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Equation-of-State Analysis of Binary Copolymer Systems. 1. Screening Effect

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ABSTRACT: The screening effect is introduced into the recently presented perturbed hard-sphere-chain (PHSC) equation of state for copolymer systems. Using reactivity ratios of copolymerization kinetics, the model first computes the number of specific monomer sequences in the copolymer consisting of monomers A and B. Some of the AB and BA monomer sequences (i.e., diads) are then replaced by BB sequences to represent the screening effect of segment B on segment A in AB and BA sequences. The essential characteristic of the screening effect is the assumption that the solution properties of a copolymer correspond to those of another copolymer whose composition differs from that of the true copolymer. The screening effect theory is used to calculate miscibility maps for several poly(styrene-*co*-methyl methacrylate) random copolymers that exhibit lower critical solution temperature behavior and significant deviation from the classical Flory–Huggins model. For a fixed temperature, there is good agreement between the theoretical miscibility map and experiment. To represent the temperature dependence of the miscibility map with temperature-independent parameters, it is necessary to consider diad interactions by modeling the copolymer consisting of monomers A and B as a terpolymer consisting of monomers A, B, and C that represent AA, BB, and AB and BA diads, respectively, of the copolymer.

Introduction

Song *et al.*[1–4] and Hino *et al.*[5] recently presented a perturbed hard-sphere-chain (PHSC) equation of state applicable to mixtures of large heteronuclear chain molecules, i.e., copolymers. The PHSC equation of state for real copolymer mixtures[5] is based on a modified form of Chiew's equation of state[6] for athermal mixtures of heteronuclear hard-sphere chains by Song *et al.*[1] The PHSC equation of state also employs a van der Waals perturbation whose parameters are related to the intermolecular potential as suggested by Song and Mason.[2] The sequence distribution in a copolymer was introduced only into the hard-sphere-chain reference state that represents repulsive interactions. The perturbation term that accounts for attractive forces was given in terms of segmental interaction energies. The segmental interaction energies depend only on the pair of segments of interest, independent of the type of segment adjacent to the segments of interest. The PHSC equation of state is able to represent lower critical solution temperature (LCST) phenomena as well as partial immiscibility with an upper critical solution temperature (UCST).

Comparison of the PHSC equation of state for copolymer systems with experiment was made for mixtures of random copolymers containing two kinds of segments; these systems are denoted as $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, where r_i is the number of effective hard spheres per molecule of component i and X and Y are segment number fractions for segment A in components 1 and 2, respectively.[5] Using the same set of intersegmental parameters at two different temperatures, calculated and experimental miscibility maps showed good agreement for the system containing poly(methyl methacrylate-*co*-butyl methacrylate) that does not exhibit a screening effect. For the system containing poly(styrene-*co*-butyl methacrylate) that exhibits a moderate screening effect, however, theory and experiment showed only semiquantitative agreement. In these systems, immiscibility is caused by LCST behavior.

A fundamental task in the development of molecular thermodynamic models for copolymer systems is inclusion of the screening effect, an effect due to sequence distribution.[7–14] To explain this effect, consider mixtures of random copolymers containing two kinds of segments. In the classical Flory–Huggins theory,[15–17] a unique interaction energy is assigned to a segment pair A and B. It is, however, conceivable that the interaction energy between a segment A in an AB or BA sequence (i.e., diad) and a segment B in an AB or BA sequence can be different from that between a segment A in an AA sequence and a segment B in an AB or BA sequence. Their difference may follow from the screening effect of segment B on segment A in AB and BA sequences which is not present in an AA sequence. The screening effect in the liquid–liquid equilibria of copolymer systems was recently reported for several systems containing two kinds of segments: mixtures of poly(styrene-*co*-methyl methacrylate) random copolymers differing in copolymer compositions.[7]

In this work, we present a simple method to include the screening effect into the previously presented PHSC equation of state for copolymer systems.[5] Theoretical miscibility maps with screening effect are computed for the system $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$. Comparison with experiment was made for mixtures containing poly(styrene-*co*-methyl methacrylate) random copolymers[7] that exhibits LCST behavior and significant deviation from the classical Flory–Huggins model.[15–17]

Theory

Equation of State for Copolymer Mixtures. Details of the PHSC equation of state are given in ref 1–5. The PHSC equation of state requires three parameters to describe the normal fluids including homopolymers: number of effective hard spheres per molecule, r; segmental diameter, σ; and nonbonded segment pair interaction energy, ϵ. These parameters were regressed

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from available volumetric and vapor–pressure data for a variety of normal fluids and several homopolymers; they are tabulated in ref 2. For a homopolymer, one of the regressed characteristic quantities is r/M, where M is the molecular weight of polymer. The procedure to define the equation-of-state parameters for copolymer systems is discussed later. The PHSC equation of state also requires at least one or two adjustable intersegmental parameters for a given pair of dissimilar segments. Intersegmental parameters can be obtained from the critical points of mixtures and from the miscibility–immiscibility boundaries of miscibility maps.

