# Equation-of-State Analysis of Binary Copolymer Systems. 3. Miscibility Maps

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ABSTRACT: The perturbed hard-sphere-chain (PHSC) equation of state for copolymer systems is applied to binary polymer mixtures containing random copolymers. Intersegmental parameters are obtained for several pairs of segments, and theoretical miscibility maps are compared with experiment for systems containing two, three, and four kinds of segments. The PHSC equation of state is able to represent immiscibility caused by lower critical solution temperature (LCST) phase behavior as well as that caused by upper critical solution temperature phase behavior. For the system poly(methyl methacrylate)/poly(acrylonitrile-*co*-styrene), theory represents the miscibility window caused by LCST behavior where miscibility changes from immiscible → miscible → immiscible as the composition of poly(acrylonitrile-*co*-styrene) random copolymer becomes rich in acrylonitrile. Using the same set of intersegmental parameters, theoretical miscibility maps and experiment show good agreement for systems containing styrene, acrylonitrile, methyl methacrylate, and cyclohexyl methacrylate.

## Introduction

Continuing demand for polymer blends with desired properties has been propelling extensive research on liquid–liquid equilibria of polymer blends.[1–5] One motivation behind these studies is the search for miscible pairs of polymers, including copolymers, which could lead to novel materials.

Miscibilities of copolymer blends have been often analyzed by the classical incompressible Flory–Huggins model,[6–8] a binary interaction model where the intramolecular and intermolecular interaction energies are expressed in terms of segmental interaction energies and copolymer compositions. These parameters can be obtained from miscibility–immiscibility boundaries on experimental miscibility maps. Segmental interaction parameters are assumed to be independent of the type of mixtures. In principle, miscibilities of copolymers at constant temperature and pressure can be predicted by the Flory–Huggins model if the relevant segmental interaction parameters are known.

Miscibilities in several binary copolymer mixtures at room temperature[9–12] were successfully predicted by the classical Flory–Huggins model[6–8] using the same set of segmental interaction parameters. In the copolymer systems where miscibilities are sensitive to temperature, however, the temperature dependence of phase behavior is difficult to predict by the Flory–Huggins model. The incompressible Flory–Huggins theory can represent only immiscibility caused by upper critical solution temperature (UCST) type phase behavior. Many copolymer blends, however, exhibit lower critical solution temperature (LCST) phase behavior at elevated temperatures arising from the free-volume effect. In the systems where immiscibility is caused by UCST behavior, the miscible copolymer composition range increases as the temperature rises. In the systems where immiscibility is caused by LCST behavior, however, the miscible copolymer composition range decreases as the temperature rises. Equation-of-state theories, rather than incompressible lattice theories, are appropriate for representing liquid–liquid equilibria of systems where immiscibility is caused by LCST behavior due to the free-volume effect. However, equation-of-state theories are also able to predict immiscibility caused by UCST behavior.

An equation of state applicable to copolymer systems is the perturbed hard-sphere-chain (PHSC) equation of state.[13–17] The PHSC equation of state[13–17] has been applied to homopolymer blends, homopolymer/copolymer mixtures, and mixtures of random copolymers containing two kinds of segments; these mixtures are denoted as $A_{r_1}/B_{r_2}$, $A_{r_1}/(C_YB_{1-Y})_{r_2}$, and $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, respectively, where $r_i$ is the number of effective hard spheres per molecule of component $i$ and $X$ and $Y$ are segment number fractions for segments A and A or C in components 1 and 2, respectively. The screening effect was introduced into the PHSC equation of state for copolymer systems in the first paper of this series.[18]

In the second paper of this series,[19] the theoretical copolymer-composition dependence of LCST was compared with experiment for mixtures of type $A_{r_1}/(C_YB_{1-Y})_{r_2}$ containing poly(methyl methacrylate-*co*-styrene) (MMA-*co*-S) and poly(acrylonitrile-*co*-styrene) (AN-*co*-S) random copolymers. These systems exhibit LCSTs in the experimentally accessible temperature range as the copolymer approaches polystyrene (i.e., as $Y \rightarrow 0$). The intersegmental parameters for the S–MMA pair were obtained from the styrene-rich region of the miscibility map for the system $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing MMA-*co*-S random copolymers.[18] Similarly, the intersegmental parameters for the S–AN pairs were obtained from the miscibility map for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing AN-*co*-S random copolymers.[19] It was shown that unique intersegmental parameters can be assigned to the S–MMA and S–AN pairs in the systems $A_{r_1}/(C_YB_{1-Y})_{r_2}$ containing MMA-*co*-S and AN-*co*-S random copolymers, respectively.

In this work, we attempt to apply the PHSC equation of state to more complicated systems using the same set of intersegmental parameters. Theoretical miscibility maps are compared with experiment for mixtures of random copolymers containing two, three, and four kinds of segments; these mixtures are denoted by $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$, and $(A_XB_{1-X})_{r_1}/$

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**Table 1. PHSC Equation-of-State Parameters for Homopolymers**[14,19]

| polymer | $r/M$ (mol/g) | $\sigma$ (Å) | $\epsilon/k_B$ (K) |
|---|---|---|---|
| polystyrene | 0.011 17 | 5.534 | 724.7 |
| polyacrylonitrile | 0.010 57 | 5.414 | 769.5 |
| poly(α-methylstyrene)[a] | 0.011 91 | 5.446 | 731.4 |
| *cis*-1,4-polybutadiene | 0.014 99 | 5.264 | 611.8 |
| poly(methyl methacrylate) | 0.014 32 | 4.850 | 655.9 |
| poly(cyclohexyl methacrylate) | 0.014 82 | 4.889 | 607.2 |
| poly(butyl methacrylate) | 0.018 99 | 4.550 | 510.8 |

[a] Parameters for poly(*o*-methylstyrene).

$(C_YD_{1-Y})_{r_2}$, respectively. Comparison of a theoretical miscibility window with experiment was made for the system poly(methyl methacrylate)/poly(acrylonitrile-*co*-styrene), a mixture of type $A_{r_1}/(C_YB_{1-Y})_{r_2}$, where the mixture is miscible over a limited copolymer composition range even though none of the three binary mixtures of relevant homopolymers is miscible. Attention is also given to the screening effect[18] in the system poly(methyl methacrylate-*co*-styrene)/poly(acrylonitrile-*co*-styrene), a mixture of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$.

## Theory

**Equation of State for Copolymer Mixtures.** Details of the PHSC equation of state for copolymer systems are given in refs 13 and 17.

Table 1 gives PHSC equation-of-state parameters for homopolymers used in this work. The equation-of-state parameters for copolymer systems are computed as discussed in the first paper of this series.[18] The weight-average molecular weight of component $i$, $M_i$ ($i$ = 1, 2 for a binary system), is used to compute equation-of-state parameters.

As discussed previously,[18,19] the PHSC equation of state requires at least one adjustable intersegmental parameter, $\kappa_{\alpha\beta}$, for a given pair of dissimilar segments α and $\beta$. An additional adjustable intersegmental parameter, $\zeta_{\alpha\beta}$, can also be introduced to relax the additivity of effective hard-sphere diameters of unlike segments α and $\beta$.

