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UCST behaviour for high-molecular-weight polymer blends and estimation of segmental χ parameters from their miscibility

Tsukasa Sato, Masaki Endo, Tomoo Shiomi* and Kiyokazu Imai†
Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan
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An upper critical solution temperature (*UCST*) type of miscibility was observed for high-molecular-weight polymer blends of poly(methyl methacrylate) (PMMA) with poly(n-butyl methacrylate) (PnBMA) and with poly(isobutyl methacrylate) (PiBMA). The blends containing random copolymers consisting of these methacrylate monomer units also showed *UCST*-type miscibility over all copolymer compositions. The segmental interaction parameters $\chi_{\mathrm{MMA/nBMA}}$, $\chi_{\mathrm{MMA/iBMA}}$ and $\chi_{\mathrm{iBMA/nBMA}}$ were estimated from the dependence of the miscibility on the copolymer composition using the Flory–Huggins theory applied to the random copolymer blends. The temperature dependence of $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ was required to be comparatively strong in the temperature range above χ_{crit}, while $\chi_{\mathrm{iBMA/nBMA}}$ did not depend so much on the temperature. Quadratic functions of temperature were more appropriate for $\chi_{\mathrm{MMA/nBMA}}$, $\chi_{\mathrm{MMA/iBMA}}$ and $\chi_{\mathrm{iBMA/nBMA}}$ than another type of function that is proportional to $1/T$. The absolute values of all $\chi_{i/j}$ estimated here were very small compared with those for other immiscible polymer blends. This means that the exchange free energy between the different methacrylate components is very small, which is considered to bring *UCST*-type miscibility to the high-molecular-weight polymer blends studied here. Copyright © 1996 Elsevier Science Ltd.

(Keywords: *UCST* behaviour; polymer blends; Flory–Huggins χ parameter)

INTRODUCTION

Miscibility in high-molecular-weight polymer blends is governed mostly by the intermolecular interactions because the contribution of the combinatorial entropy to the free energy of mixing is negligibly small. Therefore, miscibility for most miscible polymer blends found so far is caused by specific (i.e. attractive) interactions, which lead to lower critical solution temperature (*LCST*) behaviour. On the other hand, an upper critical solution temperature (*UCST*) type of miscibility occurs in the case where the dispersion force is dominant, except for the specific case where the formation and cleavage of hydrogen bonds affect miscibility[1]. Therefore, the usual *UCST*-type miscibility can be realized only when the effect of the combinatorial entropy is expected. *UCST* behaviour is usually[2,3] observed for oligomer blends and considered to be very rare for high-molecular-weight polymer blends. Only a few blends of copolymers have been observed to be of *UCST* type in spite of their high molecular weight[4,5]. In this study we found *UCST* behaviour for high-molecular-weight homopolymer blends of poly(methyl methacrylate) (PMMA) with poly(n-butyl methacrylate) (PnBMA) and with poly(isobutyl methacrylate) (PiBMA). The blends of random copolymers consisting of these methacrylate monomer units also showed *UCST* behaviour.

In this paper we will present the *UCST* behaviour for such polymer blends, together with the dependence of the miscibility on the copolymer composition for the random copolymer blends. From the copolymer composition dependence of the miscibility we estimate the Flory–Huggins interaction parameter χ between different methacrylate units. This estimation method, which has been applied to some random copolymer blends[6–9], is more convenient than the thermodynamic and scattering techniques.

EXPERIMENTAL

The characteristics of poly(methyl methacrylate) (PMMA), poly(n-butyl methacrylate) (PnBMA), poly(isobutyl methacrylate) (PiBMA), poly(methyl methacrylate-*co*-n-butyl methacrylate) (MMA/nBMA), poly(methyl methacrylate-*co*-isobutyl methacrylate) (MMA/iBMA) and poly(isobutyl methacrylate-*co*-n-butyl methacrylate) (iBMA/nBMA) are given in *Table 1*. The PMMA homopolymer was purchased from Scientific Polymer Products Inc. (Ontario). Other polymers were prepared by radical polymerization in bulk at 80°C using 1.3 wt% of azobisisobutyronitrile (AIBN) as an initiator. The conversion was controlled at 20–30% to avoid copolymer composition drift. The resulting polymers