The PHSC equation of state for mixtures of heteronuclear polymer molecules is[5]

$$\frac{p}{\varrho k_{\mathrm{B}}T} = 1 + \varrho\sum_{i=1}^{m}\sum_{j=1}^{m}x_i x_j\left[\sum_{k=1}^{r_i}\sum_{l=1}^{r_j}b_{ij,kl}g_{ij,kl}\right] - \sum_{i=1}^{m}x_i\sum_{k=1}^{r_i-1}(g_{ii,k,k+1} - 1) - \frac{\varrho}{k_{\mathrm{B}}T}\sum_{i=1}^{m}\sum_{j=1}^{m}x_i x_j\left[\sum_{k=1}^{r_i}\sum_{l=1}^{r_j}a_{ij,kl}\right] \quad (1)$$

where p is the pressure, number density $\varrho = N/V$ (N is the number of molecules, and V is the volume), k_{B} is the Boltzmann constant, T is the absolute temperature, m is the number of components, r_i and x_i are the number of effective hard spheres per molecule and the mole fraction, respectively, of component i, and subscripts k and l denote the kth and lth segments, respectively, of hard-sphere chains. Equation 1 obeys the ideal-gas limit as $\varrho \rightarrow 0$.

In eq 1, $a_{ij,kl}$ is a parameter that reflects the strength of attractive forces between the kth effective hard sphere of component i and the lth effective hard sphere of component j; $b_{ij,kl}$ represents the second virial coefficient of hard spheres or the van der Waals covolume for effective hard spheres that accounts for the excluded volume due to the repulsive forces in the Song–Mason theory;[2] $g_{ij,kl}$ is the pair radial distribution function of hard spheres when kth and lth segments of components i and j, respectively, are at contact. The pair radial distribution function is given in refs 1 and 5.

The perturbation term in eq 1 assumes random mixing of segments. Equation 1 is for the mixture of hard-sphere chains consisting of arbitrary numbers of chemically different segments, including copolymers and terpolymers consisting of two and three kinds of segments, respectively. The segments in the chain need *not* have the same size.

In the following equations, subscripts α and β denote segment type. Parameters $a_{ij,\alpha\beta}$ and $b_{ij,\alpha\beta}$ are given by[5]

$$a_{ii,\alpha\alpha} = \frac{2}{3}\pi\sigma_{i,\alpha}^{3}\epsilon_{i,\alpha}F_{\mathrm{a}}(\tilde{T}_{i,\alpha}) \quad (2)$$

$$a_{ij,\alpha\beta} = a_{j,i,\beta\alpha} = \frac{2}{3}\pi\sigma_{ij,\alpha\beta}^{3}\epsilon_{ij,\alpha\beta}\sqrt{F_{\mathrm{a}}(\tilde{T}_{i,\alpha})F_{\mathrm{a}}(\tilde{T}_{j,\beta})} \quad (3)$$

$$b_{ii,\alpha\alpha} = b_{i,\alpha} = \frac{2}{3}\pi\sigma_{i,\alpha}^{3}F_{\mathrm{b}}(\tilde{T}_{i,\alpha}) \quad (4)$$

$$b_{ij,\alpha\beta} = b_{ji,\beta\alpha} = \frac{1}{8}(b_{i,\alpha}^{1/3} + b_{j,\beta}^{1/3})^{3} \quad (5)$$

In eqs 2–4, $\sigma_{i,\alpha}$ and $\sigma_{ij,\alpha\beta}$ are the separation distances between similar and dissimilar segments, respectively, at the minimum potential energies $\epsilon_{i,\alpha}$ and $\epsilon_{ij,\alpha\beta}$, respectively, in the segment–segment pair potential. We use the following combining rules to obtain parameters $\sigma_{ij,\alpha\beta}$ and $\epsilon_{ij,\alpha\beta}$:

$$\sigma_{ij,\alpha\beta} = \sigma_{ji,\beta\alpha} = \frac{1}{2}(\sigma_{i,\alpha} + \sigma_{j,\beta}) \quad (6)$$

$$\epsilon_{ij,\alpha\beta} = \epsilon_{ji,\beta\alpha} = \sqrt{\epsilon_{i,\alpha}\epsilon_{j,\beta}}(1 - \kappa_{ij,\alpha\beta}) \quad (7)$$

and

$$\sigma_{ii,\alpha\alpha} = \sigma_{i,\alpha} \quad (8)$$

$$\epsilon_{ii,\alpha\alpha} = \epsilon_{i,\alpha} \quad (9)$$

where $\kappa_{ij,\alpha\beta}$ is an adjustable intersegmental parameter whenever $\alpha \neq \beta$.

Equation 5 follows the additivity of effective hard-sphere diameters of unlike segments and that of similar segments in different components. In eqs 2–4, F_{a} and F_{b} are the universal functions of reduced temperature defined by

$$\tilde{T}_{i,\alpha} = k_{\mathrm{B}}T/\epsilon_{i,\alpha}s(r_i) \quad (10)$$

where $s(r_i)$ is a scaling parameter that depends only on r_i. The universal functions F_{a} and F_{b} account for the temperature dependences of parameters a and b, respectively. The universal functions and the scaling parameter are given in ref 2.

Finally, an additional adjustable parameter $\zeta_{ij,\alpha\beta}$ can be introduced if necessary to relax the additivity of effective hard-sphere diameters of unlike segments such that

$$b_{ij,\alpha\beta}^{1/3} = b_{ji,\beta\alpha}^{1/3} = \frac{(b_{i,\alpha}^{1/3} + b_{j,\beta}^{1/3})}{2}(1 - \zeta_{ij,\alpha\beta}) \quad (11)$$

where $\zeta_{ij,\alpha\beta}$ is an adjustable intersegmental parameter whenever $\alpha \neq \beta$. The PHSC equation of state therefore requires at least one ($\kappa_{ij,\alpha\beta}$) and sometimes as many as two ($\kappa_{ij,\alpha\beta}$ and $\zeta_{ij,\alpha\beta}$) adjustable intersegmental parameters for a given pair of unlike segments.