**Screening Effect.** A simple method to introduce the screening effect into the PHSC equation of state is discussed in the first paper of this series.[18] The model first replaces a copolymer molecule consisting of segments A and B, $(A_XB_{1-X})_r$, by a terpolymer consisting of segments A, B, and C, which represent AA, BB, and AB and BA sequences, respectively, of a copolymer. To keep the hard-core volume of a terpolymer equal to that of a copolymer, the diameter of segment C is given by

$$\sigma_C = \left[\frac{\sigma_A^3 + \sigma_B^3}{2}\right]^{1/3} \quad (1)$$

where $\sigma_\alpha$ (α = A, B, C) is the hard-sphere diameter of segment of type α. We then introduce an adjustable parameter $\varphi$ such that the fractions $\varphi$ and $1 - \varphi$ of segments C are replaced by segments B and A, respectively. The copolymer of type $(A_XB_{1-X})_r$ is therefore assumed to have the number of segments of type A and B given by $r''_A$ and $r''_B$, respectively:

$$r''_A = n_{AA} + (n_{AB} + n_{BA})(1 - \varphi)(\sigma_C^3/\sigma_A^3) \quad (2)$$

$$r''_B = n_{BB} + (n_{AB} + n_{BA})\varphi(\sigma_C^3/\sigma_B^3) \quad (3)$$

where $n_{\alpha\beta}$ ($\alpha,\beta$ = A,B) is the number of $\alpha-\beta$ hard-sphere sequences of the copolymer of type $(A_XB_{1-X})_r$ and

$$n_{AA} + n_{AB} + n_{BA} + n_{BB} = r - 1 \quad (4)$$

In this model, $\varphi = 1$ represents complete screening of segment A by segment B in AB and BA sequences. Conversely, $\varphi = 0$ represents complete screening of segment B by segment A in AB and BA sequences. When $\varphi = (\sigma_B^3/\sigma_C^3)/2$, the screening effect vanishes.

**Calculation Procedure.** To perform phase equilibrium calculations, expressions for the spinodal and critical conditions as well as those for the chemical potential are required; they are given in ref 17. Details of phase equilibrium calculations are given in the first paper of this series.[18]

## Results and Discussion

**Systems Containing Styrene, Acrylonitrile, and α-Methylstyrene.** We first consider the miscibility map of the mixture of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ containing poly(styrene-*co*-acrylonitrile) (S-*co*-AN) and poly(α-methylstyrene-*co*-acrylonitrile) (MS-*co*-AN) random copolymers. Let segments A, B, and C represent styrene, acrylonitrile, and α-methylstyrene, respectively. In the miscibility map of the mixture of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ there is always a miscible region near the origin $X = Y = 0$. When $X = Y = 0$, there is complete miscibility because component 1 is identical to component 2.

For the system (S-*co*-AN)/(MS-*co*-AN), the intersegmental parameters for the S−MS pair can be obtained from the accurate cloud-point curves for the system polystyrene/poly(α-methylstyrene) (PS/PMS). The intersegmental parameters for the S−AN pair were obtained in the second paper of this series[19] from the miscibility map of the mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y}))_{r_2}$ containing S-*co*-AN random copolymers; they are $\kappa_{S-AN} = 0.050\,55$ and $\zeta_{S-AN} = 0$. The remaining intersegmental parameters for the AN−MS pair are determined from the miscibility−immiscibility boundary on the miscibility map of the system (S-*co*-AN)/(MS-*co*-AN).

Figure 1a compares theoretical coexistence curves with measured phase diagrams for the system PS/PMS. Because the pure-component *PVT* data for PMS are not available, we use the equation-of-state parameters of poly(*o*-methylstyrene) as those for PMS. The experimental data are from Lin and Roe,[20] who used monodisperse polymers. The characterizations of polymer samples used in ref 20 are given in Table 2. The phase diagram for the system PS58/PMS62 and that for the system PS49/PMS56 were determined by differential scanning calorimetry (dsc) and by cloud-point measurements, respectively. Using the same set of intersegmental parameters, theory is able to represent the molecular weight dependence of the UCST. The intersegmental parameters for the S−MS pair are given in Table 3.

Figure 1b compares a theoretical miscibility map with experiment for the system (S-*co*-AN)/(MS-*co*-AN). Data are from Cowie *et al.*[21] who used dsc to determine the miscibility of copolymer blends. The open circles are the miscible blends, which have only one glass-transition temperature. The blends having two glass transition temperatures of the components are considered immiscible. The theoretical miscibility map is at 25 °C for $M_1$ = 350 000 and $M_2$ = 8000. Good agreement between theory and experiment is obtained with the intersegmental parameters $\kappa_{AN-MS} = 0.064$ and $\zeta_{AN-MS} = 0$ for the AN−MS pair. Theory predicts that im-

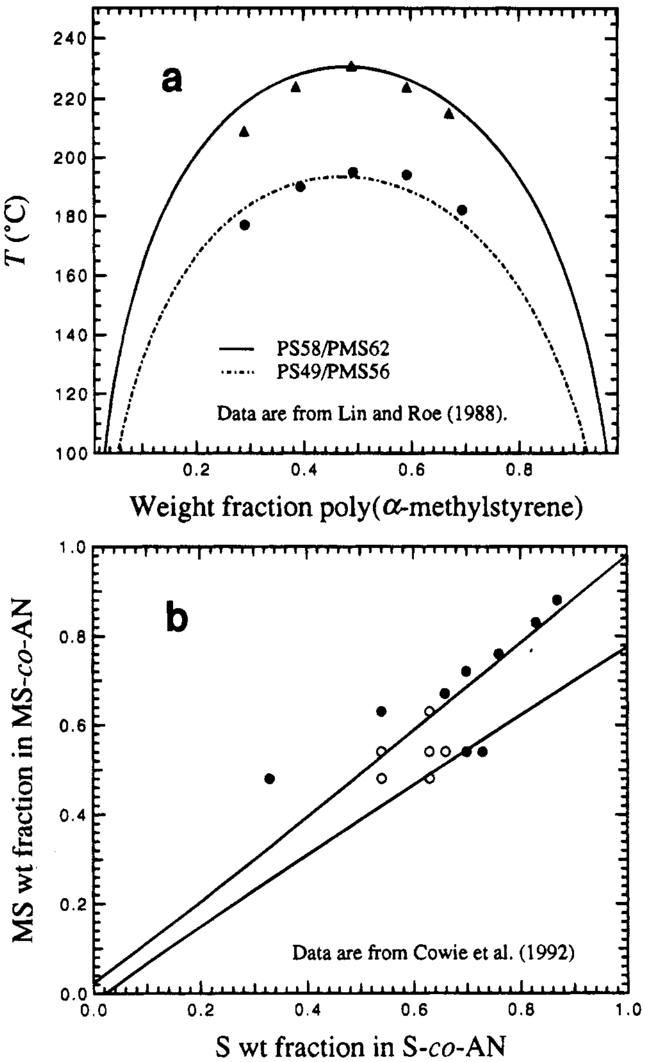

**Figure 1.** (a) Comparison of theoretical coexistence curves with experimental phase diagrams for the system PS/PMS:[20] (—) PS58/PMS62; (- · · -) PS49/PMS56; $\kappa_{\mathrm{S-MS}} = 0.000\,153$ and $\zeta_{\mathrm{S-MS}} = 0.000\,110$. (b) Miscibility map for the system (S-*co*-AN)/(MS-*co*-AN):[21] (○) miscible; (●) immiscible. Theoretical miscibility map is at 25 °C for $M_1 = 350\,000$ and $M_2 = 8000$; $\kappa_{\mathrm{S-AN}} = 0.050\,55$, $\zeta_{\mathrm{S-AN}} = 0$, $\kappa_{\mathrm{S-MS}} = 0.000\,153$, $\zeta_{\mathrm{S-MS}} = 0.000\,110$, $\kappa_{\mathrm{AN-MS}} = 0.064$, and $\zeta_{\mathrm{AN-MS}} = 0$.

