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Miscibility in blends of linear and branched poly(ethylene oxide) with methacrylate derivative random copolymers and estimation of segmental χ parameters

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Abstract

Miscibility in the blends of poly(ethylene oxide) (PEO) with *n*-hexyl methacrylate-methyl methacrylate random copolymers (HMA-MMA) and 2-ethylhexyl methacrylate-MMA random copolymers (EHMA-MMA) was evaluated using glass transition and light scattering methods. EHMA-MMA was more miscible with PEO than HMA-MMA. Both blends of PEO with HMA-MMA and EHMA-MMA showed UCST-type miscibility although homopolymer blends PEO/PMMA were predicted to be of LCST-type. This was attributed to an increase in the exchange enthalpy with increasing HMA or EHMA composition in the random copolymer. From the copolymer composition dependence of miscibility the segmental χ parameters of HMA/MMA, EHMA/MMA, EO/HMA and EO/EHMA were estimated using the Flory–Huggins theory extended to random copolymer systems. Miscibility in the blends of branched PEO with HMA-MMA whose HMA copolymer composition was 0.16 was compared with that in the linear PEO blends. The former blends were more miscible with HMA-MMA than the latter one by about 35 °C at the maximum cloud point temperature.

Keywords: Random copolymer blend; Flory–Huggins χ parameter; Branched polymer

1. Introduction

Since the middle of 1970s, polymer blends have been investigated extensively with respect to miscibility, phase separation process and practical applications [1–4]. In particular, whether the blends are miscible or immiscible is very important for making real polymeric materials. Miscibility behavior or miscibility conditions have been explained on the basis of Flory–Huggins lattice theory [5,6] and equation-of-states or free volume theory [7–10]. According to these theories, the interaction parameter χ plays an important role for miscibility. An extremely small or negative χ value is required for miscible polymer blends because the critical χ value is very small for high-molecular-weight polymer blends.

Blends containing random copolymers show unique miscibility behavior in the copolymer composition dependence, such as so-called miscibility [11–14] and immiscibility [15] windows that are caused by relatively strong repulsive and attractive interactions, respectively, between the constituent monomers in the random copolymer. Namely segmental χ parameters between different monomers play an important role in such unique miscibility behavior of the random copolymer blends. Furthermore, the degree of the segregation strength in microphase separation of block copolymers is also expressed using χ [16–18].

As mentioned above, estimation and accumulation of χ parameters for various monomer pairs are required for description of phase behavior in multicomponent systems. The χ parameters have been estimated mainly by thermodynamic [19,20] and scattering [21] methods. Another method for estimation of χ parameters has also been proposed [14,22–26]. In this method, the dependence of miscibility on the

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copolymer composition in the random copolymer blends is used. According to Flory–Huggins theory extended to random copolymer blends of $[(A_1)_{x1}(A_2)_{x2}\ldots(A_m)_{xm}]_{r1}$ and $[(B_1)_{y1}(B_2)_{y2}\ldots(B_n)_{yn}]_{r2}$, the intermolecular χ parameter can be written as [11–15,27,28]

$$\chi = \sum_{i=1}^{m}\sum_{j=1}^{n} x_i y_j \chi_{A_i/B_j} - \sum_{i=1}^{m-1}\sum_{j=i+1}^{m} x_i x_j \chi_{A_i/A_j} - \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} y_i y_j \chi_{B_i/B_j} \qquad (1)$$

where χ_{A_i/B_j} and so on are the segmental or intermonomer χ parameters and x_i and y_i are the copolymer compositions expressed with volume fractions for random copolymers 1 and 2, respectively. Putting $\chi = \chi_{crit}$ where χ_{crit} is the critical χ, the dependence of miscibility on the copolymer composition is expressed. In other words, the segmental χ parameters can be estimated by application of Eq. (1) to the experimentally obtained results. This method is applicable even to immiscible pairs. For example, in the blend of homopolymer Homo(A) and random copolymer Ran(BC), even if Homo(A) is immiscible with Homo(C), we can necessarily find a copolymer composition of the miscible-immiscible boundary when Homo(B) is miscible with Homo(A) or Homo(B) = Homo(A). Thus, we can estimate segmental χ parameters using Eq. (1).