Calculation of Monomer Sequence Distribution from Reactivity Ratios. Copolymers exhibiting the screening effect behave as if they have copolymer compositions that are different from those of the true copolymers (i.e., pseudocopolymer compositions). Therefore, a method to include the screening effect is to replace the true copolymer composition with the pseudocopolymer composition in the PHSC equation of state. In this paper, we present a systematic method to calculate the pseudocopolymer composition from the true copolymer composition using information from copolymerization kinetics.

Consider a real copolymer of type $(A_X B_{1-X})_r$, where r is the number of total monomers per molecule and X is the number fraction of monomer of type A, in which one of the monomers in the AB and BA sequences (i.e., diads) is screened by the other monomer. Since the degree-of-screening effect depends on the number of AB and BA sequences in a copolymer, the important question is how to determine the numbers of specific sequences. For a truly random copolymer, the numbers of α–β sequences, $n_{\alpha\beta}(\alpha,\beta = \mathrm{A,B})$, can be calculated from a statistical average as

$$n_{AA} = X^2(r-1);\quad n_{AB} = n_{BA} = X(1-X)(r-1);\quad n_{BB} = (1-X)^2(r-1) \tag{12}$$

The monomer sequences of real copolymers, however, may deviate from those given by eq 12. From an appropriate copolymerization-kinetic model, the monomer sequence distribution can be determined from the study of copolymerization kinetics.

Consider the terminal model of copolymerization.[18] We apply the terminal model to the copolymerization of monomers A and B, which yields the copolymer of type $(A_XB_{1-X})_r$. Kinetic equations for the terminal model are

$$\sim A^\bullet + A \rightarrow \sim A^\bullet \qquad k_{AA} \tag{13}$$

$$\sim A^\bullet + B \rightarrow \sim B^\bullet \qquad k_{AB} \tag{14}$$

$$\sim B^\bullet + A \rightarrow \sim A^\bullet \qquad k_{BA} \tag{15}$$

$$\sim B^\bullet + B \rightarrow \sim B^\bullet \qquad k_{BB} \tag{16}$$

where $\sim A^\bullet$ and $\sim B^\bullet$ are the monomer A- and monomer B-ended polymeric radicals, respectively, and $k_{\alpha\beta}$ (α,β = A,B) is the reaction rate constant of monomer β to the polymeric radical ended by monomer α.

We also define the reactivity ratios as

$$\mathcal{R}_1 = k_{AA}/k_{AB} \tag{17}$$

$$\mathcal{R}_2 = k_{BB}/k_{BA} \tag{18}$$

In the terminal model, truly random copolymers are obtained only if $\mathcal{R}_1 = \mathcal{R}_2 = 1$. On the other hand, copolymers exhibit high alternation in the monomer sequence when $\mathcal{R}_1 \ll 1$ and $\mathcal{R}_2 \ll 1$. For copolymerizations in a batch reactor, the reactivity ratios are obtained from a plot of initial copolymer composition against the monomer composition in the feed.

For sufficiently low conversions where the monomer concentrations in a batch reactor remain nearly constant, the terminal model predicts that the ratio of number fraction of segment A to that of segment B in the copolymer, Ξ, is related to the ratio of the molar concentration of monomer A to that of monomer B in the feed, ϑ, by

$$\Xi \equiv \frac{X}{1-X} = \frac{\mathcal{R}_1\vartheta + 1}{\mathcal{R}_2/\vartheta + 1} \tag{19}$$

For a known copolymer composition X, eq 34 is solved for ϑ:

$$\vartheta = \frac{-(1-\Xi) + \sqrt{(1-\Xi)^2 + 4\mathcal{R}_1\mathcal{R}_2\Xi}}{2\mathcal{R}_1} \tag{20}$$

We define $P_{\alpha\beta}$, the probability of monomer α reacting with the monomer β-ended polymeric radical; it follows that $P_{\alpha A} + P_{\alpha B} = 1$ (α,β = A,B). For a system with two monomers (A and B), we have four probabilities:

$$P_{AA} = \frac{\mathcal{R}_1\vartheta}{\mathcal{R}_1\vartheta + 1} \tag{21}$$

$$P_{AB} = 1 - P_{AA} = \frac{1}{\mathcal{R}_1\vartheta + 1} \tag{22}$$

$$P_{BB} = \frac{\mathcal{R}_2/\vartheta}{\mathcal{R}_2/\vartheta + 1} \tag{23}$$

$$P_{BA} = 1 - P_{BB} = \frac{1}{\mathcal{R}_2/\vartheta + 1} \tag{24}$$

Therefore

$$n_{AA}/n_{AB} = P_{AA}/P_{AB} = \mathcal{R}_1\vartheta \tag{25}$$

$$n_{BB}/n_{BA} = P_{BB}/P_{BA} = \mathcal{R}_2/\vartheta \tag{26}$$

where $n_{\alpha\beta}$ (α,β = A,B) is the number of $\alpha-\beta$ sequences. In addition, by neglecting the end effect (i.e., assuming that $r - 1 \cong r$)

$$r_A = rX = \frac{2n_{AA} + n_{AB} + n_{BA}}{2} \tag{27}$$

$$r_B = r(1-X) = \frac{2n_{BB} + n_{AB} + n_{BA}}{2} \tag{28}$$

where r_α (α = A,B) is the number of monomer α per molecule. Equations 25–28 are then solved for $n_{\alpha\beta}$:

$$n_{AB} = \frac{r_A(2\mathcal{R}_2/\vartheta + 1) - r_B}{2\mathcal{R}_1\mathcal{R}_2 + \mathcal{R}_1\vartheta + \mathcal{R}_2/\vartheta} \tag{29}$$

$$n_{AA} = n_{AB}\mathcal{R}_1\vartheta \tag{30}$$

$$n_{BA} = \frac{r_B(2\mathcal{R}_1\vartheta + 1) - r_A}{2\mathcal{R}_1\mathcal{R}_2 + \mathcal{R}_1\vartheta + \mathcal{R}_2/\vartheta} \tag{31}$$

$$n_{BB} = n_{BA}\mathcal{R}_2/\vartheta \tag{32}$$

When the measured monomer sequence distribution is used as the hard-sphere sequence distribution in the PHSC equation of state, the PHSC equation-of-state parameters must be obtained such that one monomer unit is represented by a single hard sphere in the model.