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* To whom correspondence should be addressed
† Present address: Department of Home Economics, Chugoku Junior College, 83 Niwase, Okayama 701-01, Japan

Table 1 Copolymer compositions[a], molecular weights[b], glass transition temperatures[c] and tacticities[a] for the polymers used in this study

Sample	Copolymer composition (mol%)	$10^{-5}\bar{M}_w$	T_g (°C)	Triad tacticity (%) mm	mr	rr
PMMA		1.0	125	4.1	34.4	61.5
PnBMA		2.7	31	4.6	35.2	60.2
PiBMA		2.6	64	4.0	32.0	64.0
MMA/nBMA-1	(MMA) 29	3.9	50			
-2	56	4.5	75	6.4	38.2	55.4
-3	71	1.8	100			
MMA/iBMA -1	(MMA) 23	2.0	75			
-2	42	3.0	82			
-3	58	2.4	91	5.2	31.3	63.5
-4	75	2.7	103			
iBMA/nBMA-1	(iBMA) 13	3.3	34			
-2	25	3.5	38	5.0	33.7	61.3
-3	33	2.6	44			
-4	53	1.9	45			
-5	60	1.5	48			
-6	75	1.5	55	4.4	36.0	59.6
-7	87	1.8	59			

[a] Determined by ^{1}H n.m.r. (270 MHz) measurement in $CDCl_3$
[b] Determined by g.p.c. measurement
[c] Midpoint in the glass transition region observed with d.s.c.

were crudely fractionated using an acetone/methanol system. The polymers obtained were purified by reprecipitation from acetone solution with a large excess of methanol, and then they were dried under vacuum. Copolymer compositions and tacticities were determined by ^{1}H n.m.r. (270 MHz) measurements using a JEOL JNM-GX270. The polymers used for tacticity determination were converted into the methyl esters previous to the n.m.r. measurements. The molecular weights ($\bar{M}_w$) were determined by gel permeation chromatography (g.p.c.) relative to polystyrene standards. The polydispersities were in the range 1.4–1.7. As shown in *Table 1*, the tacticities and molecular weights, which are important factors for miscibility, are not so different among all the polymer samples used here.

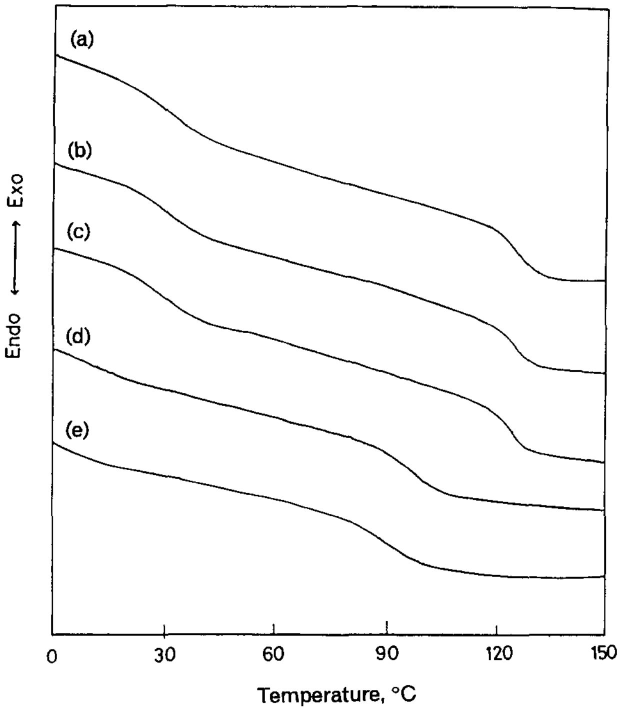

Figure 1 D.s.c. thermograms for the PMMA/PnBMA blend annealed for 30 min at 140°C (a), 150°C (b), 160°C (c), 165°C (d) and 180°C (e)

The blend samples were prepared by dissolving both component polymers in acetone and precipitating the solution into a large excess of methanol. The precipitates were dried under vacuum for at least 3 days at 60°C.

Miscibility of the blends was judged by observation of one or two glass transition temperatures (T_g) by differential scanning calorimetry (d.s.c.) using a 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 approximately 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 the initial temperature of scanning. The heating rate was 10°C min^{-1} for all the samples.

