolymer B but immiscible with homopolymer C. The copolymer employed was poly(methyl methacrylate-stat-styrene) (MMA·S), and the homopolymers were polystyrene (PS), poly(vinyl methyl ether) (PVME), and poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG), where PS is immiscible with MMA homopolymer, PVME is miscible with S but immiscible with MMA, and PEO or PEG is miscible with MMA but immiscible with S. UCST-type miscibility was observed for the PEO/MMA·S blends though the homopolymer blends PEO/PMMA had been reported to be of LCST-type. UCST-type miscibility was found for PS/MMA·S as well. On the other hand, PVME/MMA·S showed LCST-type miscibility with miscibility window-like behaviour. Such contrasting miscibility behaviour, i.e. appearances of UCST and LCST, for a series of MMA·S copolymer blends was discussed on the basis of the Flory–Patterson free volume theory. As a result, it was suggested that contribution of the free volume term decreases for PEO/MMA·S (UCST type), increases for PVME/MMA·S (LCST type) and is little changed for PS/MMA·S (UCST type), compared with that for the respective miscible component pairs, PEO/MMA, PVME/S and PS/S. Furthermore, the Flory–Huggins χ parameters between different components were estimated as a temperature-dependent function from dependence of miscibility on the copolymer composition in these blends. In this estimation, the χ parameters determined for PVME/PS and PEO/PMMA by Han *et al.* and Ito *et al.*, respectively, using neutron scattering technique were used as a standard. The miscible/immiscible boundaries drawn using the χ parameters obtained reproduced well the experimental results of the dependence of miscibility on the molecular weight as well as on the copolymer composition. Thus, it was shown that the χ parameters for immiscible pairs such as PS/PMMA, PEO/PS and PVME/PMMA can be evaluated by use of the blend type A/B·C dealt with here. © 1997 Elsevier Science Ltd.

(Keywords: UCST; LCST; copolymer blend; χ parameter; free volume theory)

INTRODUCTION

Miscibility in high molecular weight polymer blends is governed mostly by intermolecular interactions because contribution of the combinatorial entropy to mixing is negligibly small. Miscibility for most miscible polymer blends is caused by specific (i.e. attractive) interactions, which leads to lower critical solution temperature (LCST) behaviour. On the other hand, upper critical solution temperature (UCST) type miscibility occurs only in the dispersion force-dominant systems in which exchange interactions on mixing are very small. In spite of such a limited condition, UCST-type miscibility has been observed for some blends of random copolymers[1–3] as well as of homopolymers similar to each other in chemical structures[3]. In some random copolymer blends, intermolecular interactions may be adjusted by an appropriate combination of the copolymer components and by a choice of copolymer compositions. Such a property peculiar to random copolymers makes control of miscibility possible.

In the present paper, we focus on miscibility in the blends of homopolymer A with the random copolymer consisting of components B and C where homopolymer A is miscible with homopolymer B but immiscible with homopolymer C. In such copolymer blends, miscibility becomes poor with increasing immiscible copolymer component C. It is important for miscibility control to consider which appears, UCST or LCST, with an increase of component C. In this study, the blends containing poly(methyl methacrylate-stat-styrene) (MMA·S) are dealt with as such copolymer blends. The pair homopolymers are poly(vinyl methyl ether) (PVME), poly(ethylene oxide) (PEO) or poly(ethylene glycol) (PEG), and polystyrene (PS), respectively. PVME is miscible with the S component but immiscible with the MMA component, while PEG or PEO is miscible with MMA but immiscible with S.

Furthermore, the Flory–Huggins interaction parameters χ between different segments are estimated from dependence of miscibility on the copolymer composition in the above blends. This estimation method has been applied to some random copolymer blends[3–7]. Estimation of the χ parameters for polymer blends has been attempted by small-angle neutron and X-ray scattering techniques, but their application has been limited to miscible polymer blends. The method described in this paper enables us to estimate χ parameters even for immiscible pairs as well as miscible ones. If a blend type of homopolymer A/random copolymer

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B·C or A·C dealt with here is used, one can necessarily observe miscibility gaps in a measurable temperature range by adjusting contents of immiscible component C because the components A and B are miscible with or the same as each other. Therefore, we can estimate the χ parameters for immiscible pairs A/C and/or B/C from experimentally-obtained dependence of miscibility on the copolymer composition, if only random copolymer A·C or B·C can be synthesised.

EXPERIMENTAL

Poly(styrene) (PS) and poly(methyl methacrylate-stat-styrene) (MMA·S) were prepared by radical polymerisation in bulk at 80°C using 1 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 a benzene (Bz)/methanol (MeOH) system. Poly (vinyl methyl ether) (PVME) purchased from Tokyo Kasei Kogyo Co. was crudely fractionated using a Bz/hexane system. Poly(ethylene glycol) (PEG) and poly(ethylene oxide) (PEO) purchased from Scientific Polymer Products Inc. were crudely fractionated using chloroform ($CHCl_3$)/petroleum ether and Bz/petroleum ether, respectively. The PEO standard with 2.6×10^4 of molecular weight, purchased from Tosoh Co., was used without further purification and fractionation. Molecular weights were determined by GPC measurement (Tosoh Model CCPD) in tetrahydrofuran (THF) relative to the polystyrene standard, and copolymer compositions by 270 MHz ^{1}H n.m.r. (JEOL JNM GX-270) in $CDCl_3$ at 40°C. These characteristics of the polymers employed are listed in *Table 1*.