**Table 2. Characterizations of Polymer Samples Used in Reference 20**

| sample | $M_w$ | $M_w/M_n$[a] |
|---|---|---|
| PS58 | 58 400 | 1.07 |
| PS49 | 49 000 | 1.06 |
| PMS62 | 62 100 | 1.05 |
| PMS56 | 56 100 | 1.07 |

[a] $M_n$, number-average molecular weight (g/mol); $M_w$, weight-average molecular weight (g/mol).

miscibility is caused by UCST-type phase behavior. Although experimental data are not available for the entire copolymer composition range, theory predicts that the system PS/(MS-*co*-AN) is miscible when the MS-*co*-AN copolymer contains 78–98% α-methylstyrene by weight.

**Systems Containing Styrene, Acrylonitrile, and Butadiene.** A miscibility map similar to that shown in Figure 1b is also reported for mixtures of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ containing S-*co*-AN and poly(butadiene-*co*-acrylonitrile) (BD-*co*-AN) random copolymers.[22] In this system, the intersegmental parameters for three pairs of segments can be obtained from the systems containing two kinds of relevant segments. In addition to the intersegmental parameters for the S–AN pair obtained in the second paper of this series,[19] those for the BD–S pair are $\kappa_{\mathrm{BD-S}} = 0.005\,44$ and $\zeta_{\mathrm{BD-S}} = 0.001\,17$, determined from mixtures of oligomers of polystyrene (PS) and polybutadiene (PBD) in ref 17. The oligomer systems PS/PBD exhibit UCST phase behavior. The remaining intersegmental parameters for the BD–AN pair are obtained from the miscibility map for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing poly(acrylonitrile-*co*-butadiene) (AN-*co*-BD) random copolymers.

**Table 3. Intersegmental Parameters**

| binary pair | κ | ζ |
|---|---|---|
| styrene–acrylonitrile[a] | 0.050 55 | 0 |
| styrene–α-methylstyrene | 0.000 153 | 0.000 110 |
| acrylonitrile–α-methylstyrene | 0.064 | 0 |
| butadiene–styrene[b] | 0.005 44 | 0.001 17 |
| butadiene–acrylonitrile | 0.012 22<br>(0.029) | 0<br>(0) |
| methyl methacrylate–styrene | −0.002 73 | −0.003 5 |
| methyl methacrylate–acrylonitrile | 0.032 49 | 0 |
| cyclohexyl methacrylate–styrene[a] | 0.001 936 | −0.001 718 |
| cyclohexyl methacrylate–acrylonitrile[a] | 0.042 17 | −0.003 17 |
| cyclohexyl methacrylate–methyl methacrylate | 0.015 07 | 0.008 06 |
| butyl methacrylate–methyl methacrylate[b] | −0.001 58 | −0.001 |
| butyl methacrylate–styrene | 0.010 85[b]<br>(0.012 5) | −0.002[b]<br>−0.002 |
| butyl methacrylate–acrylonitrile | 0.063 95<br>(0.045 08) | 0<br>0 |

[a] Reference 19. [b] Reference 17.

Figure 2a compares a theoretical miscibility map with experiment for the system $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing AN-*co*-BD random copolymers. Data are from Cowie *et al.*[22] obtained by dsc. Unfortunately, the AN-*co*-BD copolymers used by Cowie *et al.* are highly polydisperse ($M_w \cong 284\,000$ g/mol, $M_w/M_n = 1.5$–$11$; $M_n \equiv$ number-average molecular weight). It is therefore difficult to determine the intersegmental parameter for the BD–AN pair accurately from the data shown in Figure 2a. We obtain two sets of intersegmental parameters $\kappa_{\mathrm{BD-AN}} = 0.012\,22$ and $0.029$ by assuming $\zeta_{\mathrm{BD-AN}} = 0$. Theoretical miscibility maps in Figure 2a are at 25 °C for $M_1 = M_2 = 284\,000$. The miscible area predicted by the theory with $\kappa_{\mathrm{BD-AN}} = 0.029$ is slightly smaller than that predicted by theory with $\kappa_{\mathrm{BD-AN}} = 0.01222$.

Figure 2b compares a theoretical miscibility map with experiment[22] for the system (S-*co*-AN)/(BD-*co*-AN). The theoretical miscibility map is at 25 °C for $M_1 = 324\,000$ and $M_2 = 284\,000$. Theory predicts that immiscibility is caused by UCST phase behavior. The theoretical miscibility map is very sensitive to the intersegmental parameter for the BD–AN pair, $\kappa_{\mathrm{BD-AN}}$. Theory predicts that the system (S-*co*-AN)/(BD-*co*-AN) becomes immiscible as $\kappa_{\mathrm{BD-AN}}$ varies from 0.012 22 to 0.029, although the miscibility map in Figure 2a does not vary significantly in this range for $\kappa_{\mathrm{BD-AN}}$. Agreement between theoretical miscibility map and experiment cannot be obtained by simply adjusting $\kappa_{\mathrm{BD-AN}}$.

In the system (S-*co*-AN)/(BD-*co*-AN), the deviation of theoretical miscibility map from experiment may be caused by the polydispersity effect as well as by the probability that polybutadiene can assume several microstructures. The intersegmental parameters for the BD–S pair may also be inaccurate because they are obtained from data for mixtures of oligomers.

The origin of immiscibility in this system also needs to be clarified. Cowie *et al.*[22] mentioned that, in the