RESULTS AND DISCUSSION

Phase diagram of UCST-*type miscibility*

In *Figure 1*, as examples, are shown the d.s.c. thermograms for the PMMA/PnBMA blend with a weight ratio of 50/50 wt%. The blend sample was annealed for 30 min at each temperature. Two glass transition temperatures were observed for the blend when annealed at 140–160°C, while one glass transition temperature was observed for the blend when annealed at 165 and 180°C. This indicates that the blend changes to miscible from immiscible between 160 and 165°C. *Figure 2* shows the d.s.c. thermograms for the PMMA/PnBMA blend annealed for 30 min at 150 and 180°C and for 15 h at 130°C, in that order. As shown in *Figure 2*, the blend changes to immiscible from miscible when the temperature is decreased from 180 to 130°C. In other words, the miscibility change of the blend is reversible. Also, no weight loss was observed by thermogravimetric analysis for the blend annealed for 200 min at 165°C. *Figure 3* shows a phase diagram obtained from observations of glass transition temperatures for PMMA/PnBMA blends with various blend ratios. This phase diagram demonstrates that the PMMA/PnBMA blends evidently have *UCST*-type miscibility. The PMMA/PiBMA blends were also found to have *UCST*-type miscibility. Earlier examples of high-molecular-weight polymer blends having *UCST*-type miscibility had only been found for random copolymer blends, while the *UCST*-type behaviour found here is for blends consisting of two homopolymers analogous to each other in chemical structure.

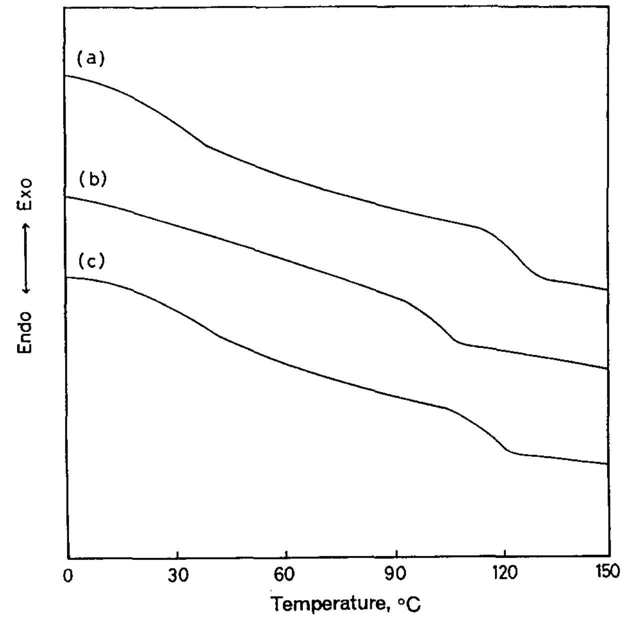

Figure 2 D.s.c. thermograms for the PMMA/PnBMA blend annealed for 30 min at 150°C (a), 180°C (b) and for 15 h at 130°C (c), in that order

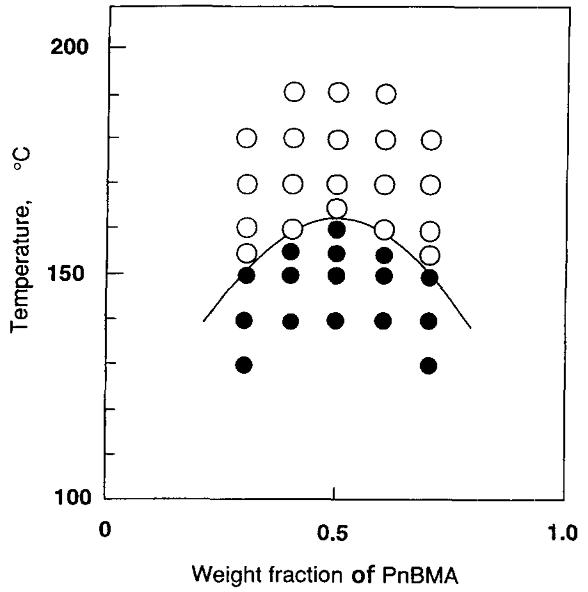

Figure 3 Phase diagram for PMMA/PnBMA blends: (○) miscible; (●) immiscible

It is expected to be very rare that a *UCST* appear for a blend of polymers with high molecular weights. According to the equation-of-state theory[10–12], we have two kinds of temperature dependence of the Flory–Huggins molecular interaction parameter χ_{12}, as shown in *Figure 4*. The *UCST* appears only when the temperature dependence of the molecular χ_{12} is type c and when the minimum of curve c (*Figure 4*) is smaller than the value of χ_{crit} given by