Screening Effect. Consider a heteronuclear hard-sphere chain that represents a real copolymer of type $(A_XB_{1-X})_r$. The rigorous approach to introduce the screening effect into the model is to represent a copolymer consisting of segments A and B by a terpolymer consisting of segments A, B, and C that represent AA, BB, and AB and BA sequences, respectively, of the copolymer. Figure 1b shows the hard-sphere sequence of the terpolymer that represents the copolymer having the hard-sphere sequence shown in Figure 1a. The numbers of segment of type A, B, and C in a terpolymer are given by r_A', r_B', and r_C', respectively; they are related to the numbers of $\alpha-\beta$ sequences $n_{\alpha\beta}$ (α,β = A,B) of a copolymer, eqs 29–32, by

$$r_A' = n_{AA} \tag{33}$$

$$r_B' = n_{BB} \tag{34}$$

$$r_C' = n_{AB} + n_{BA} \tag{35}$$

To keep the hard-core volume of a terpolymer equal to that of a copolymer, the diameter of segment C, σ_C, is

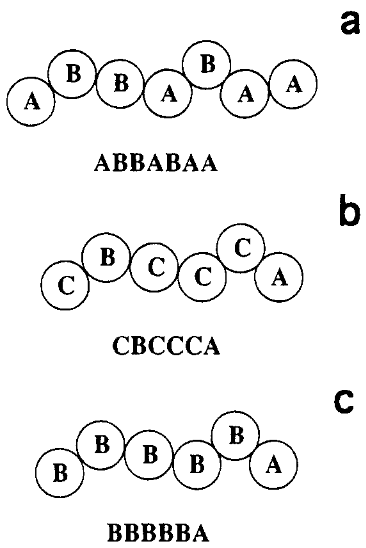

Figure 1. (a) Hard-sphere sequence of a copolymer consisting of segments A and B; (b) hard-sphere sequence of a terpolymer consisting of segments A, B, and C that represent AA, BB, and AB and BA sequences (i.e., diads), respectively, of a copolymer shown in Figure 1a; and (c) hard-sphere sequence of a copolymer obtained by replacing all the segments C in the terpolymer shown in Figure 1b by segments B, i.e., complete screening of segment A by segment B in AB and BA sequences.

given by

$$\sigma_C = \left[\frac{\sigma_A^3 + \sigma_B^3}{2}\right]^{1/3} \tag{36}$$

Representation of a copolymer by a terpolymer, however, is not practical because many sets of intersegmental parameters are required. For example, three sets of intersegmental parameters are required to represent the simplest copolymer mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$. To simplify the problem, we introduce an adjustable parameter φ, which is the fraction of segments C in a terpolymer that represents segments B. Parameter $1 - \varphi$ is the fraction of segments C in a terpolymer that represents segments A. Figure 1c shows the hard-sphere sequence of the copolymer obtained by replacing all segments C in the terpolymer shown in Figure 1b by segments B, i.e., $\varphi = 1$, which corresponds to the complete screening of segment A by segment B in AB and BA sequences (i.e., diads). After replacing segments C by segments A and B, the number of segments of type A and that of type B are given by r''_A and r''_B, respectively:

$$r''_A = r'_A + r'_C(1 - \varphi)(\sigma_C^3/\sigma_A^3) \tag{37}$$

$$r''_B = r'_B + r'_C\varphi(\sigma_C^3/\sigma_B^3) \tag{38}$$

The factors σ_C^3/σ_A^3 and σ_C^3/σ_B^3 in eqs 37 and 38, respectively, are introduced to keep the hard-core volume of a molecule constant. When $\varphi = (\sigma_B^3/\sigma_C^3)/2$, there is no screening effect.

In the presence of a screening effect, the copolymer of type $(A_XB_{1-X})_r$ is assumed to have the total number of segments, r^*, and the number fraction of segment of type A, X^*, given by

$$r^* = r''_A + r''_B \tag{39}$$

$$X^* = r''_A/r \tag{40}$$

where r''_A and r''_B are given by eqs 37 and 38, respectively.

The present model is based on the assumption that when an AB or BA diad is interacting with another diad, the screening effect of segment B on segment A in an AB or BA diad reduces the contact frequency between the segment A in an AB or BA diad and a segment belonging to the other diad. In the perturbation term of eq 1, for a given mixture composition, the contact frequency between a pair of segments depends only on the copolymer composition as given by random mixing of segments. Parameter φ introduced here systematically adjusts the contact frequency between a pair of segments A and B.

Calculation Procedure

Phase Equilibrium Calculation. Details of phase equilibrium calculations are given in ref 5. The theoretical miscibility map at constant temperature computed in this paper gives the boundary between total miscibility and partial miscibility. In the mixture where immiscibility is caused by LSCT behavior, the LCST of a pair of miscible copolymers in the theoretical miscibility map is higher than the temperature of the system. Conversely, the UCST of a pair of miscible copolymers is lower than the temperature of the system in the mixture where immiscibility is caused by UCST behavior. A theoretical miscibility map, therefore, tells us that if the copolymer compositions of a pair of copolymers are in the miscible region, mixtures of these copolymers form a single homogeneous phase in all proportions.