Films of PS/MMA·S and PVME/MMA·S for cloud point measurements were cast from 5 wt% solutions in THF on a glass plate; the solvent was evaporated at room temperature, and the cast films were further dried under vacuum for 3 days at a temperature above their glass transition temperatures (T_g). Blends of PVME/MMA·S and PEO (or PEG)/MMA·S for DSC measurements were prepared by dissolving both component polymers in a common good solvent and then precipitating the solution into a large excess of common non-solvent. Combinations of common good/non-solvents employed for PVME/MMA·S and PEO (or PEG)/MMA·S were THF/MeOH and $CHCl_3$/petroleum ether, respectively. The precipitates were dried under vacuum for at least 3 days above their T_g.

In the cloud point measurements the films were annealed for at least 30 min at a miscible temperature, and then were cooled and heated for PS/MMA·S and PVME/MMA·S, respectively, up to an immiscible region at the rate of 1–2°C min^{-1}. The cloud point was determined by detecting a sudden increase in intensity of He–Ne laser light scattered from the film. Another miscibility measurement was conducted by observation of T_g using a differential scanning calorimeter (d.s.c.), Seiko I&E Ltd DSC 20 with an SSC/580 thermal controller and data system. Sample sizes were approximately 20 mg for the blends and 10 mg for the pure polymers. The blends were annealed in the d.s.c. apparatus for more than 30 min at a desired temperature and then were rapidly cooled to an initial temperature of scanning. The heating rate was 10°C min^{-1} for all the samples.

RESULTS

UCST and LCST-type miscibility for blends containing random copolymer MMA·S

UCST-type miscibility was observed for the blends of PS with MMA·S copolymer. *Figure 1* shows an example of a

Table 1 Copolymer compositions and molecular weights of the polymers

Sample	MMA cont., mol%[a]	$10^{-4}\,\bar{M}_w$[b]	$\bar{M}_w/\bar{M}_n$[b]
(PS/MMA·S) and (PVME/MMA·S) systems			
PS	–	2.6	2.4
PVME8.7	–	8.7	1.9
PVME2.2	–	2.2	3.1
MMA·S13	13	2.2	1.7
MMA·S22	22	2.1	2.5
MMA·S28	28	2.7	1.8
MMA·S41	41	2.5	2.2
MMA·S54	54	3.3	2.1
MMA·S71	71	3.6	2.1
(PEG or PEO/MMA·S) system			
PEG0.5	–	0.5	1.1
PEO2.6[c]	–	2.6	1.2
PEO10	–	10[d]	–
PEO30	–	30[d]	–
PEO90	–	90[d]	–
MMA·S46	46	9.1	1.7
MMA·S64	64	11.0	1.7
MMA·S67	67	12.7	1.7
MMA·S73	73	12.4	1.7
MMA·S83	83	12.6	1.7

[a] Determined by 270 MHz ^{1}H n.m.r. measurement in $CDCl_3$
[b] Determined by GPC measurement relative to the polystyrene standard
[c] TSK standard PEO SE-2 (Tosoh Co)
[d] Nominal values

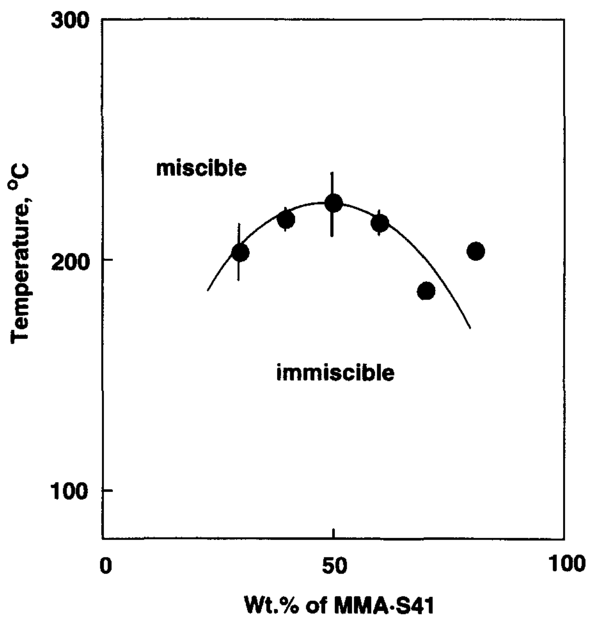

Figure 1 Cloud point curve for PS/MMA·S41 blends

UCST-type phase diagram for PS/MMA·S41 determined by cloud point measurements. *Figure 2* shows dependence of miscibility on the copolymer composition obtained from cloud point measurements at 50/50 wt% blend ratio. As shown in *Figure 2*, although miscibility gaps could be observed for the copolymers containing 28, 41 and 54 mol% of MMA, the blend of the copolymer containing 71 mol% of MMA remained immiscible till thermal decomposition occurred, while the blends of the copolymers containing less than 28 mol% of MMA kept miscible above glass transition temperatures.

The blends of PEG or PEO with MMA·S also showed UCST-type miscibility. *Figure 3* indicates copolymer composition dependence of miscibility for these blends with various molecular weights of PEG or PEO at 50/50 blend ratio. The miscible region of the copolymer composition is narrower as the molecular weight of PEO is larger. It should be noted that miscibility behaviour of the PEO/MMA·S copolymer blends is UCST-type although the homopolymer blends PEO/PMMA have been reported to be of LCST-type miscibility[8]. This is discussed in a later section.