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

where r_1 and r_2 are the numbers of segments for polymers 1 and 2, respectively. Since the χ_{crit} value is very small for high-molecular-weight polymer blends, the *UCST* usually does not appear. The *UCST* may be observed only if the minimum of curve c is small enough to be below χ_{crit}. This may be realized when both the exchange energy and the free volume difference, which are indicated by curves a and b, respectively, in *Figure 4*, are very small. This situation is, of course, uncommon. For the present PMMA/PnBMA and PMMA/PiBMA blends, the differences in both free volume and interaction energy between the two polymers are expected to be very small because these component polymers are analogous to each other in chemical structure. Thus, the combinations of polymers used in this study may correspond to the case for the appearance of a *UCST*, as discussed above.

Dependence of miscibility on copolymer composition and estimation of segmental interaction parameters

Figures 5–9 show the dependence of miscibility on copolymer composition at a 50/50 wt% blend ratio for blends which contain random copolymers consisting of different methacrylate units. As shown in these figures, all the blends have *UCST*-type miscibility over all the copolymer compositions investigated here. We will

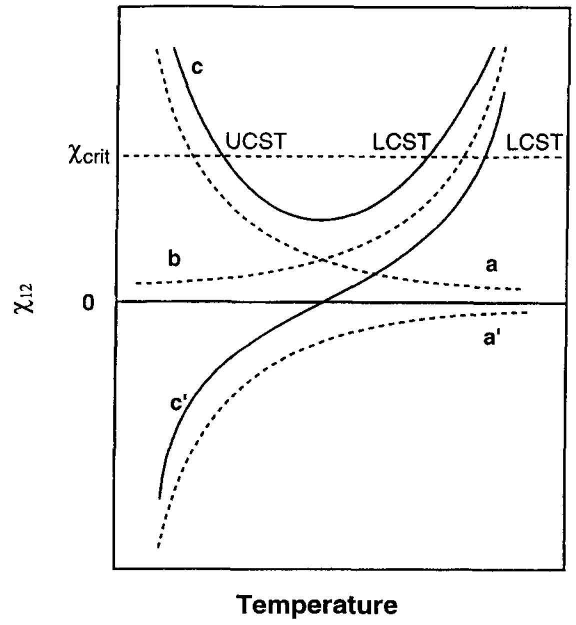

Figure 4 Schematic illustration of the temperature dependence of χ_{12}: (a, a′) the exchange energy terms; (b) the free volume term; (c, c′) χ_{12} = (a) + (b) and χ_{12} = (a′) + (b), respectively

estimate the segmental interaction parameters $\chi_{i/j}$ using the copolymer composition dependence of miscibility for these random copolymer blends.

According to the Flory–Huggins theory[13,14], the Gibbs free energy change per segment on mixing for r_1-mer and r_2-mer systems can be written as

$$\Delta G/RT = (\varphi_1/r_1)\ln\varphi_1 + (\varphi_2/r_2)\ln\varphi_2 + \chi_{12}\varphi_1\varphi_2 \quad (2)$$