An experimental miscibility map is usually obtained for binary equimass mixtures. The difference between the miscibility map that provides the boundary between total and partial miscibilities and the miscibility map for a fixed mixture composition, however, is small because the phase diagrams of polymer blends are flat near the critical point. As a first approximation, the measured phase separation temperature of an equimass mixture can be taken as the critical temperature of the mixture.

In this paper, all the theoretical calculations were performed for liquids at zero pressure, an excellent approximation when the systems of interest are in the liquid state near atmospheric pressure.

Equation-of-State Parameters. In comparing theory with experiment, the equation-of-state parameters for copolymer mixtures are obtained as follows. Consider component 1, a copolymer of type $(A_XB_{1-X})_{r_1}$. We use the regressed parameters ϵ_A, σ_A, and r/M of a homopolymer consisting of segment A reported in ref 2 as the characteristic parameters of segment A in copolymers; here M is the molecular weight. These parameters were obtained from pure-component pressure–volume–temperature (*PVT*) data.

For monodisperse polymers, the choice of average molecular weight has little effect on the calculation of phase equilibria. For polydisperse systems, however, it is not obvious which average molecular weight to use. The effect of molecular weight distribution of polystyrene on the cloud points of the system poly(vinyl methyl ether)/polystyrene (PVME/PS) was reported by Nishi and Kwei.[19] The system PVME/PS is known to exhibit LCST behavior. These authors simulated the effect of molecular weight distribution of PS on the cloud points of equimass blends by mixing different amounts of monodisperse PS of known molecular weights. Although PVME was polydisperse, Nishi and Kwei showed that, for a given weight-average molecular weight, M_W, of PS, the cloud points in the system PVME/PS containing polydisperse PS agree well with those containing monodisperse PS. Therefore, we use the weight-average molecular weight of polymer to compute the equation-of-state parameters.

When the copolymer composition in weight fraction and the weight-average molecular weight are known, simple stoichiometry gives Ω_A, the total mass of segment A per mole of copolymer; Ω_A is then multiplied by r/M of the homopolymer consisting of segment A to obtasin $r_{1,A}$, the number of effective hard spheres of type A. A similar calculation is performed to obtain $r_{1,B}$, the number of effective hard spheres of type B.

Results and Discussion

Screening Effect on Theoretical Miscibility Map. Within the framework of incompressible Flory–Huggins theory,[15-17] Braun *et al.*[7] have discussed the screening effect on the miscibility map for the mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing two kinds of segments. The systems $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ that exhibit a screening effect are mixtures containing poly(styrene-*co*-methyl methacrylate), poly(styrene-*co*-butyl methacrylate), and poly(*p*-chlorostyrene-*co*-butyl methacrylate) random copolymers.[7] For the system containing poly(styrene-*co*-butyl methacrylate) random copolymers, the theoretical miscibility map computed by the PHSC equation of state and experiment showed semiquantitative agreement without introducing the screening effect.[5]

Braun *et al.*[7] suggested that the screening effect is more apparent in the mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ than in more complicated systems such as mixtures of type $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ and $(A_XB_{1-X})_{r_1}/(C_YD_{1-Y})_{r_2}$ containing three and four kinds of segments, respectively. This suggestion probably follows because in the systems $(A_XB_{1-X})_{r_1}/(C_YB_{1-Y})_{r_2}$ and $(A_XB_{1-X})_{r_1}/(C_YD_{1-Y})_{r_2}$, a variety of miscibility maps can be obtained by simply adjusting the intersegmental parameters. In the system $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, however, the classical Flory–Huggins[15-17] theory predicts only one kind of miscibility map: a pair of copolymers is miscible when the copolymer-composition difference $|X - Y|$ is less than the critical copolymer composition difference $|X - Y|_c$, which is independent of the copolymer compositions X and Y. Therefore, any effect that violates the assumptions of Flory–Huggins theory would cause deviation of observed miscibility maps from those predicted by Flory–Huggins theory.

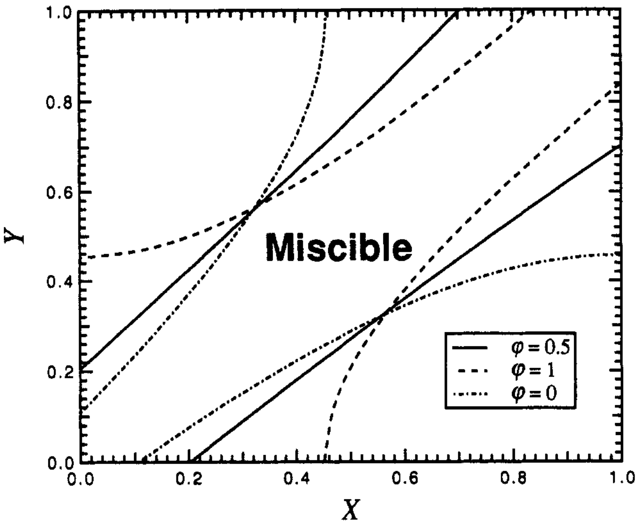

Figure 2. Screening effect on the miscibility map for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$: $r_1 = r_2 = 10\,000$, $\sigma_B/\sigma_A = 1.0$, $\epsilon_B/\epsilon_A = 1.05$, $\kappa_{AB} = -0.003\,45$, $\zeta_{AB} = -0.002$, $p = 0$, $\tilde{T}_A = k_BT/\epsilon_A = 0.7$, $\mathscr{R}_1 = \mathscr{R}_2 = 1$; (—) $\varphi = 0.5$, no screening; (- - -) $\varphi = 1$, complete screening of segment A by segment B in AB and BA diads; (– • –) $\varphi = 0$, complete screening of segment B by segment A in AB and BA diads. Theory predicts that immiscibility is caused by LCST behavior.