In this paper, we will present the dependence of miscibility on the copolymer composition obtained experimentally in the blends of poly(ethylene oxide) (PEO) with random copolymers containing methacrylate derivatives, and from those results the segmental χ parameters will be estimated.

Furthermore, we will compare the miscibility in the blends of branched PEO with that of linear one. Molecular shape such as ring and branch may affect miscibility.

Finally we will discuss which appears, UCST or LCST, in random copolymer blends, compared with that in homopolymer blends composed of the same component monomers as those contained in the random copolymer. Even if Homo(A)/Homo(B) blends show LCST (or UCST) behavior, there is a possibility that a UCST (or LCST) appears in Homo(A)/Ran(BC) blends.

2. Experimental

Two kinds of random copolymers composed of methyl methacrylate (MMA) and *n*-hexyl methacrylate (HMA) and of MMA and 2-ethylhexyl methacryalte (EHMA) were prepared by free radical polymerization. The monomers used for copolymerization were purified as follows: after the polymerization inhibitor was removed, the monomers were dried with calcium hydride and sodium sulfate anhydride and then distilled under reduced pressure. The removal of the inhibitor was performed in a common method for MMA and EHMA and through the column containing alumina for HMA. Copolymerization was carried out in degassed bulk at 80 °C using 1.0 wt% of AIBN. The conversion was controlled to be within 20% to avoid copolymer composition drift. The resulting polymers were crudely fractionated with a benzene/methanol system.

Linear PEO standards with three kinds of molecular weights, purchased from Tosoh Co. were used without further purification and fractionation. Branched PEO (BPEO) was synthesized by free radical polymerization of methacrylate-type of PEG macromonomer in a degassed 50 wt% benzene solution for 72 h at 100 °C using di-*t*-butyl peroxide (2 wt% to the amount of the macromonomer) as an initiator. The PEG macromonomer was synthesized by the reaction of methacryloyl chloride with CH_3O–PEG—ONa, in which PEG monomethyl ether (kindly supplied by NOF Co. Japan) whose molecular weights was 5200, was used as an original PEG. The resulting BPEO products were fractionated by GPC column fractionation.

Molecular weights and their distribution for MMA random copolymers were determined by common GPC measurements in THF relative to the polystyrene standard, and copolymer compositions by ^{1}H NMR (JEOL JMX-GM 270) in $CDCl_3$ at 40 °C. The molecular weight for BPEO was determined using GPC with a LALLS detector (LS-8000, Tosoh). The number of arms in BPEO is estimated to be 4–5 from the molecular weights of BPEO and the original macromonomer. The characteristics of the polymers employed here are listed in Table 1.

Blend samples were prepared by cast from 5 wt% chloroform or THF solutions. Miscibility was judged by two methods: measurements of cloud points and observation of glass transition temperature, T_g. In the cloud point

Table 1
Characteristics of polymers

Sample	$10^{-4}\,\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$[a]	T_g[b] (°C)	HMA or EHMA[c] (mol%)
HMA-MMA				
−7	5.3	1.6	98	7.8
−10	5.9	1.6	91	10.4
−13	5.4	1.6	84	13.0
−16	6.2	1.7	84	16.0
−17	6.2	1.5	76	17.2
−19	5.4	1.6	72	19.0
−21	5.3	1.5	68	21.1
EHMA-MMA				
−8	14	1.8	112	7.7
−11	14	1.9	90	11.0
−18	15	2.1	83	18.4
−27	17	1.7	73	26.9
−31	16	2.0	63	31.0
PMMA	10		125	
PEO 2.6[d]	2.6	1.09		
PEO 17[d]	17	1.04		
PEO 91[d]	91	1.08		
BPEO[e]	2.3	1.2		

[a] Determined by GPC measurement in THF, relative to polystyrene standard.
[b] Determined by DSC measurement.
[c] Determined by ^{1}H NMR measurement.
[d] TSK standard PEO, molecular weight and its distribution are nominal.
[e] Determined by GPC-LALLS measurement.