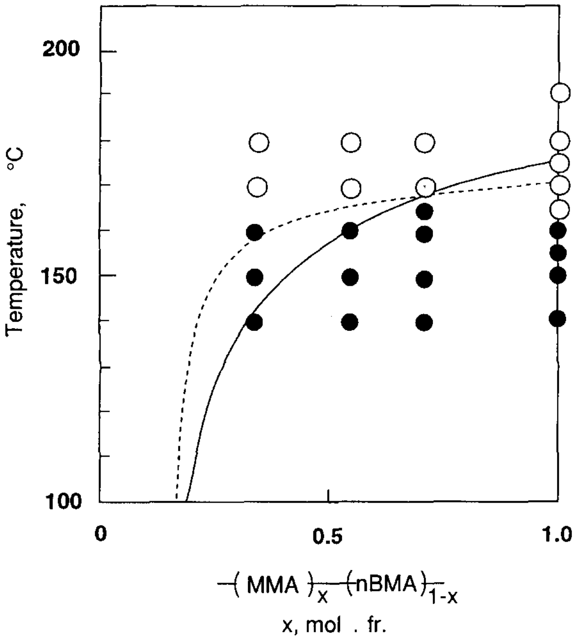

Figure 5 Dependence of miscibility on copolymer composition for MMA/nBMA·PnBMA blends: (○) miscible; (●) immiscible. The broken and solid lines are miscible/immiscible boundary lines calculated with $\chi_{\mathrm{MMA/nBMA}} = a + b/T$ and $\chi_{\mathrm{MMA/nBMA}} = aT^2 + bT + c$, respectively

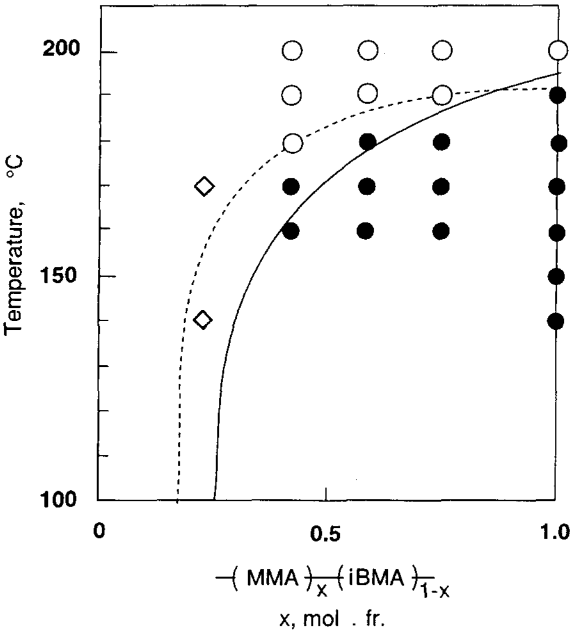

Figure 6 Dependence of miscibility on copolymer composition for MMA/iBMA·PiBMA blends: (○) miscible; (●) immiscible; (◇) behaviour when the difference between the two T_g values is small. The broken and solid lines are miscible/immiscible boundary lines calculated with $\chi_{\mathrm{MMA/iBMA}} = a + b/T$ and $\chi_{\mathrm{MMA/iBMA}} = aT^2 + bT + c$, respectively

where φ_1 and φ_2 are the segment or volume fractions of r_1-mer and r_2-mer, respectively. For a mixture of two general random copolymers **1** $([(A_1)_{x_1}(A_2)_{x2}\ldots(A_m)_{xm}]_{r1})$ and **2** $([(B_1)_{y1}(B_2)_{y2}\ldots(B_n)_{yn}]_{r2})$, we can write the molecular χ_{12} per segment between copolymers **1** and **2** as[15-19]

$$\chi_{12} = \sum_{i=1}^{m}\sum_{j=1}^{n} x_i y_j \chi_{\mathrm{A}i/\mathrm{B}j} - \sum_{i=1}^{m-1}\sum_{j=i+1}^{m} x_i x_j \chi_{\mathrm{A}i/\mathrm{A}j} - \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} y_i y_j \chi_{\mathrm{B}i/\mathrm{B}j} \quad (3)$$

where $\chi_{\mathrm{A}i/\mathrm{B}j}$ and so on are the segmental interaction parameters between the different segments A_i, B_j and so on, and x_i and y_j are the copolymer compositions expressed with volume fractions for copolymers 1 and 2, respectively. At the critical state the molecular χ_{12} equals χ_{crit}, i.e.

$$\chi_{12} = \chi_{\mathrm{crit}} \quad (4)$$

Therefore, the segmental $\chi_{i/j}$ can be estimated from equations (3) and (4) if the critical state is known. In the estimation of the $\chi_{i/j}$ in this study, the critical concentration was assumed to be close to 50 wt% regardless of the polydispersity, as shown in *Figure 3*. The segment size was taken to be an MMA monomer unit, and the numbers of segments for the copolymer were taken as the average for a series of copolymers used. Also, the segmental $\chi_{i/j}$ was assumed to be independent of the blend ratio and the copolymer composition.