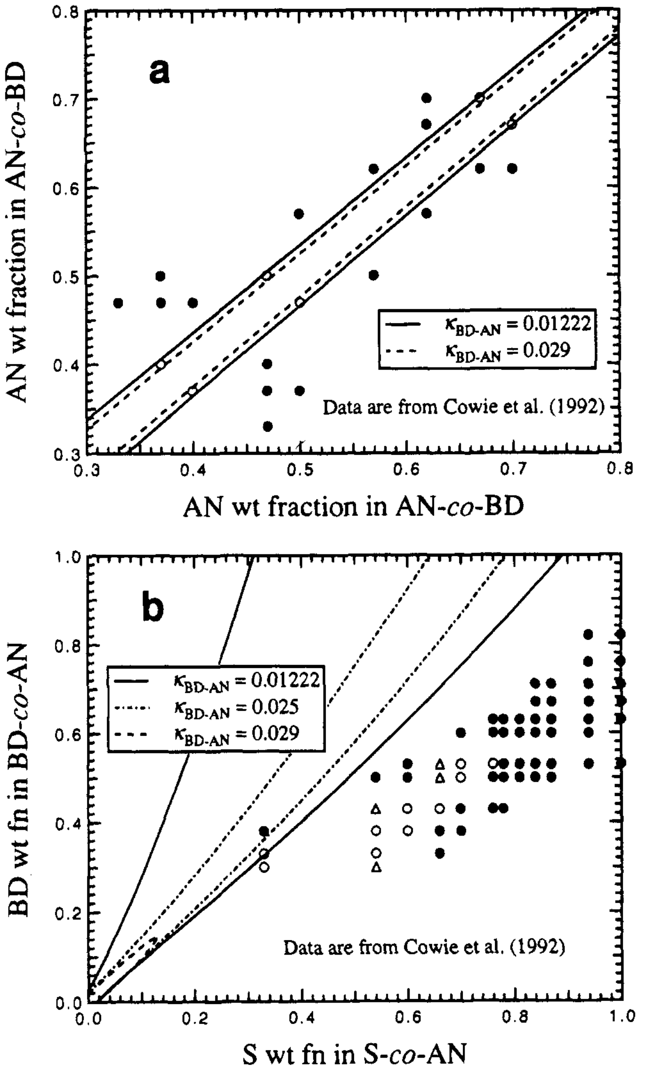

**Figure 2.** (a) Miscibility map for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing AN-*co*-BD:[22] (○) miscible; (●) immiscible. Theoretical miscibility map is at 25 °C for $M_1 = M_2 = 284\,000$: (—) $\kappa_{BD-AN} = 0.012\,22$, $\zeta_{BD-AN} = 0$; (- - -) $\kappa_{BD-AN} = 0.029$, and $\zeta_{BD-AN} = 0$. (b) Miscibility map for the system (S-*co*-AN)/(BD-*co*-AN):[22] (○) miscible; (△) partially miscible; (●) immiscible. Theory is at 25 °C for $M_1 = 324\,000$ and $M_2 = 284\,000$; $\kappa_{S-AN} = 0.050\,55$, $\zeta_{S-AN} = 0$, $\kappa_{BD-S} = 0.005\,44$, $\zeta_{BD-S} = 0.001\,17$, and $\zeta_{BD-AN} = 0$.

system (S-*co*-AN)/(BD-*co*-AN), miscible blends exhibit LCST phase behavior at elevated temperatures. In addition, Ougizawa and Inoue[23] reported that the system (S-*co*-AN)/(BD-*co*-AN) containing 75% styrene and 60% butadiene by weight in S-*co*-AN and BD-*co*-AN, respectively, shows both an UCST and a LCST in the temperature-composition phase diagram with complete miscibility between UCST and LCST. The simultaneous occurrence of an UCST and a LCST is also reported for the high-molecular-weight system polybutadiene/poly(styrene-*co*-butadiene) containing 45% styrene[24] by weight in the copolymer. The phase behavior of the system (S-*co*-AN)/(BD-*co*-AN) appears to be very complicated.

An important conclusion from the theoretical calculations shown in Figure 2a,b is that, in the system having limited miscibility, the theoretical miscibility map can be very sensitive to slight changes in intersegmental parameters.

**System Poly(methyl methacrylate)/Poly(acrylonitrile-*co*-styrene).** The phase behavior of copolymer systems containing methyl methacrylate, styrene, and acrylonitrile has been extensively studied.[25–28] The mixture poly(methyl methacrylate) (PMMA)/(AN-*co*-S) is known to exhibit a miscibility window caused by LCST phase behavior. In this system, miscibility changes from immiscible → miscible → immiscible as the copolymer content of acrylonitrile in AN-*co*-S rises, even though none of the three relevant binary mixtures of homopolymers is miscible. The system PMMA/(AN-*co*-S) is miscible at room temperature when the copolymer contains approximately 9–35% acrylonitrile by weight. Suess *et al.*[25] and Cowie and Lath[27] reported that the LCST in the system PMMA/(AN-*co*-S) containing approximately 10–25% acrylonitrile by weight lies above the thermal degradation temperature of the mixture. The exact miscible copolymer composition range and phase separation temperatures, however, may depend on the sample preparation and the heating rates of cloud-point measurements as well as on the molecular weight and polydispersity of the polymer samples.

Three mixtures of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ can be obtained from MMA, S, and AN segments: the systems (MMA-*co*-AN)/(S-*co*-AN), (AN-*co*-MMA)/(S-*co*-MMA), and (MMA-*co*-S)/(AN-*co*-S). We attempt to fit the miscibility maps of these systems using the same set of intersegmental parameters. The intersegmental parameters for the S–AN pair are $\kappa_{S-AN} = 0.050\,55$ and $\zeta_{S-AN} = 0$, obtained from the miscibility map of the mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-*co*-AN random copolymers.[19] Because of the screening effect discussed in the first paper of this series,[18] however, the intersegmental parameters for the MMA–S pair cannot be obtained from the miscibility map of the mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-*co*-MMA random copolymers. We obtain the intersegmental parameters for the MMA–S and MMA–AN pairs from the miscibility window of the system PMMA/(AN-*co*-S).

Figure 3a compares the theoretical miscibility window with experimental data by Suess *et al.*[25] for the system PMMA/(AN-*co*-S). The solid circles are the LCSTs determined by cloud-point measurements. The open and solid squares are the miscible and immiscible blends, respectively, containing 60% PMMA by weight at 50 °C. Curves are the theoretical LCSTs for $M_1 = 43\,000$ and $M_2 = 162\,000$. The intersegmental parameters for the MMA–S and MMA–AN pairs were obtained by assuming that, at 166 °C, the immiscibility–miscibility and miscibility–immiscibility boundaries lie at 9.4 and 34.6% acrylonitrile by weight, respectively. For given intersegmental parameters for the S–AN pair, $\kappa_{S-AN}$ and $\zeta_{S-AN}$, it was found that there is only one set of intersegmental parameters $\kappa_{MMA-S}$ and $\kappa_{MMA-AN}$ for $\zeta_{MMA-S} = \zeta_{MMA-AN} = 0$ which satisfy the above-mentioned conditions. Additional intersegmental parameter $\zeta_{MMA-S}$ was introduced to change the width of the miscibility window. The intersegmental parameters for the MMA–AN pair are the same ($\kappa_{MMA-AN} = 0.032\,49$ and $\zeta_{MMA-AN} = 0$) in the three curves shown in Figure 3a.

The experimental data in Figure 3a show that the LCST does not vary significantly between 25 and 35 wt % acrylonitrile and that the width of the miscibility window is almost independent of temperature below about 170 °C. On the other hand, the theoretical miscibility window is a smooth curve. It is therefore not possible to obtain good agreement between theory and experiment over a wide temperature range.