measurements, the blend film was first annealed for at least 30 min at a miscible temperature, and then cooled to an immiscible region. The cloud point was determined by detecting a sudden increase in intensity of He–Ne laser light scattered from the film in the cooling process. The cooling rate was 1–2 °C/min for the linear PEO blends, while for the branched PEO blends the cloud points were determined by extrapolating the results at 1, 3 and 5 °C/min. The extrapolated temperature was higher than that at 1 °C/min by about 5 °C. In the T_g method, T_g was observed for the 50 wt% blend with a DSC20 apparatus made by SEIKO I & E Ltd. Usually miscibility is judged by observation of one or two T_gs corresponding to a miscible or immiscible state, respectively. However, T_g of PEO is not detected so easily because of a crystalline polymer. The glass transition and melting temperatures of PEO are around −50 and 60 °C, respectively. Therefore, when a glass transition temperature of methacrylate copolymers was observed in the range of 60–130 °C, the blend was judged to be immiscible (see T_g of MMA copolymers shown in Table 1.). The sample was first annealed for 30 min–8 h at a desired temperature in the DSC apparatus, and then rapidly quenched to 60 °C. Immediately after that, DSC measurements were performed at a heating rate of 10 °C min^{-1}.

3. Results

3.1. Miscibility

UCST-type miscibility was observed for the blends of PEO with HMA-MMA random copolymers. Fig. 1 shows a phase diagram determined by the light scattering and glass transition measurements for the PEO2.6/HMA-MMA16 blends. Although an appearance of UCST should be very rare for high-molecular-weight polymer blends as mentioned in Section 1, UCST-type miscibility has found for some random copolymer blends and for homopolymer blends composed of homologous polymers [25,26,29,30]. Fig. 2 indicates the dependence of miscibility on the HMA copolymer composition at 50/50 wt/wt blend ratio for PEO/HMA-MMA blends with various molecular weights of PEO. Regardless of the molecular weight of PEO, as shown in Fig. 2, a miscibility gap can be found at 0.13–0.16 of HMA copolymer composition. This indicates that the copolymer composition affects miscibility more significantly than the molecular weight in the PEO/HMA-MMA systems. Here, it should be noted that although the miscibility behavior of the homopolymer blends PEO/PMMA has been reported to be an LCST-type, PEO/HMA-MMA blends are of UCST-type. This is discussed in a later section.

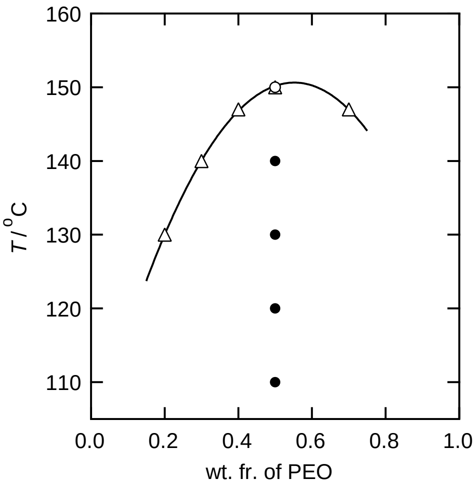

Fig. 1. Phase diagram for the PEO2.6/HMA-MMA16 blends. The triangles are the cloud points measured in the light scattering method. The open and closed circles indicate miscible and immiscible points, respectively, determined by the T_g method.

PEO/EHMA-MMA blends also showed UCST-type miscibility as indicated in the phase diagram of Fig. 3. The dependence of miscibility on the EHMA copolymer composition is shown in Fig. 4. As shown in Fig. 4, the miscible region of the copolymer composition in the EHMA-MMA blends is larger than that in the blends with HMA-MMA, and also the miscibility is more dependent on the copolymer composition as well as the molecular weight. These suggest that an attractive interaction between PEO and EHMA is stronger than that between PEO and HMA.