Figure 2 shows the screening effect on the theoretical miscibility map at constant temperature for a mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$. If a pair of X and Y are in the miscible region, a pair of copolymers with these compositions form a single homogeneous phase in all proportions. The copolymers in this system are assumed to be truly random copolymers. The numbers of $\alpha-\beta$ hard-sphere sequences, $n_{\alpha\beta}$ (α,β = A,B), are therefore given by eq 12. For a known total number of monomers, r, and number fraction of segments of type A, X, the copolymer of type $(A_XB_{1-X})_r$ is assumed to have the total number of monomers, r^*, and the number fraction of segments of type A, X^*, given by eqs 39 and 40, respectively. Since the hard-sphere diameter of segment A is equal to that of segment B, $\varphi = 0.5$ represents the system where there is no screening effect. On the other hand, $\varphi = 1$ and $\varphi = 0$ correspond to the complete screening of segment A by segment B and that of segment B by segment A, respectively, in AB and BA sequences in a copolymer. Theory predicts the immiscibility is caused by LCST behavior.

In the miscibility map for a mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$, there is always a miscible region near the diagonal line $X = Y$; when $X = Y$, component 1 is identical to component 2 and there is complete miscibility. A pair of copolymers is therefore miscible when the copolymer-composition difference $|X - Y|$ is less than the critical copolymer-composition different $|X - Y|_c$. In the system shown in Figure 2, $|X - Y|_c$ is nearly independent of the copolymer compositions X and Y in the absence of a screening effect (i.e., when $\varphi = 0.5$), in accord with the prediction of Flory–Huggins theory.[15-17] For $\varphi = 1$, the screening effect results in a significantly wider miscible area for small X and Y. Conversely, the miscible area becomes wider at large X and Y for $\varphi = 0$. The screening effect results in strong dependence of $|X - Y|_c$ on the copolymer compositions.

As discussed by Koningsveld and Kleintjens,[20] the dependence of critical copolymer-composition difference $|X - Y|_c$ on the copolymer compositions can also be caused by the difference in the segmental interaction surface areas. Koningsveld and Kleintjens[20] modified the Flory–Huggins theory such that the interaction surface area per segment depends on the type of segment comprising the copolymer. The resulting model is able to predict that $|X - Y|_c$ depends on the copolymer composition. In the modeling calculations shown in ref 20, however, $|X - Y|_c$ is nearly a linear function of copolymer composition. In the miscibility maps with a screening effect shown in Figure 2, $|X - Y|_c$ increases sharply as $X \rightarrow 1$ for $\varphi = 0$ and as $X \rightarrow 0$ for $\varphi = 1$.

A miscibility map similar to that for the system $\varphi = 1$ in Figure 2 was also obtained by Braun *et al.*,[7] who modified the incompressible Flory–Huggins model (which predicts UCST-type phase behavior) by replacing AB and BA sequences by BB sequences. The PHSC equation of state is able to explain the screening effect in

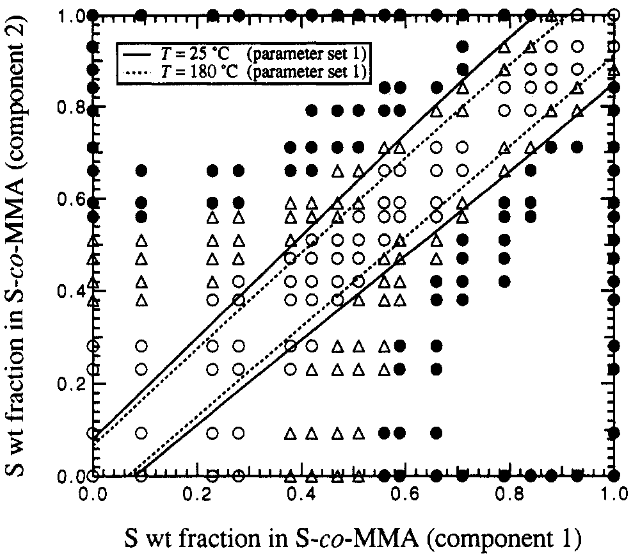

Figure 3. Comparison of theoretical miscibility maps with experiment for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing poly(styrene-*co*-methyl methacrylate) random copolymers ($M_w \cong 150\,000$ g/mol, $M_w/M_n \cong 1.7$): $M_1 = M_2 = 150\,000$; parameter set 1, $\kappa_{S-MMA} = -0.02125$, $\zeta_{S-MMA} = -0.02$. Poly(styrene-*co*-methyl methacrylate) copolymers are denoted as S-*co*-MMA, where S and MMA represent styrene and methyl methacrylate segments, respectively. Theory predicts that immiscibility is caused by LCST behavior. Data are from Braun *et al.*:[7] (○) miscible at 25 and 180 °C, (△) miscible at 25 °C but immiscible at 180 °C, and (●) immiscible at 25 and 180 °C.