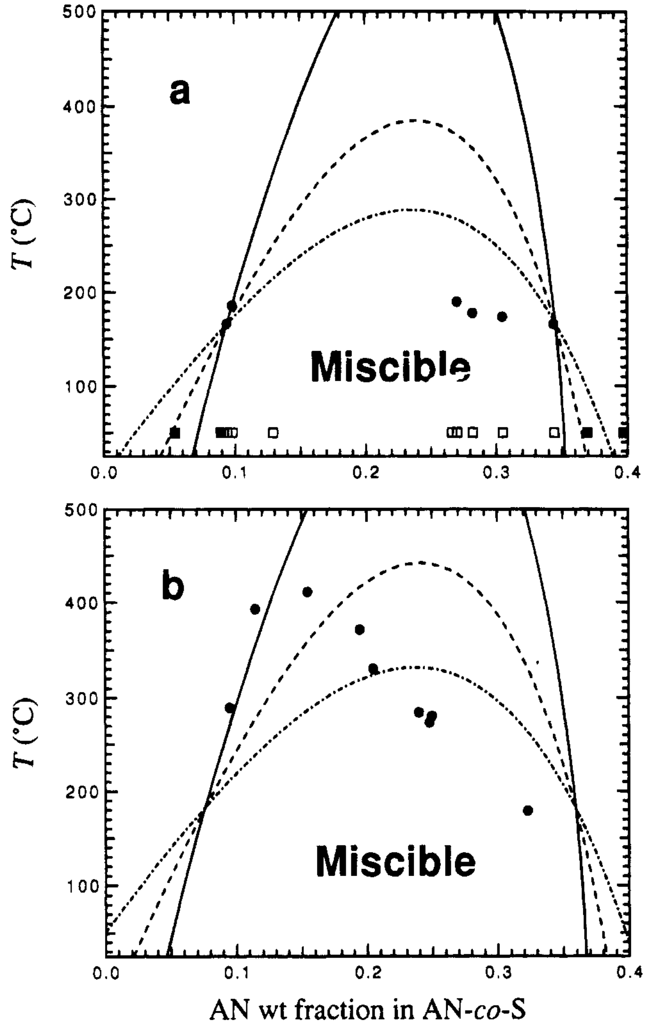

**Figure 3.** Miscibility window for the system PMMA/(AN-co-S):[25,26] $\kappa_{MMA-AN} = 0.032\,49$, $\zeta_{MMA-AN} = 0$, $\kappa_{S-AN} = 0.050\,55$, and $\zeta_{S-AN} = 0$. (—) $\kappa_{MMA-S} = -0.002\,73$, $\zeta_{MMA-S} = -0.0035$; (- - -) $\kappa_{MMA-S} = -0.004\,31$, $\zeta_{MMA-S} = -0.0045$; (···) $\kappa_{MMA-S} = -0.006\,69$, $\zeta_{MMA-S} = -0.006$ (a) Theoretical LCST for $M_1$ = 43 000 and $M_2$ = 162 000: (●) LCST,[15] (□) miscible,[15] and (■) immiscible.[15] (b) Theoretical spinodal for equimass mixtures of $M_1$ = 100 000 and $M_2$ = 150 000: (●) cloud points of equimass mixtures.[16]

A miscibility window for the system PMMA/(AN-co-S) is also reported by Fowler *et al.*,[26] who used the PMMA of higher molecular weight ($M_w$ = 105 400 g/mol, $M_w/M_n$ = 2.0) than that used by Suess *et al.*[25] ($M_w$ = 43 000 g/mol, $M_w/M_n$ = 1.72). The molecular weight and polydispersity factor of AN-co-S copolymers are roughly the same for both experiments. Figure 3b compares the cloud points from Fowler *et al.*[26] with the theoretical spinodal for equimass mixtures. The theoretical spinodal is calculated using the intersegmental parameters obtained in Figure 3a with $M_1$ = 100 000 and $M_2$ = 150 000. Theory predicts that in the system PMMA/(AN-co-S) the LCST increases as the molecular weight of PMMA, $M_1$, rises. Theory also predicts that the LCST decreases as the molecular weight of AN-co-S copolymer, $M_2$, rises. Although the cloud points for $M_1$ = 100 000 from Fowler *et al.*[26] are higher than those for $M_1$ = 43 000 from Suess *et al.*,[25] it is not clear whether the LCST indeed increases with rising molecular weight of PMMA in the system PMMA/(AN-co-S) because the measured phase separation temperature could depend on sample preparation and polydispersity. Equation-of-state theories, however, are able to represent such a molecular weight dependence of LCST because the unfavorable equation-of-state effect, which results from compressibility disparities, could decrease as the difference in molecular sizes declines.

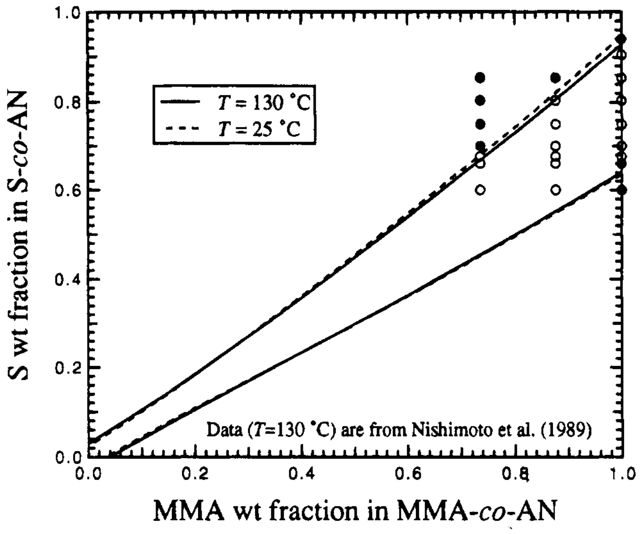

**Figure 4.** Comparison of theoretical miscibility map with experiment for the system (MMA-co-AN)/(S-co-AN):[28] (○) miscible at 130 °C; (●) immiscible at 130 °C. Theory is for $M_1$ = $M_2$ = 150 000: $\kappa_{MMA-S} = -0.002\,73$, $\zeta_{MMA-S} = -0.0035$, $\kappa_{MMA-AN} = 0.032\,49$, $\zeta_{MMA-AN} = 0$, $\kappa_{S-AN} = 0.050\,55$, and $\zeta_{S-AN} = 0$.

We use $\kappa_{MMA-S} = -0.002\,73$ and $\zeta_{MMA-S} = -0.0035$ as the intersegmental parameters for the MMA–S pair. With these parameters, theory slightly overestimates the miscible copolymer composition range near the immiscibility–miscibility boundary at room temperature.

**Systems Containing Methyl Methacrylate, Styrene, and Acrylonitrile.** We next compare theoretical miscibility maps with experiment for various systems containing methyl methacrylate, styrene, and acrylonitrile segments using the intersegmental parameters obtained from Figure 3a.

Figure 4 compares a theoretical miscibility map with experiment for mixtures of the type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ containing MMA-co-AN and S-co-AN random copolymers. Data at 130 °C are from Nishimoto *et al.*[28] A similar miscibility map is also reported at room temperature by Cowie and Lath.[27] As expected from the temperature dependence of the miscibility window in the system PMMA/(AN-co-S) shown in Figure 3a, the theoretical miscibility map is not sensitive to the temperature between 25 and 130 °C. Theory and experiment are in good agreement.

Figure 5 compares a theoretical miscibility map with experiment for mixtures of the type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ containing AN-co-MMA and S-co-MMA random copolymers.[27] In the theoretical miscibility map, there is a small miscible area near the origin $X = Y = 0$. Theory predicts that this system is essentially immiscible, consistent with experiment.

Figure 6 compares a theoretical miscibility map with experiment at room temperature for mixtures of the type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ containing MMA-co-S and AN-co-S random copolymers.[29,30] In this system, miscibility changes from immiscible → miscible → immiscible as the acrylonitrile content in component 2 rises from zero wt % acrylonitrile. As expected from Figure 3a, theory overestimates the miscible area near the immiscibility–miscibility boundary. The intersegmental parameters were obtained at 166 °C; better agreement between the theoretical miscibility map and experiment at 25 °C is

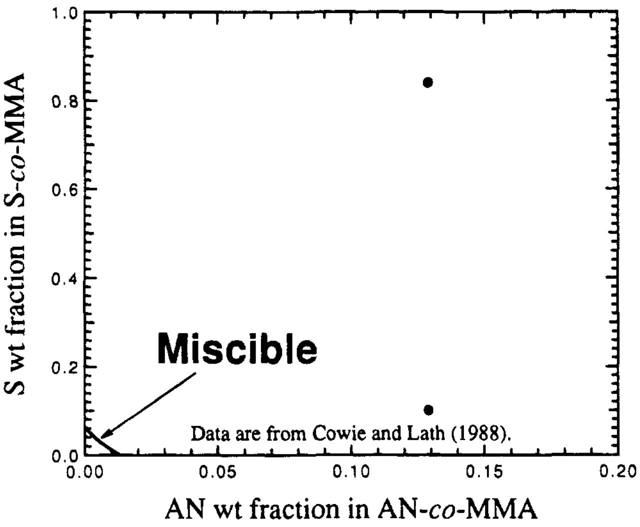

**Figure 5.** Comparison of theoretical miscibility map with experiment at room temperature[27] for the system (AN-*co*-MMA)/S-*co*-MMA): (●) immiscible. Theory is at 25 °C for $M_1 = M_2 = 150\,000$. Intersegmental parameters are the same as those used in Figure 4.