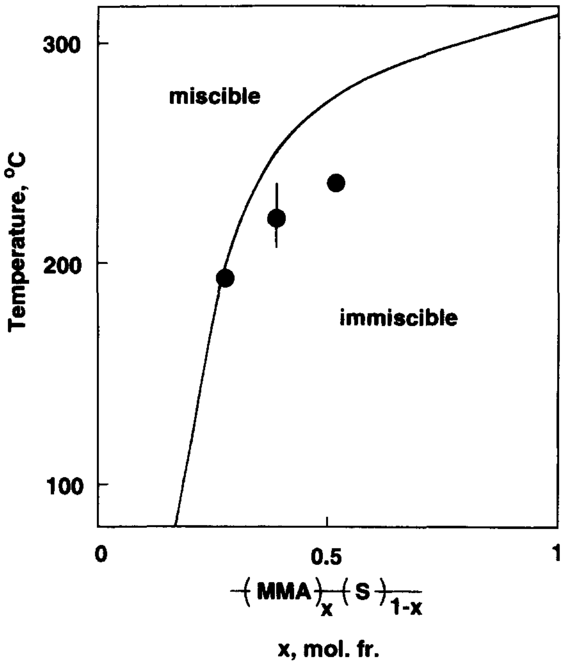

Figure 2 Dependence of miscibility on the copolymer composition for the PS/MMA·S blends obtained by cloud point measurements. The solid line is a calculated miscible/immiscible boundary line

An appearance of UCST in high molecular weight polymer blends is rare. Polymer blends can be miscible when the Flory–Huggins interaction parameter χ is smaller than a critical value of χ, χ_{crit}, given by

$$\chi_{\mathrm{crit}} = (r_1^{-1/2} + r_2^{-1/2})^2/2 \qquad (1)$$

where r_1 and r_2 are the numbers of segments for polymers 1 and 2, respectively. Since the χ_{crit} for high molecular weight blends is very small, most miscible blends found so far are attractive force-dominant systems whose χ values are negative. In this case, according to the temperature dependence of χ (*Figure 4*) described by the Flory–Patterson theory[9–12], only LCST appears owing to the free volume effect as indicated by the curve (c'). An appearance of UCST is limited to dispersion force-dominant systems in which the temperature dependence of χ is U-shaped as shown by the curve (c). Even in those systems an appearance of UCST is rare because χ values for usual polymer blends are not so small. UCST-type miscibility has been found for homopolymer pairs similar to each other in chemical structure[3] and some random copolymer blends[1–3].

Figure 5 shows an LCST-type phase diagram for PVME8.7/MMA·S28 obtained by cloud point measurements. *Figure 6* shows the copolymer composition dependence of miscibility for blends of MMA·S with PVME8.7 and PVME2.2, respectively, determined by d.s.c. measurements at 50/50 wt% blend ratio. As shown in *Figure 6*, the miscible temperature regions for the copolymer blends become larger in a range of small copolymer composition of MMA rather than those for the PVME/PS homopolymer blends corresponding to $x = 0$. This miscibility behaviour, like a so-called miscibility window, may be explained by more attractive interactions between MMA·S and PVME caused by the repulsion effect between the copolymer components MMA and S.

Estimation of segmental interaction parameters from miscibility

According to the Flory–Huggins theory extended to multicomponent systems, dependence of miscibility on the copolymer composition can be explained using the molecular interaction parameter χ expressed in terms of the segmental interaction parameters $\chi_{i/j}$ between the different constituent monomers. For a mixture of homopolymer A and random copolymer B_x-C_{1-x}, the molecular interaction parameter χ can be written as[13–17]

$$\chi = x\chi_{\mathrm{A/B}} + (1-x)\chi_{\mathrm{A/C}} - x(1-x)\chi_{\mathrm{B/C}} \qquad (2)$$

where x is the copolymer composition expressed with volume fraction of the copolymer. Since the parameter χ equals χ_{crit} at the critical state, the segmental $\chi_{i/j}$ can be estimated from the copolymer composition dependence of miscibility obtained experimentally using equation (2) if χ_{crit} is known. In estimation of $\chi_{i/j}$, the critical concentration was assumed to be 50 wt%, as shown in *Figures 1* and *5*, in neglect of polydispersities of molecular weights. The segment volume was taken to be the same value as molar mass of a styrene monomer unit. The numbers of segments for the