Table 1. PHSC Equation-of-State Parameters for Homopolymers[2]

polymer	r/M (mol/g)	σ(Å)	ϵ/k_B (K)
polystyrene	0.011 17	5.534	724.7
	(0.009 602)[a]	(5.854)[a]	(786.2)[a]
poly(methyl methacrylate)	0.014 32	4.850	655.9
	(0.009 988)[a]	(5.545)[a]	(797.6)[a]

[a] This work; $r/M = 1/M^*$, where M^* is the molecular weight of the monomer.

the system where immisicibility is caused by LCST behavior.

Comparison with Experiment. Systems Containing Styrene and Methyl Methacrylate. Figure 3 compares a theoretical miscibility map with experimental data reported by Braun *et al.*[7] for a mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing poly(styrene-*co*-methyl methacrylate) random copolymers ($M_w \cong 150\,000$, $M_w/M_n \cong 1.7$; $M_n \equiv$ number-average molecular weight). Poly(styrene-*co*-methyl methacrylate) random copolymers are denoted as S-*co*-MMA, where S and MMA represent styrene and methyl methacrylate segments, respectively. The PHSC equation-of-state parameters for polystyrene and poly(methyl methacrylate) are given in Table 1. Let segments A and B represent styrene and methyl methacrylate, respectively. In this system, immiscibility is caused by LCST behavior. Open and solid circles are the pairs of copolymers that are miscible and immiscible, respectively, at both 25 and 180 °C. Open triangles denote the pairs of copolymers that are miscible at 25 °C but are immiscible at 180 °C. The miscible area decreases as the temperature rises because a pair of miscible copolymers eventually becomes immiscible as the temperature is raised above the LCST of the mixture. The experimental miscibility map shown in Figure 3 is similar to that shown in Figure 2 with $\varphi = 1$; in this system segment A (styrene) is completely screened by segment B (methyl methacrylate) in AB and BA sequences.

Table 2. Intersegmental Parameters for Figures 3 and 4

binary pair	κ_{AB}	ζ_{AB}
styrene−methyl methacrylate		
parameter set 1	−0.021 25	−0.02
parameter set 2	−0.005 66	−0.004
parameter set 3	−0.056 27	−0.04

The intersegmental parameters for the styrene−methyl methacrylate (S−MMA) pair, parameter set 1, were obtained as follows. We first preset ζ_{S-MMA} to −0.02 and then solve for κ_{S-MMA} by assuming that at 25 °C the boundary between miscible and immiscible regions at $\omega_{1,A} = 1.0$ lies at $\omega_{2,A} = 0.85$, where $\omega_{i,A}$ is the weight fraction of styrene in component i. Intersegmental parameters are given in Table 2. With these parameters, theory predicts that immisicibility is caused by LCST behavior. Agreement between theory and experiment is good in the styrene-rich region of the miscibility map at both 25 and 180 °C. Parameter set 1 therefore may be used as the intersegmental parameters for the S−MMA pair in the systems PVME/(MMA-*co*-S) and (tetramethyl Bisphenol A polycarbonate)/(MMA-*co*-S), where the mixtures exhibit phase separation in the experimentally accessible temperature range when methyl methacrylate content in the MMA-*co*-S copolymer is less than about 35% by weight.

Better agreement between theory and experiment is obtained if the screening effect is considered. For the copolymerization of styrene with methyl methacrylate at 60 °C, the reactivity ratios, eqs 17 and 18, are[7]

$$\mathcal{R}_1 = k_{AA}/k_{AB} = 0.522 \tag{41}$$

$$\mathcal{R}_2 = k_{BB}/k_{BA} = 0.482 \tag{42}$$

where subscripts A and B represent styrene and methyl methacrylate monomers, respectively. Using these reactivity ratios, for known copolymer composition and total number of monomers per molecule, the numbers of $\alpha-\beta$ (α,β = A,B) monomer sequences per molecule of component i, $n_{i,\alpha\beta}$(i = 1,2; α,β = A,B), are computed by eqs 29−32.

To use the monomer sequences calculated from the reactivity ratios as the hard-sphere sequences in the PHSC equation of state, equation-of-state parameters of homopolymers must be obtained by assuming that one monomer is represented by a single sphere in the model. The PHSC equation-of-state parameters ϵ and σ for polystyrene and poly(methyl methacrylate) were regressed from the same *PVT* data used in ref 2 by presetting r/M to $1/M^*$, where M^* is the molecular weight of monomer. The PHSC equation-of-state parameters for polystyrene and poly(methyl methacrylate) obtained in this manner are given in parentheses in Table 1.

Figure 4 compares a theoretical miscibility map (with screening effect) with experiment for a mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing S-*co*-MMA random copolymers.[7] The theoretical miscibility map was calculated by assuming complete screening of the styrene segment by the methyl methacrylate segment in the S−MMA and MMA−S sequences (i.e., $\varphi = 1$). The origin of the screening effect, however, is not obvious. Braun *et al.* speculated that the acetoxyl group of methyl methacrylate segment screens the π electron cloud of the phenyl group in the styrene segment.[7]

In Figure 4, parameter set 2 was obtained by assuming that $\zeta_{S-MMA} = -0.004$ and that at 25 °C the boundary between miscible and immiscible regions at $\omega_{1,A} = 1.0$