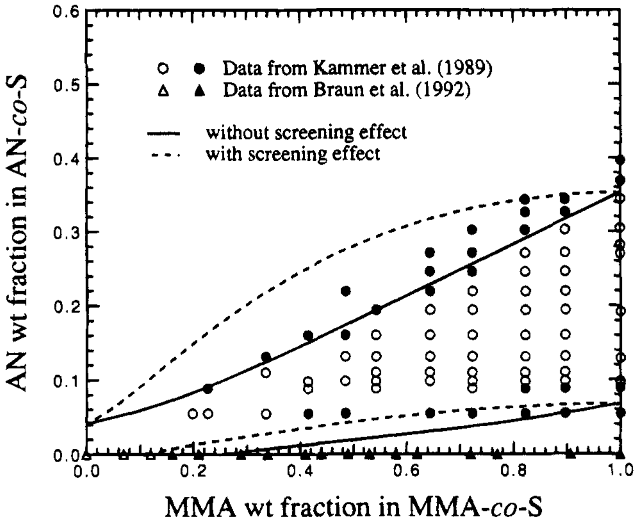

**Figure 6.** Comparison of theoretical miscibility map with experiment at room temperature for the system (MMA-*co*-S)/(AN-*co*-S):[29,30] (○, △) miscible; (●, ▲) immiscible. Theory is at 25 °C for $M_1 = 43\,000$ and $M_2 = 162\,000$. The screening effect is introduced by replacing the MMA–S and S–MMA sequences with the MMA–MMA sequence as discussed in the text. Intersegmental parameters are the same as those used in Figures 4 and 5.

obtained if the intersegmental parameters are obtained at 25 °C. The predicted miscibility–immiscibility boundary agrees well with experiment.

An interesting question is whether the system (MMA-*co*-S)/(AN-*co*-S) exhibits the screening effect. As discussed in the first paper of this series,[18] mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-*co*-MMA random copolymers exhibit the screening effect. In this system, a simple model proposed in ref 18 indicates that the styrene segment is screened by the methyl methacrylate segment in the S–MMA and MMA–S sequences; these sequences behave essentially as MMA–MMA sequences. It is therefore possible that a similar screening effect is observed in the MMA-*co*-S copolymer in the system (MMA-*co*-S)/(AN-*co*-S).

The first paper of this series[18] gives details of the method to include the screening effect into the PHSC equation of state. We replace all of the S–MMA and MMA–S sequences by the MMA–MMA sequences, i.e., $\varphi = 0$ in eqs 2 and 3, with segments A and B representing methyl methacrylate and styrene, respectively. As discussed in ref 18, to use the number of monomer sequences calculated from the measured reactivity ratios of copolymerization as the number of hard-sphere sequences, $n_{\alpha\beta}$ ($\alpha,\beta$ = A,B) in the model, the equation-of-state parameters must be obtained such that one monomer is represented by a single sphere in the model. The equation-of-state parameters used in this work, however, are those that give the best fit to the pure-component *PVT* data; these parameters do not assume that one monomer corresponds to a single sphere in the PHSC equation of state. Therefore, we assume that the number of hard-sphere sequences of a copolymer of type $(A_XB_{1-X})_r$ are given by that of a truly random copolymer:

$$n_{AA} = X^2(r-1),\quad n_{AB} = n_{BA} = X(1-X)(r-1),\quad n_{BB} = (1-X)^2(r-1) \qquad (5)$$

The broken curves in Figure 6 are calculated by assuming that the S–MMA and MMA–S hard-sphere sequences of MMA-*co*-S copolymer behave as the MMA–MMA sequences, i.e., $\varphi = 0$ in eqs 2 and 3, with segments A and B representing methyl methacrylate and styrene, respectively. For a given methyl methacrylate content in the MMA-*co*-S copolymer, agreement of the theoretical immiscibility–miscibility boundary with experiment seems to be improved as the screening effect is included. The difference between the solid and broken curves, however, is small. In addition, the theory with screening effect clearly overestimates the miscible area near the miscibility–immiscibility boundary. Therefore, the screening effect in the MMA-*co*-S copolymer in the system (MMA-*co*-S)/(AN-*co*-S) is not as apparent as that in the system $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-*co*-MMA random copolymers. The screening effect in the system (MMA-*co*-S)/(AN-*co*-S) may be important only when the AN-*co*-S copolymer contains a very small amount of acrylonitrile.

The results shown in Figures 4–6 imply that the intersegmental parameters do not depend on the type of mixture in the systems, (MMA-*co*-AN)/(S-*co*-AN), (AN-*co*-MMA)/(S-*co*-MMA), and (MMA-*co*-S)/(AN-*co*-S). A question, however, still remains regarding the intersegmental parameters for the MMA–S pair obtained in Figure 3a. Figure 7 compares a theoretical miscibility map with screening effect with experiment for mixtures of the type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-*co*-MMA random copolymers.[30] The screening effect is introduced by the same procedure used to include the screening effect in the system (MMA-*co*-S)/(AN-*co*-S); the S–MMA and MMA–S sequences are replaced by the MMA–MMA sequences. The number of specific sequences is given by eq 5 with segments A and B representing styrene and methyl methacrylate segments, respectively. The complete screening of styrene by methyl methacrylate in the S–MMA and MMA–S sequences corresponds to $\varphi = 1$ in eqs 2 and 3. The screening effect is included in both components 1 and 2. Although the temperature dependence of the miscibility map is not correctly predicted, the parameters used in Figure 7 seem to be of the correct order of magnitude.

We next consider mixtures of the type $(A_XB_{1-X})_{r_1}/(C_YD_{1-Y})_{r_2}$ containing four kinds of segments which requires six sets of intersegmental parameters.

**Systems Containing Cyclohexyl Methacrylate, Methyl Methacrylate, Acrylonitrile, and Styrene.**

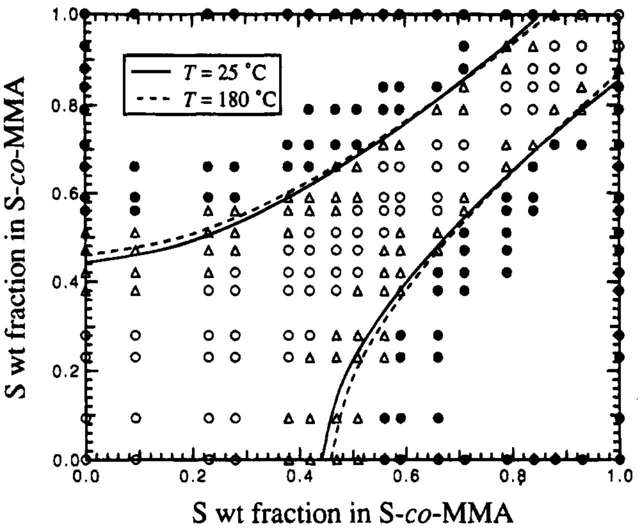

**Figure 7.** Miscibility maps with screening effect for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-co-MMA random copolymers[30] ($M_w \cong 150\,000$ g/mol, $M_w/M_n \cong 1.7$): (○) miscible at 25 and 180 °C; (△) miscible at 25 °C but immiscible at 180 °C; (●) immiscible at 25 and 180 °C. Theoretical miscibility maps are for $M_1 = M_2 = 150\,000$ with $\kappa_{S-MMA} = -0.002\,73$ and $\zeta_{S-MMA} = -0.003$. The screening effect is introduced by replacing the MMA–S and S–MMA sequences with the MMA–MMA sequences as discussed in the text.