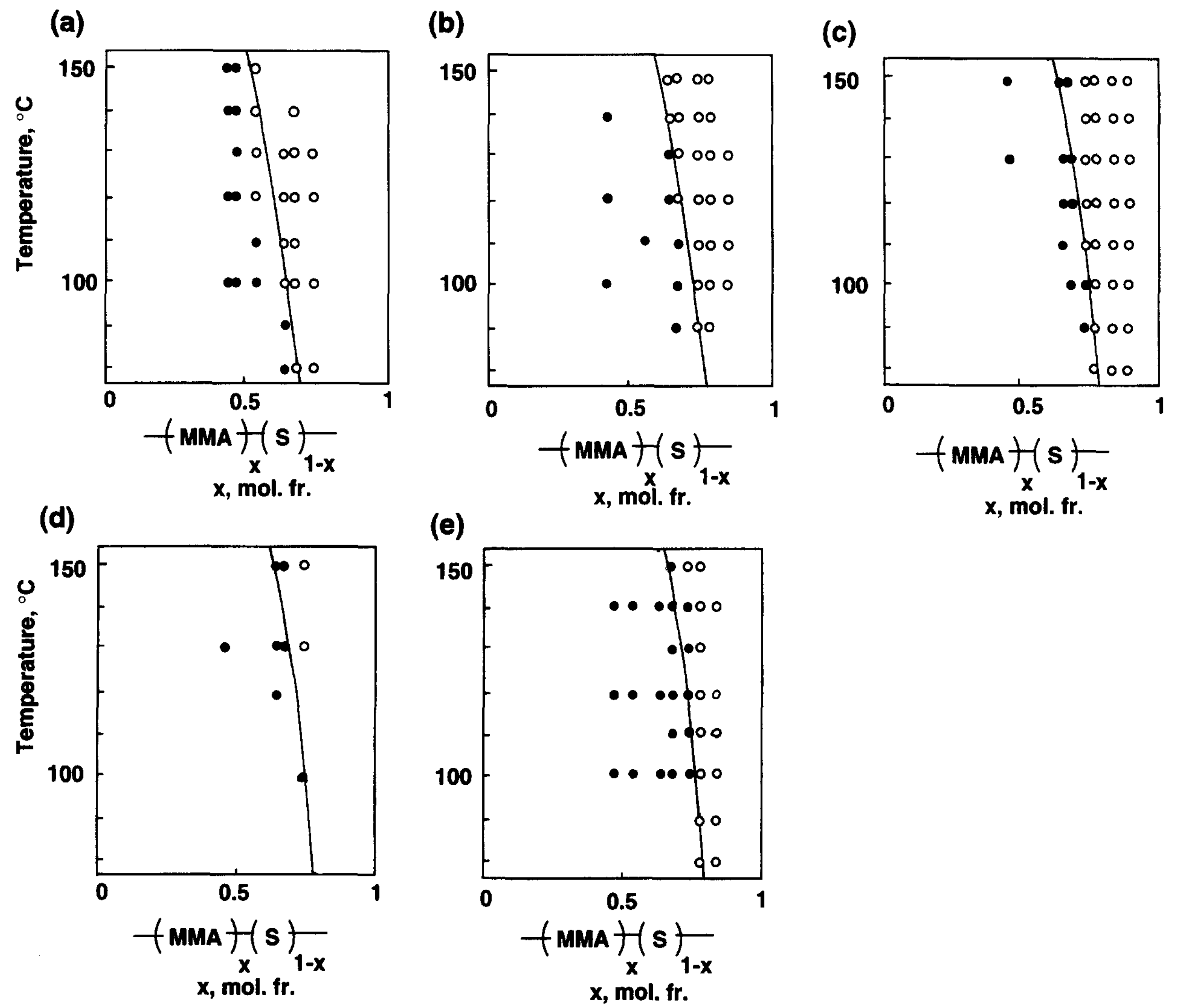

Figure 3 Dependence of miscibility on the copolymer composition for the blends of MMA·S with (a) PEG0.5, (b) PEO2.6, (c) PEO10, (d) PEO30, and (e) PEO90 obtained by d.s.c measurements: (○) miscible, (●) immiscible. The solid lines are calculated miscible/immiscible boundaries

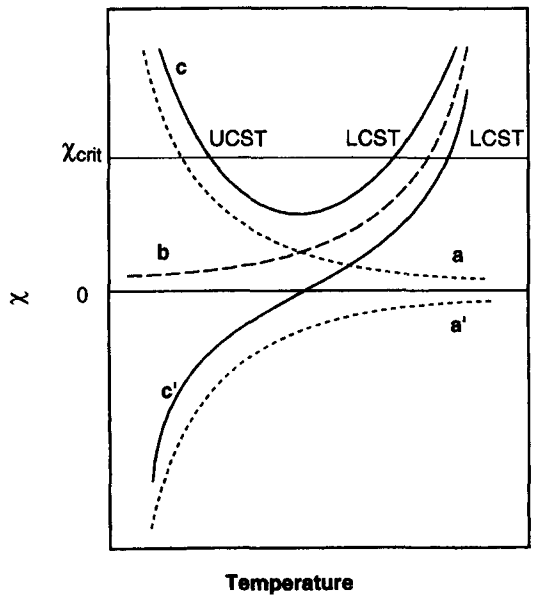

Figure 4 Schematic illustration of temperature dependence of χ: (a and a') the exchange enthalpy terms which correspond to positive and negative exchange enthalpy parameters X_{12}, respectively; (b) the free volume term; (c and c') $\chi = (a) + (b)$ and $\chi = (a') + (b)$, respectively

copolymers were taken as an average for a series of copolymers used for each blend system: the values of χ_{crit} are 8.43×10^{-3} for PS/MMA·S, 15.2×10^{-3}, 4.35×10^{-3}, 1.94×10^{-3}, 1.18×10^{-3} and 0.831×10^{-3} for the