3.2. Estimation of segmental interaction parameters

According to the Flory–Huggins theory extended to multicomponent systems, as shown in Eq. (1), the 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 i and j. For a mixture of homopolymer A and random copolymer B_yC_{1-y}, the molecular interaction parameter χ can be rewritten from Eq. (1), as

$$\chi = y\chi_{A/B} + (1-y)\chi_{A/C} - y(1-y)\chi_{B/C} \tag{2}$$

where y is the copolymer composition expressed with volume fraction. At the critical state the χ parameter equals a critical value of χ, χ_{crit}, given by

$$\chi_{crit} = \frac{(r_1^{-1/2} + r_2^{-1/2})^2}{2} \tag{3}$$

where r_1 and r_2 are the numbers of segments for polymers 1 and 2, respectively. Therefore, when χ_{crit} is known, the segmental $\chi_{i/j}$ can be estimated from the copolymer composition dependence of miscibility obtained experimentally using Eq. (2).

In estimation of $\chi_{i/j}$, the critical concentration was assumed to be 50 wt%. The segment volume was taken to be the same value as molar mass of a MMA monomer unit. The molecular weights for the HMA-MMA and EHMA-MMA copolymers were taken as averages for a series of copolymers: 5.6 and 15.2×10^4 for HMA-MMA and EHMA-MMA, respectively. Also, the segmental $\chi_{i/j}$ was assumed to be independent of

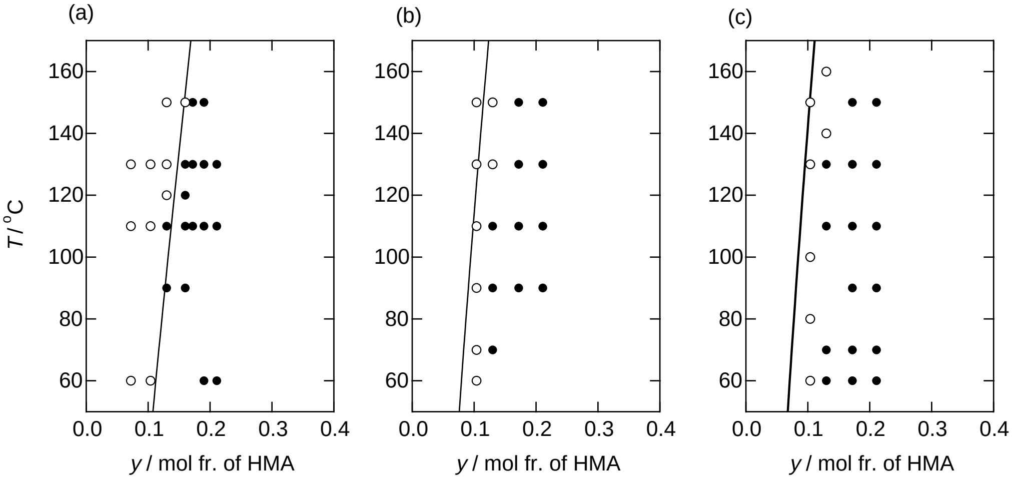

Fig. 2. Dependence of miscibility on the copolymer composition for the PEO/HMA-MMA blends with various molecular weights of PEO at 50/50 wt/wt blend ratio: the molecular weight of PEO, (a) 2.6×10^4; (b) 17×10^4; (c) 91×10^4. The open and closed circles indicate miscible and immiscible points, respectively. The solid lines are the calculated boundary lines.

the blend ratio, copolymer composition and molecular weight. The temperature dependence was expressed as

$$\chi_{i/j} = a + b/T \tag{4}$$

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

First, Eq. (2) was applied to the PMMA/HMA-MMA and PMMA/EHMA-MMA blends to estimate the $\chi_{i/j}$ values for MMA/HMA and MMA/EHMA, respectively. In the type of these blends A/B_yA_{1-y}, Eq. (2) can be simplified as

$$\chi = y^2\chi_{A/B} \tag{5}$$

Although miscibility for these blends is not shown in any figures, PMMA homopolymer with a molecular weight of 10×10^4 was miscible and immiscible with HMA-MMA13 and HMA-MMA17, respectively, and the blends of PMMA with EHMA-MMA series were found to have a miscible-immiscible boundary between the copolymer compositions of EHMA-MMA-8 and -11. In both PMMA blends with HMA-MMA and EHMA-MMA series, no temperature dependence of miscibility was observed in the temperature range of 100–170 °C investigated here. On the basis of these experimental results, the segmental $\chi_{i/j}$ values for MMA/HMA and MMA/EHMA were determined using Eqs. (5) and (3) on the assumptions that the boundary copolymer compositions were $y_{HMA}=0.15$ and $y_{EHMA}=0.094$, respectively, and that the $\chi_{i/j}$ is independent of temperature in the range investigated here. The segmental $\chi_{i/j}$ estimated thus for MMA/HMA and MMA/EHMA are