For a mixture of the random copolymer $1(\mathrm{A}_x/\mathrm{B}_{1-x})$ and the homopolymer 2 (B) such as MMA/nBMA·PnBMA or MMA/iBMA·PiBMA, equation (3) can be reduced to

$$\chi_{12} = x^2\chi_{\mathrm{A/B}} \quad (5)$$

where the segmental $\chi_{\mathrm{A/B}}$ corresponds to $\chi_{\mathrm{MMA/nBMA}}$ or $\chi_{\mathrm{MMA/iBMA}}$ in MMA/nBMA·PnBMA and MMA/iBMA·PiBMA, respectively. Using equations (4) and (5), we can estimate $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ from the experimental results shown in *Figures 5* and *6*, respectively. In the vicinity of the *UCST*, as shown in *Figure 4*, the interaction parameter χ_{12} decreases with temperature to lower than χ_{crit} at the miscible state. Then, as an approximation, we can formulate the temperature dependence of $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ as

$$\chi_{i/j} = a + b/T \quad (6)$$

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

When the miscible/immiscible boundary line calculated from equation (5) is fitted to the experimental line for the MMA/nBMA·PnBMA blends, as shown by the broken line in *Figure 5*, the segmental $\chi_{\mathrm{MMA/nBMA}}$ is given as

$$\chi_{\mathrm{MMA/nBMA}} = -0.216 + 95.7/T \quad (7)$$

In the same way, the following expression for the parameter $\chi_{\mathrm{MMA/iBMA}}$ was obtained from the experimental results for the MMA/iBMA·PiBMA blends (*Figure 6*)

$$\chi_{\mathrm{MMA/iBMA}} = -0.157 + 73.1/T \quad (8)$$

The parameters $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ given by equations (7) and (8) become negative at 170 and 191°C, respectively. According to the equation-of-state theory above, the intermolecular χ_{12} for *UCST*-type miscibility is always positive and its temperature dependence is U-shaped. Therefore, $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ should be positive in the temperature range studied here at least. Even if somewhat different values are taken for the constants *a* and *b*, the temperature dependence is not improved very much since the form of the function that is proportional to $1/T$ is not changed. As another approximation, therefore, we put these segmental interaction parameters $\chi_{i/j}$ into a quadratic function of temperature

$$\chi_{i/j} = aT^2 + bT + c \tag{9}$$

where *a*, *b* and *c* are constants. For the miscible/immiscible boundary lines expressed by the solid lines in *Figures 5* and *6*, respectively, the segmental interaction parameters $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ are given by

$$\chi_{\mathrm{MMA/nBMA}} = 2.50 \times 10^{-6}T^2 - 2.33 \times 10^{-3}T + 0.541 \tag{10}$$

$$\chi_{\mathrm{MMA/iBMA}} = 1.30 \times 10^{-6}T^2 - 1.28 \times 10^{-3}T + 0.243 \tag{11}$$

In equations (10) and (11) the segmental $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ are always positive.

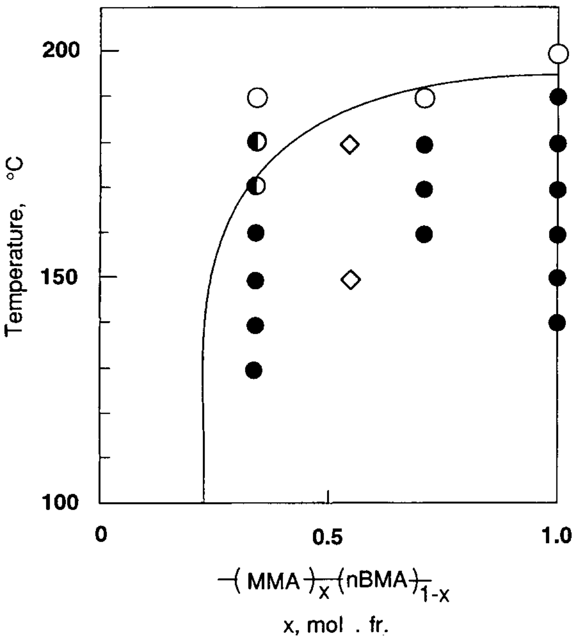

Figure 7 Dependence of miscibility on copolymer composition for MMA/nBMA·PiBMA blends: (○) miscible; (●) immiscible; (◇) behaviour when the difference between the two T_g values is small; (◐) miscible when annealed for 30 min but immiscible when annealed for 90 min. The solid line is the calculated miscible/immiscible boundary line