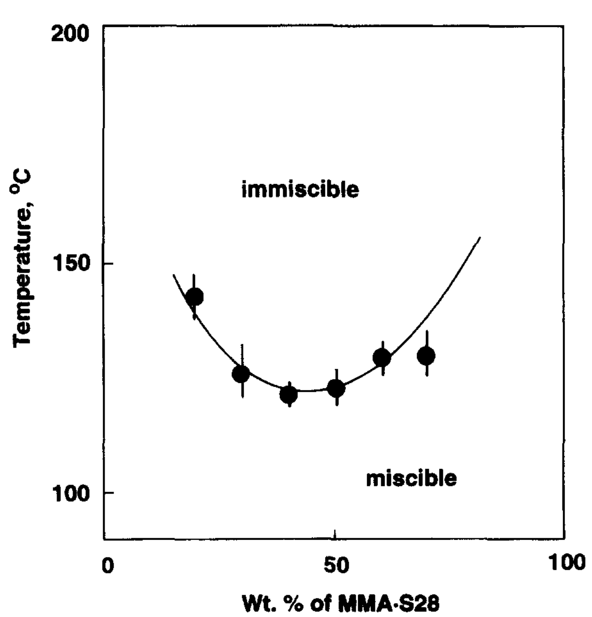

Figure 5 Cloud point curve for PVME8.7/MMA·S28 blends

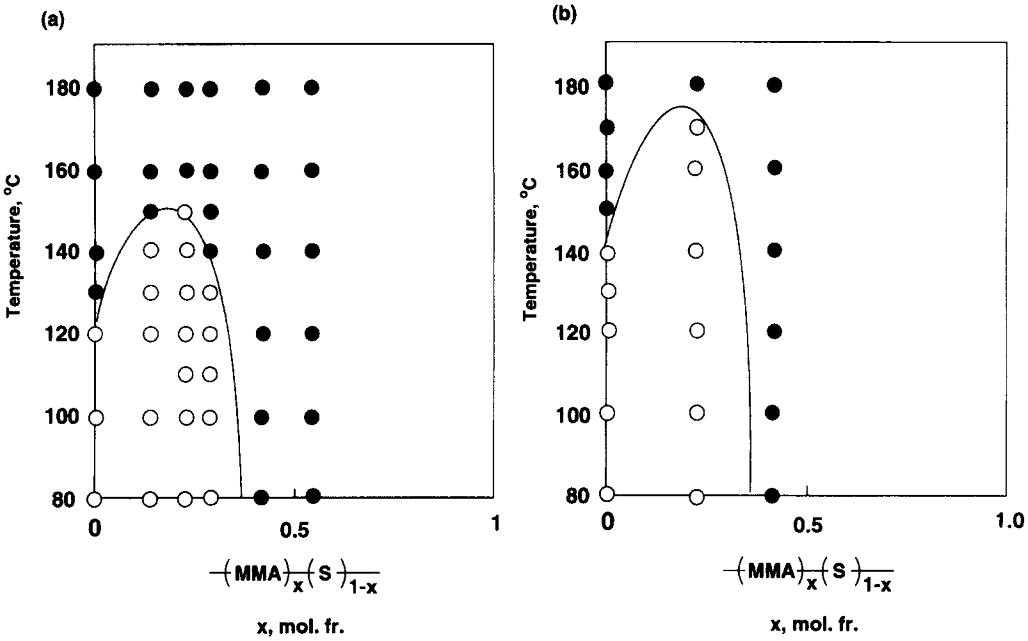

Figure 6 Dependence of miscibility on the copolymer composition for (a) PVME8.7/MMA·S and (b) PVME2.2/MMA·S obtained by d.s.c. measurements: (○) miscible, (●) immiscible. The solid lines are calculated miscible/immiscible boundaries

blends with PEG0.5, PEO2.6, PEO10, PEO30 and PEO90, respectively, and 4.57×10^{-3} and 8.42×10^{-3} for the blends with PVME8.7 and PVME2.2, respectively. Also, the segmental $\chi_{i/j}$ was assumed to be independent of the blend ratio, copolymer composition and molecular weight. If χ is put to depend on both the blend ratio and copolymer composition, a relation between them may be required. The temperature dependence of $\chi_{i/j}$ was expressed as

$$\chi_{i/j} = a + b/T \tag{3}$$

where a and b are constants and T is the temperature expressed in Kelvin.

First, equation (2) was applied to the PS/MMA·S system, in which the expression of the interaction χ in equation (2) can be simplified as

$$\chi = x^2 \chi_{\mathrm{A/B}} \tag{4}$$

where the segmental $\chi_{\mathrm{A/B}}$ corresponds to $\chi_{\mathrm{S/MMA}}$. When the miscible/immiscible boundary line calculated using equations (3) and (4) is given as shown by the solid line in *Figure 2*, the segmental $\chi_{\mathrm{S/MMA}}$ is expressed by

$$\chi_{\mathrm{S/MMA}} = -0.50 + 290/T \tag{5}$$

The calculated line differs somewhat from the experimental result, as shown in *Figure 2*. This difference may be reduced by using the parameter $\chi_{\mathrm{S/MMA}}$ dependent on the copolymer composition.

Next, equation (2) was applied to PEO (or PEG)/MMA·S systems, where $\chi_{\mathrm{A/B}}$, $\chi_{\mathrm{A/C}}$ and $\chi_{\mathrm{B/C}}$ correspond to $\chi_{\mathrm{EO/MMA}}$ (or $\chi_{\mathrm{EG/MMA}}$), $\chi_{\mathrm{EO/S}}$ (or $\chi_{\mathrm{EG/S}}$) and $\chi_{\mathrm{S/MMA}}$, respectively. Ito *et al.*[18] obtained $\chi_{\mathrm{EO/MMA}}$ for the blends of 50 wt% PEO with a mixture of protonated and deuterated PMMA at 80°C from small-angle neutron scattering (SANS) measurements, as

$$\chi_{\mathrm{EO/MMA}} = -5.0 \times 10^{-3} \tag{6}$$

Although miscibility in deuterated systems is affected by the isotope effect as described later, $\chi_{\mathrm{EO/MMA}}$ obtained by them was adopted here without modification because that effect on miscibility in the PEO/PMMA system is not known. The parameter $\chi_{\mathrm{EO/S}}$ was estimated so as to reproduce the experimental results in *Figure 3* using $\chi_{\mathrm{S/MMA}}$ and $\chi_{\mathrm{EO/MMA}}$ obtained above. When $\chi_{\mathrm{EO/S}}$ is put as

$$\chi_{\mathrm{EO/S}} = -0.60 + 309/T \tag{7}$$

the miscible/immiscible boundary lines calculated are obtained as shown in *Figure 3(a–e)*. Although the calculated results slightly deviate from the experimental ones at high temperatures, the dependence of miscibility on the molecular weight as well as on the copolymer composition is reproduced well. The deviation at high temperatures may come from the fact that the parameter $\chi_{\mathrm{EO/MMA}}$ was taken to be independent of temperature.