$$\chi_{MMA/HMA} = 0.0512 \tag{6}$$

$$\chi_{MMA/EHMA} = 0.0554 \tag{7}$$

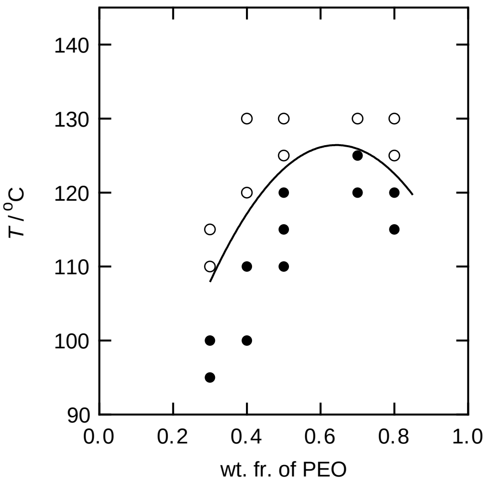

Fig. 3. Phase diagram for the PEO2.6/EHMA-MMA31 blends, determined by the T_g method.

In the estimation of these parameters, the copolymer composition converted from the chemically defined monomer to MMA monomer-based one was used.

Next, the segmental $\chi_{i/j}$'s for PEO/HMA and PEO/EHMA were determined by application of Eq. (2) to the PEO blends, where $\chi_{A/B}$, $\chi_{A/C}$ and $\chi_{B/C}$ correspond to $\chi_{EO/HMA}$ (or $\chi_{EO/EHMA}$), $\chi_{EO/MMA}$ and $\chi_{MMA/HMA}$ (or $\chi_{MMA/EHMA}$), respectively. $\chi_{MMA/HMA}$ and $\chi_{MMA/EHMA}$ were already determined above. $\chi_{EO/MMA}$ cannot be estimated from miscibility because PEO is completely miscible with PMMA in all the temperature range. Ito et al. [31] obtained $\chi_{EO/MMA}$ for the 50/50wt blends of PEO with a mixture of protonated and deuterated PMMA at 80 °C from small-angle neutron scattering measurements, as

$$\chi_{EO/MMA} = -5.0\times10^{-3} \tag{8}$$

Although the miscibility in deuterated systems is somewhat different from that in protonated ones, their $\chi_{EO/MMA}$ was adopted without any modification. Using these $\chi_{i/j}$ parameters, $\chi_{EO/HMA}$ and $\chi_{EO/EHMA}$ were determined so that the calculated boundaries for PEO2.6/HMA-MMA and PEO2.6/EHMA-MMA blends could fit the respective experimental ones as shown by the solid lines in Figs. 2(a) and 4(a). Here, the calculations were performed on the basis of the segmental