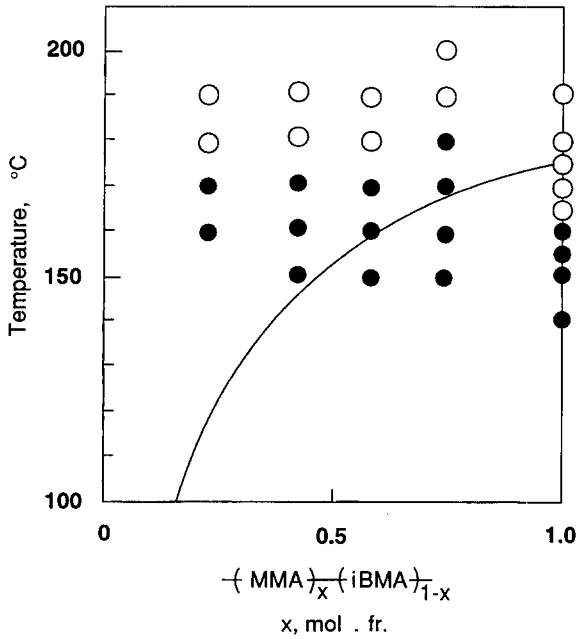

Figure 8 Dependence of miscibility on copolymer composition for MMA/iBMA·PnBMA blends: (○) miscible; (●) immiscible. The solid line is the calculated miscible/immiscible boundary line

Next, equation (3) was applied to the blend systems MMA/nBMA·PiBMA, MMA/iBMA·PnBMA and iBMA/nBMA·MMA/iBMA-4 (75 mol% MMA) shown in *Figures 7–9*, respectively. For a mixture of random copolymer **1** (A_x/B_{1-x}) and homopolymer **2** (C) such as MMA/nBMA·PiBMA or MMA/iBMA·PnBMA, equation (3) can be rewritten as

$$\chi_{12} = x\chi_{\mathrm{A/C}} + (1-x)\chi_{\mathrm{B/C}} - x(1-x)\chi_{\mathrm{A/B}} \tag{12}$$

In the application of equation (12) to these systems, the intersegmental $\chi_{\mathrm{iBMA/nBMA}}$ is required in addition to the $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$ determined earlier. In our previous study[19], a film of the PiBMA/PnBMA blend remained clear up to about 230°C, at which the blend became brown. Since the PiBMA/PnBMA blend consists of polymers analogous to each other in structure, this blend is also expected to have *UCST*-type miscibility. We now express the intersegmental

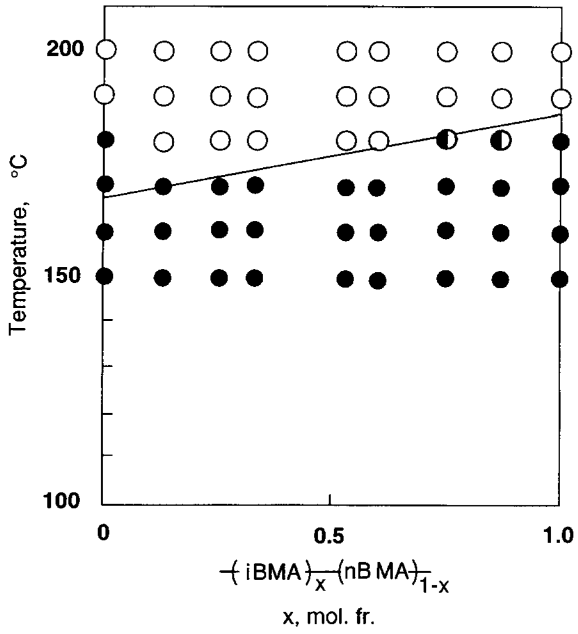

Figure 9 Dependence of miscibility on copolymer composition for iBMA/nBMA·MMA/iBMA-4 (75 mol% MMA): (○) miscible; (●) immiscible; (◐) miscible when annealed for 30 min but immiscible when annealed for 90 min. The solid line is the calculated miscible/immiscible boundary line