A miscibility map for mixtures of poly(cyclohexyl methacrylate-co-methyl methacrylate) (CHMA-co-MMA) and AN-co-S random copolymers is reported by Nishimoto *et al.*[31] In this system, all of the necessary six sets of intersegmental parameters can be obtained from the following three mixtures of type $A_{r_1}/(C_YB_{1-Y})_{r_2}$: PMMA/(AN-co-S), PCHMA/(AN-co-S), and PS/(CHMA-co-MMA).

The intersegmental parameters for the CHMA–S and CHMA–AN pairs were obtained in the second paper of this series;[19] they are given in Table 3. The mixture of PCHMA and PS is miscible up to about 240 °C.[31] The mixture of PCHMA and AN-co-S copolymer also shows LCST phase behavior. The intersegmental parameters among methyl methacrylate, acrylonitrile, and styrene segments are the same as those used in Figures 4–7. The remaining intersegmental parameters for the CHMA–MMA pair are obtained from the copolymer-composition dependence of phase separation temperatures in the system PS/(CHMA-co-MMA).[31]

Figure 8 compares the copolymer-composition dependence of theoretical LCST with the cloud points of equimass mixtures[31] for the system PS/(CHMA-co-MMA). Although the molecular weights of copolymers and complete phase diagrams are not reported, this system is shown to exhibit LCST phase behavior. The theoretical curve is for $M_1 = M_2 = 200\,000$. The intersegmental parameters for the CHMA–MMA pair were obtained by assuming that, for the copolymer containing 28.5% cyclohexyl methacrylate by weight, the critical temperature and mixture composition are 150 °C and 13 wt % PS, respectively. Under these assumptions, the calculated critical compositions may not agree with the measured critical compositions. The difference between the calculated LCST and the measured phase separation temperature for equimass mixtures, however, would be small because the phase diagram in this system is flat near the LCST.

Figure 9 compares a theoretical miscibility map with experiment[31] for the system (CHMA-co-MMA)/(AN-co-S). Theory and experiment are in excellent agreement. Theory predicts that the miscible area decreases with temperature because in this system immiscibility is caused by LCST phase behavior.

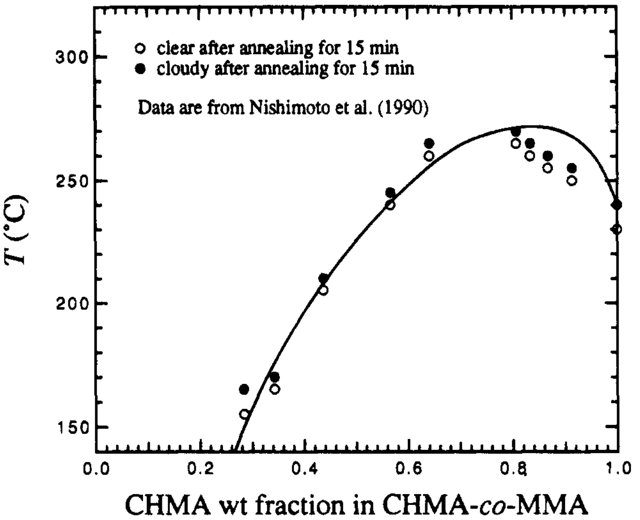

**Figure 8.** Comparison of theoretical LCST with the phase separation temperatures of equimass mixtures for the system PS/(CHMA-co-MMA):[31] $M_1 = M_2 = 200\,000$, $\kappa_{S-MMA} = -0.002\,73$, $\zeta_{S-MMA} = -0.0035$, $\kappa_{CHMA-S} = 0.0019\,36$, $\zeta_{CHMA-S} = -0.001\,718$, $\kappa_{CHMA-MMA} = 0.01507$, and $\zeta_{CHMA-MMA} = 0.008\,06$.

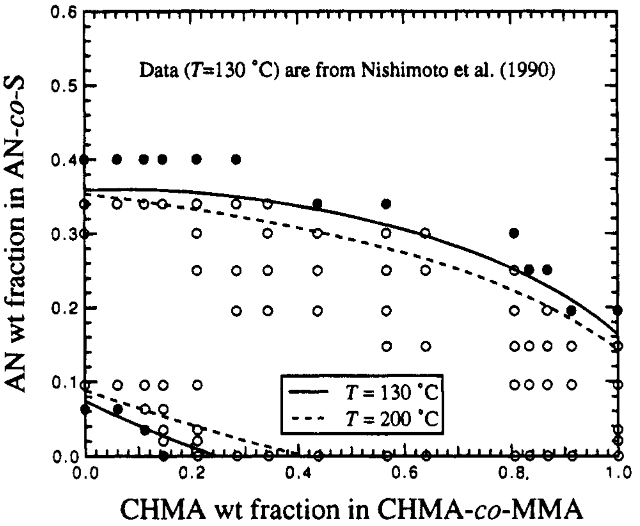

**Figure 9.** Comparison of theoretical miscibility map with experiment for the system (CHMA-co-MMA)/(AN-co-S):[31] (○) miscible at 130 °C; (●) immiscible at 130 °C. Theory is for $M_1 = M_2 = 200\,000$. Intersegmental parameters are given in Table 3.

**Systems Containing Butyl Methacrylate, Methyl Methacrylate, Acrylonitrile, and Styrene.** A partial miscibility map for mixtures of poly(butyl methacrylate-co-methyl methacrylate) (BMA-co-MMA) and AN-co-S random copolymers is reported by Kammer and Piglowski.[32] The system (BMA-co-MMA)/(AN-co-S) is obtained by simply replacing cyclohexyl methacrylate segment by butyl methacrylate in the system (CHMA-co-MMA)/(AN-co-S) shown in Figure 8. Poly(butyl methacrylate) (PBMA) and PS are known to be immiscible. PBMA and AN-co-S random copolymer are also reported to be immiscible.[26] Therefore, it is expected that the miscible area is smaller in the system (BMA-co-MMA)/(AN-co-S) than in the system (CHMA-co-MMA)/(AN-co-S).