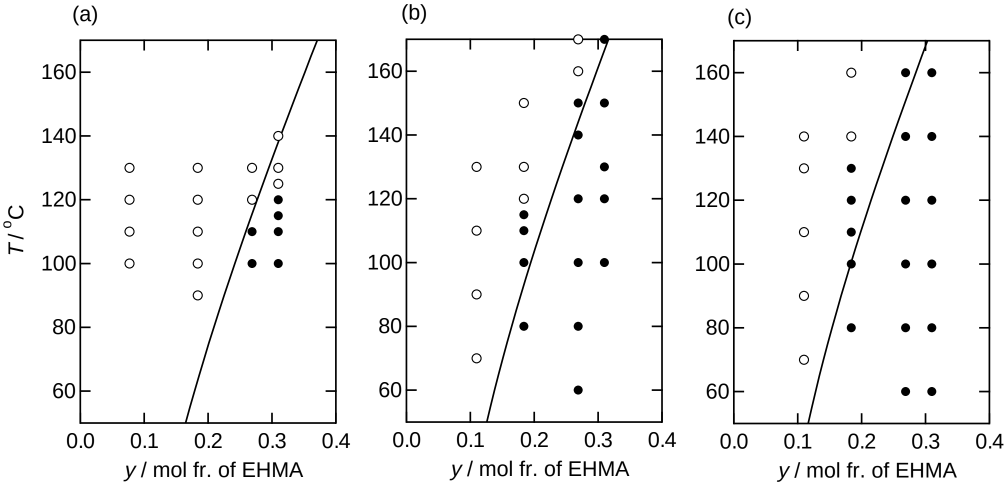

Fig. 4. Dependence of miscibility on the copolymer composition for the PEO/EHMA-MMA blends with various molecular weights of PEO at 50/50 wt/wt blend ratio: the molecular weight of PEO, (a) 2.6×10^4; (b) 17×10^4; (c) 91×10^4. The open and closed circles indicate miscible and immiscible points, respectively. The solid lines are the calculated boundary lines.

copolymer composition in which the segment size was taken to be of an MMA monomer, and the calculated boundary lines were converted to those expressed in the chemically defined copolymer composition. The $\chi_{i/j}$ parameters thus obtained are listed in Table 2.

These $\chi_{i/j}$ parameters were applied to the other blends with a different molecular weight of PEO. As shown in Figs. 2(b) and (c) and 4(b) and (c), although the calculated immiscible region was overestimated for a series of HMA-MMA blends, as a whole the calculated boundary lines can reproduce the experimental ones.

3.3. Comparison of miscibility between the blends of linear and branched PEO

In Fig. 5 the phase diagrams obtained from light scattering measurements are compared between the blends of linear and branched PEO (LPEO and BPEO, respectively) with HMA-MMA16. Even though the molecular weights of PEO are almost the same as each other, the maximum cloud temperature in the blends of LPEO is higher than that in the BPEO blends by about 35 °C, that is, BPEO is more miscible with HMA-MMA16 than LPEO.

The difference in miscibility of these systems may come from compactness of BPEO molecules. In addition, we may point out that methyl groups on the end of the branched chain in BPEO also contribute to miscibility. EHMA-MMA copolymers in which EHMA has more methyl groups than HMA are more miscible with PEO than HMA-MMA copolymers.

Table 2
χ parameters for various pairs

Pair	χ parameter	Temperature range (K)	At 413 K
HMA/MMA	0.0512	333–443	
EHMA/MMA	0.0554	333–443	
EO/HMA	$0.006+30/T$	333–433	0.0786
EO/EHMA	$-0.042+35/T$	333–443	0.0427
EO/MMA[a]	-0.005	353	
*n*BMA/MMA[b]	$-0.216+95.7/T$	413–463	0.0157
iBMA/MMA[b]	$-0.150+73.1/T$	413–473	0.0270

[a] Ref. [31].
[b] Ref. [25].

4. Discussion

The homopolymer blends PEO/PMMA is considered to be of LCST-type miscibility because the χ parameter is negative.

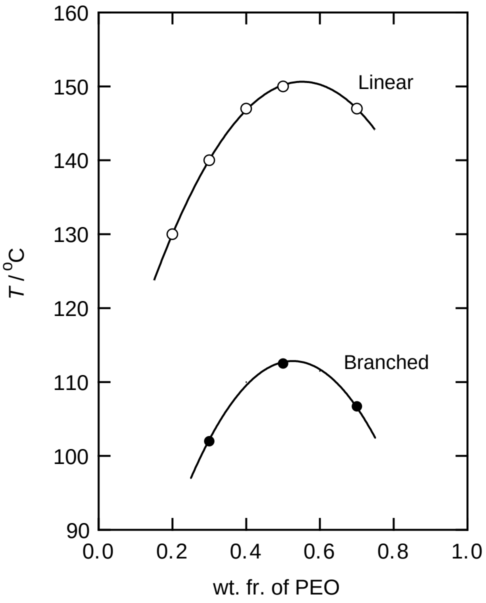

Fig. 5. Phase diagrams obtained by the light scattering method for the blends of linear PEO2.6 and branched PEO, respectively, with HMA-MMA16.