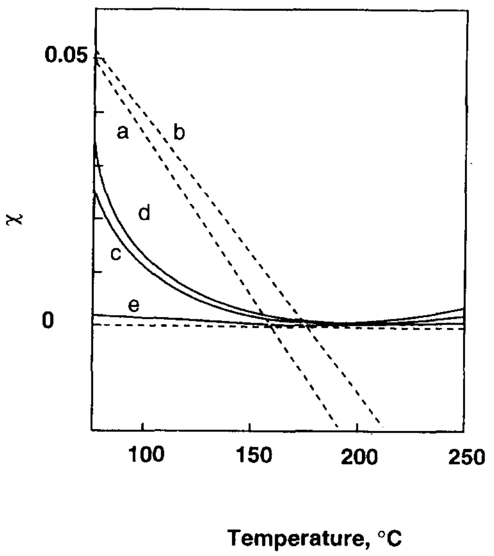

Figure 10 Types of temperature dependence for the $\chi_{i/j}$ estimated in this study: (a, b) $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$, respectively, expressed by $a+b/T$; (c–e) $\chi_{\mathrm{MMA/nBMA}}$, $\chi_{\mathrm{MMA/iBMA}}$ and $\chi_{\mathrm{iBMA/nBMA}}$, respectively, expressed by aT^2+bT+c

$\chi_{\mathrm{iBMA/nBMA}}$ as a quadratic function of temperature. When the miscible/immiscible boundary line calculated from equation (12) is fitted to the experimental line for the MMA/nBMA·PiBMA blend, as shown by the solid line in *Figure 7*, the segmental $\chi_{\mathrm{iBMA/nBMA}}$ is given by

$$\chi_{\mathrm{iBMA/nBMA}} = 1.00 \times 10^{-7}T^2 - 8.46 \times 10^{-5}T + 0.0179 \qquad (13)$$

The value of $\chi_{\mathrm{iBMA/nBMA}}$ estimated here is smaller than χ_{crit} up to about 230°C, which is in agreement with the miscibility of the PiBMA/PnBMA blend described in our previous study[19].

The three $\chi_{i/j}$ parameters obtained thus are applied to the MMA/iBMA · PnBMA and iBMA/nBMA·MMA/iBMA-4 blends in *Figures 8* and *9*, respectively. As shown in *Figure 8*, the calculated boundary line reproduces satisfactorily the experimental line for the MMA/iBMA·PnBMA blends. For a mixture of random copolymers **1** (A_x/B_{1-x}) and **2** (C_y/D_{1-y}) such as iBMA/nBMA·MMA/iBMA-4, the molecular χ_{12} can be written as

$$\begin{aligned}\chi_{12} = {} & xy\chi_{\mathrm{A/C}} + x(1-y)\chi_{\mathrm{A/D}} + y(1-x)\chi_{\mathrm{B/C}} \\ & + (1-x)(1-y)\chi_{\mathrm{B/D}} \\ & - x(1-x)\chi_{\mathrm{A/B}} - y(1-y)\chi_{\mathrm{C/D}} \qquad (14)\end{aligned}$$

As shown in *Figure 9*, the calculated miscible/immiscible boundary line does not depend so much on the copolymer composition and agrees fairly well with the experimental line.

Remarks

Usually, a blend of A_x/B_{1-x} and B becomes more miscible as x decreases. As shown in *Figures 5* and *6*, however, the miscible/immiscible boundary temperature for the MMA/nBMA·PnBMA and MMA/iBMA·PiBMA blends does not depend so much on the copolymer composition over a wide range of compositions. This may be a result of the strong temperature dependence of $\chi_{\mathrm{MMA/nBMA}}$ and $\chi_{\mathrm{MMA/iBMA}}$. Such a temperature dependence can be expressed by equation (7) or (8) as proportional to $1/T$, although these $\chi_{i/j}$ values become negative too rapidly, as shown in *Figure 10*. On the other hand, the quadratic functions of temperature given by equations (10) and (11) do not become negative and can reproduce satisfactorily the copolymer composition dependence of the miscible/immiscible boundary lines.

Also, it should be noted that the absolute values of all the $\chi_{i/j}$ obtained here are small compared with such values for other immiscible polymer pairs. In particular, the value of $\chi_{\mathrm{iBMA/nBMA}}$ is very small. This means that the exchange free energies between different methacrylate components are small, leading to miscible blends with a *UCST*.

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