Finally, equation (2) was applied to the PVME/MMA·S system, where $\chi_{\mathrm{A/B}}$, $\chi_{\mathrm{A/C}}$ and $\chi_{\mathrm{B/C}}$ correspond to $\chi_{\mathrm{VME/MMA}}$, $\chi_{\mathrm{VME/S}}$ and $\chi_{\mathrm{MMA/S}}(= \chi_{\mathrm{S/MMA}})$, respectively. Since $\chi_{\mathrm{S/MMA}}$ has been determined already, $\chi_{\mathrm{VME/MMA}}$ and $\chi_{\mathrm{VME/S}}$ are estimated here. Han *et al.*[19] evaluated the parameter $\chi_{\mathrm{VME/S}}$ from SANS measurements for the blends of PVME with deuterated PS (PSD), as a function of concentration of PSD and temperature. Their result gives $\chi_{\mathrm{PVME/PSD}} = 0.084 - 34.7/T$ by extrapolating the PSD concentration to zero and converting to the value per styrene monomer. Miscibility for the blends of PVME with PSD and with protonated PS (PSH) differs from each other. The former blends are more miscible than the latter[20]. In fact, the boundary temperatures for the PVME/PS homopolymer blends calculated using the parameter $\chi_{\mathrm{VME/S}}$ obtained by Han *et al.*[19] were higher than the experimental boundaries shown at $x = 0$ in *Figure 6*. Such a difference in interactions between protonated and deuterated systems is due to the difference in vibrational modes between C–H and C–D bonds[21]. Bates and Wignal[22] and also Singh and Van Hook[23] formulated the χ parameter accounting for the differences in segment volumes and van der Waals forces coming from such an isotope effect. The χ parameter characterising this effect depends on temperature. Therefore, the temperature-dependent term of the parameter $\chi_{\mathrm{VME/S}}$ was somewhat modified to fit the experimental miscible/immiscible boundary for the PVME/PS homopolymer blends as

$$\chi_{\mathrm{VME/S}} = 0.084 - 31.6/T \qquad (8)$$

The $\chi_{\mathrm{VME/S}}$ value given by equation (8) is somewhat larger than above $\chi_{\mathrm{PVME/PSD}}$. This tendency is seen in comparison of $\chi_{\mathrm{PVME/PSD}}$ with $\chi_{\mathrm{PVME/PSH}}$[24] obtained by correction for $\chi_{\mathrm{PSH/PSD}}$. $\chi_{\mathrm{VME/MMA}}$ was determined from the experimental results of PVME/MMA·S shown in *Figure 6* using $\chi_{\mathrm{VME/S}}$ and $\chi_{\mathrm{S/MMA}}$ obtained above. When the segmental $\chi_{\mathrm{VME/MMA}}$ is taken to be

$$\chi_{\mathrm{VME/MMA}} = -0.37 + 212/T \qquad (9)$$

the calculated miscible/immiscible boundaries are obtained as shown by the solid lines in *Figure 6*. As shown in *Figure 6*, the calculated lines reproduce very well both the dependences of miscibility on the copolymer composition and molecular weight.

Figure 7 shows temperature dependence of $\chi_{i/j}$ estimated in this study together with that for EO/MMA obtained by Ito *et al.*[18] As shown in this figure, $\chi_{\mathrm{MMA/S}}$ is larger than the other interaction parameters. This implies that a repulsion effect between MMA and S exists in the blends containing the MMA·S copolymer as observed in miscibility behaviour of PVME/MMA·S. Also, the temperature dependence of χ shows that the enthalpic term is negative for the pairs VME/S and EO/MMA and positive for the S/MMA, EO/S and VME/MMA pairs.

DISCUSSION

In the present copolymer blends, although both homopolymer blends of PEO/PMMA and PVME/PS show LCST-type miscibility, UCST appears for the PEO/MMA·S blends while LCST for the PVME/MMA·S blends. The PS/MMA·S blends also show UCST-type miscibility. Generally there are two possibilities that a UCST or LCST appears in a measurable temperature range for the blends of homopolymer A with random copolymer B·C where the homopolymer pair A/B is miscible but A/C immiscible. According to the Flory–Patterson theory[9–12], the molecular interaction parameter χ consists of the exchange enthalpy and free volume difference terms. When in the A/C pair the contribution of the enthalpy term to immiscibility is larger than that of the free volume term in a measurable temperature range, UCST may appear for the copolymer blends A/B·C. On the other hand, LCST appears when the contribution of the free volume term is larger.

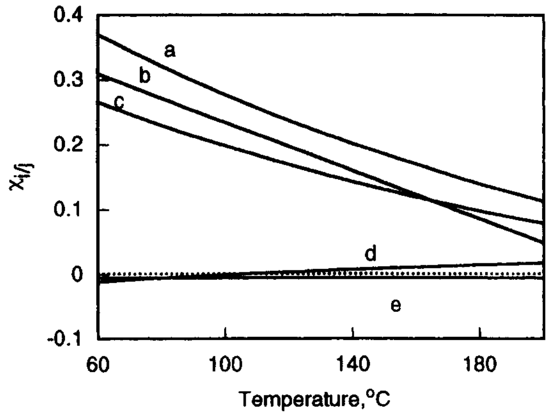

Figure 7 Temperature dependence of $\chi_{i/j}$ for (a) S/MMA, (b) EO/S, (c) VME/MMA, (d) VME/S, and (e) EO/MMA