The intersegmental parameters for the BMA–MMA and BMA–S pairs were obtained in ref 17 from the miscibility maps of mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing BMA-co-MMA and S-co-BMA random co-

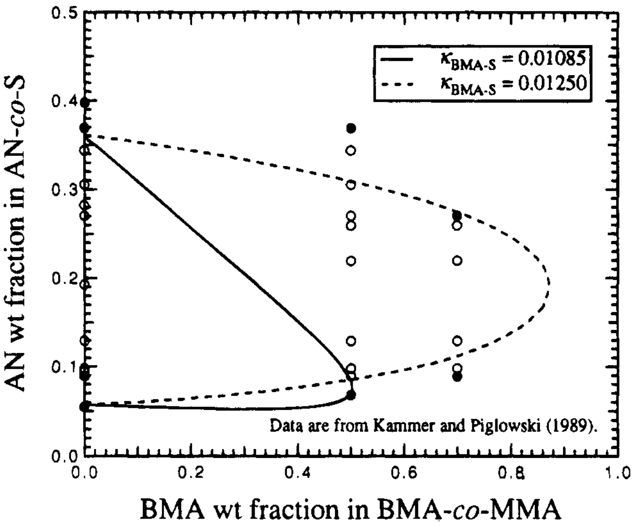

**Figure 10.** Comparison of theoretical miscibility map with experiment at room temperature for the system (BMA-*co*-MMA)/(AN-*co*-S):[25,32] (○) miscible; (●) immiscible. Theory is at 25 °C for $M_1$ = 100 000 and $M_2$ = 150 000: (—) $\kappa_{BMA-S}$ = 0.0125, $\zeta_{BMA-S} = -0.002$, $\kappa_{BMA-AN}$ = 0.063 95, and $\zeta_{BMA-AN}$ = 0; (- - -) $\kappa_{BMA-S}$ = 0.010 85, $\zeta_{BMA-S} = -0.002$, $\kappa_{BMA-AN}$ = 0.045 08, and $\zeta_{BMA-AN} = 0$.

polymers, respectively, which show LCST-type phase behavior. They are $\kappa_{BMA-MMA} = -0.001\,58$, $\zeta_{BMA-MMA} = -0.001$, $\kappa_{BMA-S} = 0.010\,85$, and $\zeta_{BMA-S} = -0.002$. The system $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-*co*-BMA random copolymers also exhibits a moderate screening effect having the miscibility map similar to that for the system containing S-*co*-MMA random copolymers shown in Figure 7. Theory, however, was able to obtain semiquantitative agreement with experiment without introducing the screening effect. All of the necessary intersegmental parameters (except those for the BMA–AN pair) are now obtained. We obtain the intersegmental parameters for the BMA–AN pair by using the partial information of the miscibility map for the system (BMA-*co*-MMA)/(AN-*co*-S).

Figure 10 compares a theoretical miscibility map with experiment at room temperature for the system (BMA-*co*-MMA)/(AN-*co*-S). The intersegmental parameters for the BMA–AN pair were obtained by assuming $\zeta_{BMA-AN} = 0$ and that the miscibility–immiscibility boundary lies at $\omega_{BMA} = 0.5$ and $\omega_{AN} = 0.085$, where $\omega_{BMA}$ and $\omega_{AN}$ are the weight fractions of butyl methacrylate and of acrylonitrile in BMA-*co*-MMA and AN-*co*-S copolymers, respectively. With these intersegmental parameters, however, theory (solid curve) underestimates the miscible area. The uncertainty in intersegmental parameters is most likely in those for the BMA–S pair because they were obtained from the miscibility map of the system $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing BMA-*co*-S random copolymers exhibiting the screening effect. Good agreement with experiment is obtained if the same fitting procedure is repeated by slightly adjusting one of the intersegmental parameters for the BMA–S pair, $\kappa_{BMA-S}$, to 0.0125. In that event, theory predicts that the system PBMA/(AN-*co*-S) is immiscible, consistent with the experiment of Fowler *et al.*[26]

## Conclusions

The perturbed hard-sphere-chain equation of state is able to represent immiscibility caused by lower critical solution temperature phase behavior as well as the immiscibility due to upper critical solution temperature phase behavior. Theoretical miscibility maps are compared with experiment for binary mixtures of copolymers containing two, three, and four kinds of segments.

For the systems $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ studied in this work, intersegmental parameters for as many as two pairs of segments are obtained from the systems containing two kinds of relevant segments. The remaining intersegmental parameters are obtained from data for the system $A_{r_1}/(C_YB_{1-Y})_{r_2}$. For the system $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$, theoretical miscibility maps are in good agreement with experiment except for the system poly(styrene-*co*-acrylonitrile)/poly(butadiene-*co*-acrylonitrile). The theoretical miscibility map and experiment show excellent agreement for the system $(A_XB_{1-X})_{r_1}/(C_YD_{1-Y})_{r_2}$ containing poly(cyclohexyl methacrylate-*co*-methyl methacrylate) and poly(acrylonitrile-*co*-styrene) random copolymers, where intersegmental parameters are obtained from three mixtures of type $A_{r_1}/(C_YB_{1-Y})_{r_2}$.

In the copolymer systems studied in this work, theoretical miscibility maps and experiment show good agreement using the same set of intersegmental parameters. Total prediction using the intersegmental parameters obtained from the system containing two kinds of segments only, however, remains to be carried out together with the measurements of miscibility maps and phase diagrams of relevant copolymer systems using monodisperse copolymers.

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## References and Notes

(1) Paul, D. R., Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978.
(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.
(3) Schmitt, B. J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 273.
(4) Solc, K., Ed. *Polymer Compatibility and Incompatibility: Principles and Practices*; MMI Press Symposium Series; Harwood Academic Publishers GmbH: New York, 1982; Vol. 2.
(5) Krause, S. *Pure Appl. Chem.* **1986**, *58*, 1553.
(6) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(7) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(8) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(9) Cowie, J. M. G.; Lath, D. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 103.
(10) Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. *Polymer* **1990**, *31*, 486.
(11) Cowie, J. M. G.; Reid, V. M. C.; McEwen, I. J. *Polymer* **1990**, *31*, 905.
(12) Bell, S. Y.; Cowie, J. M. G.; McEwen, I. J. *Polymer* **1994**, *35*, 786.
(13) Song, Y.; Lambert, S. M.; Prausnitz, J. M. *Macromolecules* **1994**, *27*, 441.
(14) Song, Y.; Lambert, S. M.; Prausnitz, J. M. *Ind. Eng. Chem. Res.* **1994**, *33*, 1047.
(15) Song, Y.; Lambert, S. M.; Prausnitz, J. M. *Chem. Eng. Sci.* **1994**, *49*, 2765.
(16) Song, Y.; Lambert, S. M.; Prausnitz, J. M., paper presented at AIChE meeting in St. Louis, November 1993.
(17) Hino, T.; Song, Y.; Prausnitz, J. M. *Macromolecules* **1994**, *27*, 5681.
(18) Hino, T.; Song, Y.; Prausnitz, J. M. *Macromolecules* **1995**, *28*, xxxx.
(19) Hino, T.; Prausnitz, J. M. *Macromolecules* **1995**, *28*, xxxx.
(20) Lin, J. L.; Roe, R. J. *Polymer* **1988**, *29*, 1227.
(21) Cowie, J. M. G.; Elexpuru, E. M.; McEwen, I. J. *Polymer* **1992**, *33*, 1993.

(22) Cowie, J. M. G.; Harris, J. H.; McEwen, I. J. *Macromolecules* **1992**, *25*, 5287.

(23) Ougizawa, T.; Inoue, T. *Polym. J.* **1986**, *18*, 521.

(24) Ougizawa, T.; Inoue, T.; Kammer, H. W. *Macromolecules* **1985**, *18*, 2092.

(25) Suess, M.; Kressler, J.; Kammer, H. W. *Polymer* **1987**, *28*, 957.

(26) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.

(27) Cowie, J. M. G.; Lath, D. *Makromol. Chem., Macromol. Symp.* **1988**, *16*, 103.

(28) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Polymer* **1989**, *30*, 1279.

(29) Kammer, H. W. *Acta Polym.* **1986**, *40*, 75.

(30) Braun, D.; Yu, D.; Kohl, P. R.; Gao, X.; Andradi, L. N.; Manger, E.; Hellmann, G. P. *J. Polym. Sci., Polym. Phys. Ed.* **1992**, *30*, 577.

(31) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Macromolecules* **1990**, *23*, 3633.

(32) Kammer, H. W.; Piglowski, J. *Acta Polym.* **1989**, *40*, 363.

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