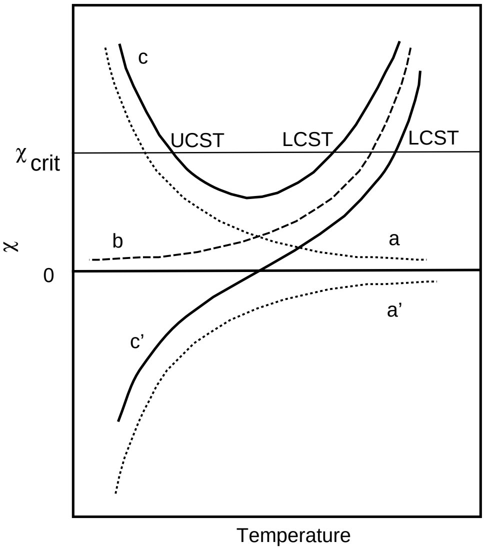

Fig. 6. Schematic illustration of temperature dependence of χ based on free volume or equation-of-states theory: (*a* and *a'*) the exchange enthalpy terms corresponding to positive and negative exchange enthalpies, respectively; (b) the free volume term; (*c* and *c'*) $\chi=(a)+(b)$ and $\chi=(a')+(b)$, respectively.

In spite of that, both PEO/HMA-MMA and PEO/EHMA-MMA blends showed UCST-type miscibility. We reported in the previous paper [26] that although both homopolymer blends of PEO/PMMA and poly(vinyl methyl ether)/polystyrene (PVME/PS) showed LCST-type miscibility, UCST appeared for PEO/(MMA-stat-styrene) (PEO/MMA-S) blends while LCST for PVME/MMA-S, where both homopolymer blends of PEO/PS and PVME/PMMA are immiscible systems.

Such contrastive miscibility behavior of the random copolymer blends was discussed in detail based on the free volume theory [26]. According to the theory, we can express the temperature dependence of χ as shown in Fig. 6. The χ parameter consists of the exchange enthalpy (EH) and free volume difference (FV) terms. UCST is caused by the positive EH term, while LCST by the FV term. In the blends of homopolymer A with random copolymer B–C where the homopolymer pair A/B is miscible but A/C immiscible, when in the A/C pair the contribution of the positive EH term to χ is larger than that of the FV term, UCST may appear with increasing C composition in the B–C copolymer. On the other hand, LCST may appear when the FV term contributes more greatly to immiscibility than the EH term. In the previous paper [26], it was shown that the FV term was smaller in PEO/PMMA than in PEO/PS, which suggests that an increase in the contribution of the EH term for the copolymer blend PEO/MMA-S causes UCST. In PVME/MMA-S, on the other hand, it was concluded that the appearance of LCST was due to the fact that the FV term was larger in PVME/PMMA than in PVME/PS.

In the present copolymer blends PEO/HMA-MMA and PEO/EHMA-MMA, although we have no information on the FV and EH terms, the EH term is predicted to be larger with increasing HMA or EHMA composition. As shown in Table 2, the χ parameters of HMA/MMA and EHMA/MMA pairs are considerably larger than those of nBMA (*n*-butyl methacrylate)/MMA and iBMA (isobutyl methacrylate)/MMA, which means that a longer alkyl side group weakens the polarities of methacrylate. Therefore, the exchange enthalpy in PEO/HMA and PEO/EHMA pairs is considered to be larger than that of PEO/MMA pair. This may lead to the fact that the PEO blends with HMA-MMA and EHMA-MMA are of UCST-type.

5. Conclusion

The miscibility in the random copolymer blends of PEO/HMA-MMA and PEO/EHMA-MMA was experimentally evaluated. Although PEO/PMMA blends are predicted to have LCST-type miscibility, the miscibility behavior of the blends with the random copolymers, HMA-MMA and EHMA-MMA, was of UCST-type.

The χ parameters of PEO/HMA, PEO/EHMA and HMA/EHMA pairs were estimated from the copolymer composition dependence of miscibility in the random copolymer blends.

The branched PEO was more miscible with the HMA-MMA random copolymer than the linear PEO, which indicates that more compact polymer molecules are more miscible.

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