According to the simple expression by Patterson[11,12], the molecular interaction parameter χ per molar core volume can be written as

$$\chi/M_1\nu^*_{1,\mathrm{sp}} = p^*_1/RT^*_1[(X_{12}/p^*_1)\tilde{\nu}_1^{1/3}/(\tilde{\nu}_1^{1/3} - 1)] + p^*_1/RT^*_1[\tau^2\tilde{\nu}_1^{1/3}/2(4/3 - \tilde{\nu}_1^{1/3})] \qquad (10)$$

where $\chi_{1,\mathrm{sp}}{}^*$, $p_1{}^*$ and $T_1{}^*$ are the specific core volume, characteristic pressure and characteristic temperature of polymer 1, $\tilde{\nu}_1$ is the reduced volume of polymer 1 and M_1 is the molecular weight. The first term on the right-hand side of equation (10) is the contribution of exchange enthalpy characterised by the parameter X_{12}, and the second term the free volume difference characterised by τ given by

$$\tau = 1 - T^*_1/T^*_2 \qquad (11)$$

Two kinds of temperature dependences of the χ parameter can be drawn depending on the sign of X_{12} as shown schematically in *Figure 4*. Here, we estimate only the free volume difference term (*FV*) for the homopolymer pairs according to equation (10) because we have no data of X_{12} applicable to the simple expression of χ in equation (10). Taking account of the χ curves in *Figure 7*, the enthalpic term for the PVME/PS and PEO/PMMA pairs corresponds to curve (a') in *Figure 4* and that for PVME/PMMA, PEO/PS and PMMA/PS to curve (a).

The solid lines in *Figure 8* indicate the temperature dependence of the *FV* term calculated for the respective homopolymer pairs using the characteristic parameters listed in *Table 2*. Here, the reduced volume $\tilde{\nu}$ was obtained from the reduced equation-of-state[9,10]

$$\tilde{T} = (\tilde{\nu}^{1/3} - 1)/\tilde{\nu}^{4/3} \qquad (12)$$

where

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

The broken lines, which indicate the enthalpic term, in *Figure 8* were drawn arbitrarily by taking into account the

Table 2 Characteristic parameters obtained at indicated temperatures

Characteristic parameters	PEO (70°C)[a]	PMMA (100°C)	PS (100°C)[d]	PVME (100°C)[e]
T^* (K)	6532	8399[b]	7948	7051
p^* (J cm^{-3})	677	630[c]	506	483
$\nu_{\mathrm{sp}}{}^*$ (cm^3 g^{-1})	0.7558	0.7336[b]	0.8205	0.8173

[a] Ref. 25
[b] Ref. 26
[c] Ref. 27
[d] Ref. 28
[e] Ref. 29

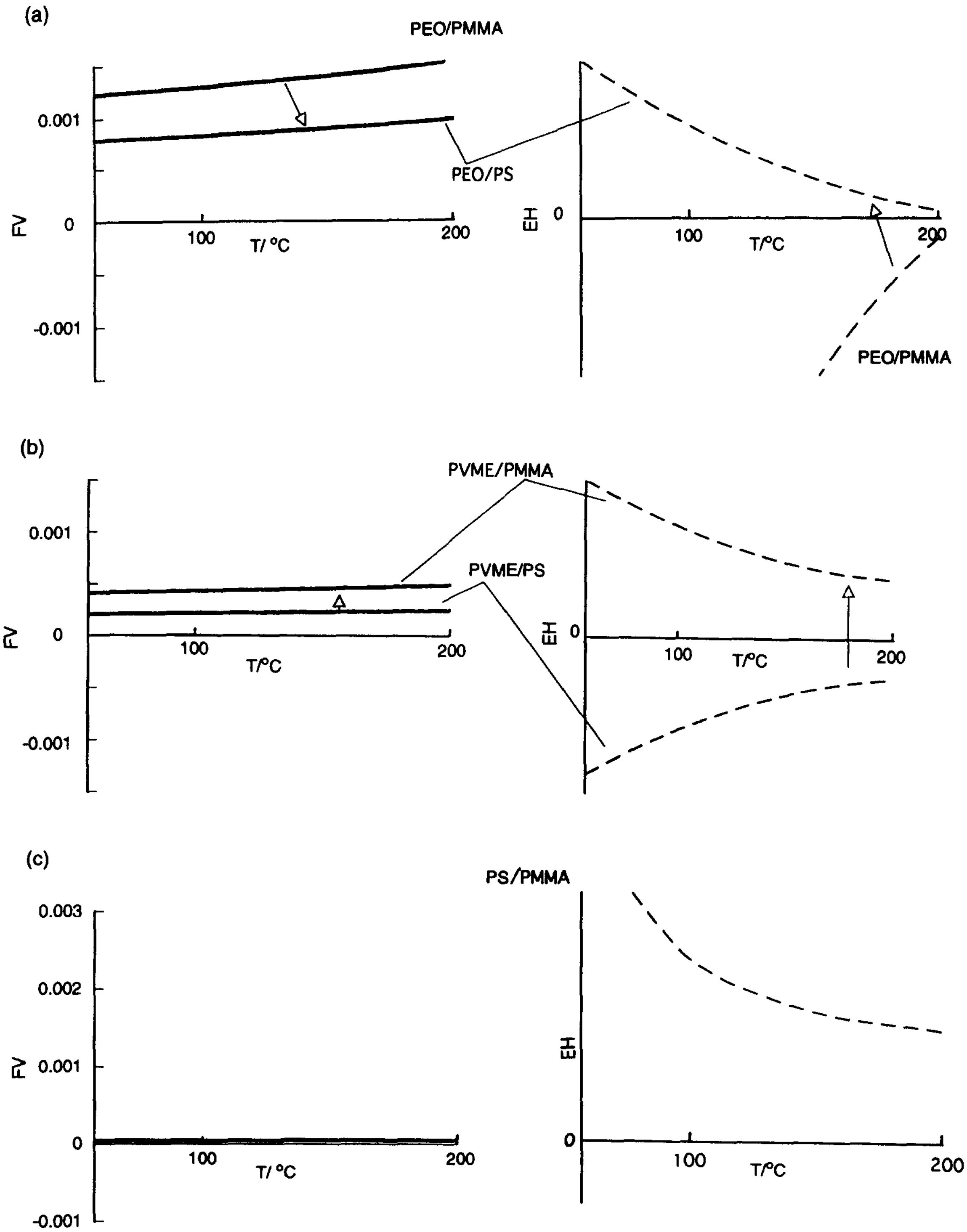

Figure 8 Temperature dependences of the free volume difference term, *FV*, and the enthalpic terms, *EH*, for the homopolymer/homopolymer pairs of (a) PEO/PMMA and PEO/PS, (b) PVME/PS and PVME/PMMA, and (c) PS/PMMA. The solid lines indicate the *FV* term calculated according to the second term of equation (10), and the broken lines the enthalpic term arbitrarily drawn

χ curves in *Figure 7*. As shown in *Figure 8*(a), the *FV* values for PEO/PS are smaller than those for PEO/PMMA. This suggests that the contribution of free volume difference to immiscibility in the PEO/MMA·S blends becomes small by containing the styrene component in the copolymer molecules rather than that in the homopolymer blends PEO/PMMA, while the enthalpic term changes from negative to positive. Namely, immiscible behaviour occurring with increasing the styrene component in the MMA·S copolymer is caused by the enthalpic contribution, which leads to UCST-type miscibility. On the other hand, the *FV* contribution in PVME/PMMA is larger than that in PVME/PS and also the enthalpic term becomes positive from negative (*Figure 8b*) This means that immiscibility in the copolymer blends PVME/MMA·S comes from both the enthalpic and *FV* contributions. Taking into account that the PVME/PS homopolymer blends are of LCST-type, the PVME/MMA·S blends may show LCST-type miscibility in a small content of the MMA component. As shown in *Figure 8c*, the contribution of the *FV* term in PS/PMMA is very small. It suggests that an immiscible situation for the PS/MMA·S blend is caused by the enthalpic term, namely UCST appears for this system.

REFERENCES

1. Ougizawa, T., Inoue, T. and Kammer, H., *Macromolecules*, 1985, **18**, 2089.
2. Ueda, H. and Karasz, F. E., *Macromolecules*, 1985, **18**, 2719.
3. Sato, T., Endo, M., Shiomi, T. and Imai, K., *Polymer*, 1996, **37**, 2131.
4. Shiomi, T., Karasz, F. E. and MacKnight, W. J., *Macromolecules*, 1986, **19**, 2644.
5. Brannock, G. R., Barlow, J. W. and Paul, D. R., *Journal of Polymer Science, Polymer Physics Edition*, 1991, **29**, 413.
6. Cimmino, S., Karasz, F. E. and MacKnight, W. J., *Journal of Polymer Science, Polymer Physics Edition*, 1992, **30**, 49.
7. Cowie, J. M. G., Reid, V. M. C. and McEwen, I. J., *Polymer*, 1990, **31**, 905.
8. Fernandes, A. C., Barlow, J. W. and Paul, D. R., *Journal of Applied Polymer Science*, 1986, **32**, 5481.
9. Flory, P. J., *Journal of the American Chemical Society*, 1965, **87**, 1833.
10. Flory, P. J., *Discussions of the Faraday Society*, 1970, **49**, 7.
11. Patterson, D. and Robard, A., *Macromolecules*, 1978, **11**, 690.
12. Patterson, D., *Polymer Engineering Science*, 1982, **22**, 64.
13. Kambour, R. P., Bendler, J. T. and Bopp, R. C., *Macromolecules*, 1983, **16**, 753.
14. ten Brinke, G., Karasz, F. E. and MacKnight, W. J., *Macromolecules*, 1983, **16**, 1827.
15. Paul, D. R. and Barlow, J. W., *Polymer*, 1984, **25**, 487.
16. Simha, R. and Branson, H., *Journal of Chemical Physics*, 1944, **12**, 253.
17. Stockmayer, W. H., Moore, L. D. Jr., Fixman, M. and Epstein, B. N., *Journal of Polymer Science*, 1955, **16**, 517.
18. Ito, H., Russell, T. P. and Wignall, G. D., *Macromolecules*, 1987, **20**, 2213.
19. Han, C. C., Bauer, B. J., Clark, J. C., Muroga, Y., Matsushita, Y., Okada, M., Tran-cong, Q., Chang, T. and Sanchez, I. C., *Polymer*, 1988, **29**, 2002.
20. Lin, J.-L. and Roe, R.-J., *Macromolecules*, 1987, **20**, 2168.
21. Buckinghan, A. D. and Hentschel, H. G. E., *Journal of Polymer Science, Polymer Physics Edition*, 1980, **18**, 853.
22. Bates, F. S. and Wignal, G. D., *Physical Review Letters*, 1986, **57**, 1429.
23. Singh, R. R. and Van Hook, W. A., *Macromolecules*, 1987, **20**, 1855.
24. Hammouda, B., Briber, R. M. and Bauer, B. J., *Polymer*, 1992, **33**, 1785.
25. Booth, C. and Devoy, C. J., *Polymer*, 1971, **12**, 309.
26. Olabisi, O. and Simha, R., *Macromolecules*, 1975, **8**, 206.
27. Manzini, G. and Crescenzi, V., *Gazzetta Chimica Italiana*, 1974, **104**, 51.
28. Höcker, H., Blake, G. J. and Flory, P. J., *Transactions of the Faraday Society*, 1971, **67**, 2251.
29. Shiomi, T., Hamada, F., Nasako, T., Yoneda, K., Imai, K. and Nakajima, A., *Macromolecules*, 1990, **23**, 229.