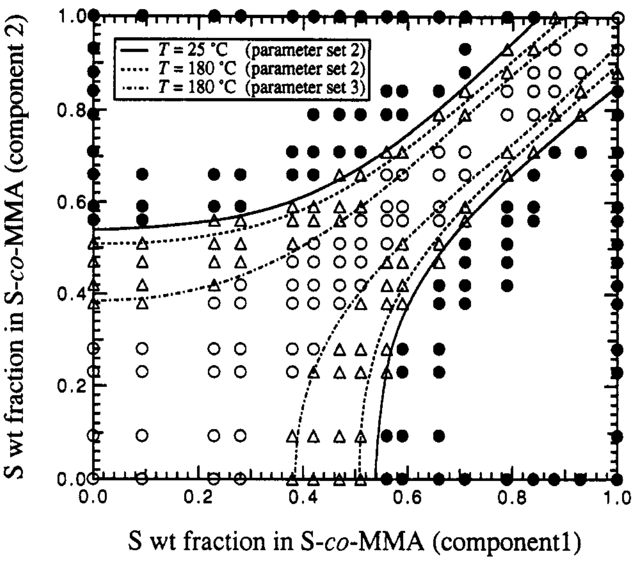

Figure 4. Comparison of theory (with screening effect) with experiment for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing poly(styrene-*co*-methyl methacrylate) random copolymers[7] ($M_1 = M_2 = 150\ 000$): parameter set 2, $\kappa_{\text{S-MMA}} = -0.00566$, $\zeta_{\text{S-MMA}} = -0.004$; parameter set 3, $\kappa_{\text{S-MMA}} = -0.05627$, $\zeta_{\text{S-MMA}} = -0.04$. Poly(styrene-*co*-methyl methacrylate) copolymers are denoted as S-*co*-MMA, where S and MMA represent styrene and methyl methacrylate segments, respectively. Theoretical miscibility maps assume complete screening of the S segment by the MMA segment in the S−MMA and MMA−S sequences. Theory predicts that immiscibility is caused by LCST behavior.

lies at $\omega_{2,A} = 0.85$. Similarly, parameter set 3 was obtained by assuming that $\zeta_{\text{S-MMA}} = -0.04$ and that at 180 °C the boundary between miscible and immiscible regions at $\omega_{1,A} = 1.0$ lies at $\omega_{2,A} = 0.94$. Theory predicts that immiscibility is caused by LCST behavior at both 25 and 180 °C.

Upon introducing the screening effect, theory and experiment show good agreement in the entire copolymer composition range. The temperature dependence of the miscibility map, however, is not predicted by using the same set of intersegmental parameters. It is also not possible to represent the temperature dependence of the miscibility map by letting parameter φ be temperature dependent. One possible implication is that the degree of screening depends on the copolymer composition. As shown in Figure 3, theory and experiment can show good agreement in the styrene-rich region of miscibility map without introducing the screening effect.

To represent the temperature dependence of the miscibility map using the same set of intersegmental parameters, it is necessary to consider diad interactions by replacing a copolymer by a terpolymer as shown in Figure 1. In this method, a copolymer of type $(A_XB_{1-X})_r$ is modeled as a terpolymer consisting of segments A, B, and C that represent AA, BB, and AB and BA sequences (i.e., diads), respectively, of a copolymer. Therefore, in a terpolymer, fractions of segments A and B are equal to those of AA and BB diads, respectively, of a copolymer $(A_XB_{1-X})_r$. Similarly, the fraction of segment C is given by the fraction of AB and BA diads of a copolymer. Diad fractions of a copolymer are computed from eqs 29−32. The diameter of segment C, σ_C, is given by eq 36; the parameter ϵ for segment C is assumed to be given by

$$\epsilon_C = \sqrt{\epsilon_A \epsilon_B} \qquad (43)$$

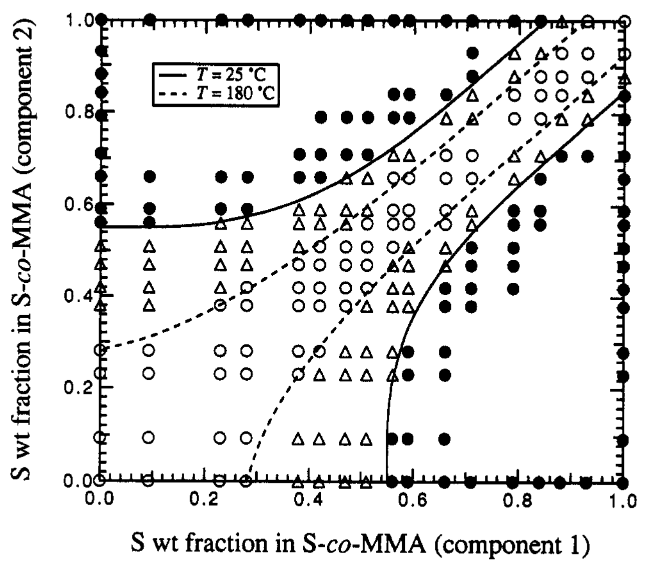

Figure 5. Comparison of theory with experiment for the system shown in Figures 3 and 4. The theoretical miscibility map is calculated by considering diad interactions. S-*co*-MMA copolymer is modeled as a terpolymer consisting of segments A, B, and C that represent SS, MMAMMA, and SMMA and MMAS diads, respectively, of a S-*co*-MMA copolymer. Theory predicts that immiscibility is caused by LCST behavior. Intersegmental parameters are temperature independent; they are given in Table 3.

In this approach, theory requires three sets of intersegmental parameters to represent a mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing two kinds of segments.

Figure 5 compares a theoretical miscibility map with experiment for the system shown in Figures 3 and 4.[7] The theoretical miscibility map was calculated by replacing a copolymer by a terpolymer as discussed above. In a terpolymer representing a S-*co*-MMA copolymer, segments A, B, and C represent SS, MMAMMA, and SMMA and MMAS diads, respectively, of a S-*co*-MMA copolymer.

Three sets of intersegmental parameters are obtained as follows. We first preset the intersegmental parameters between segments A and B and those for segments B and C. Intersegmental parameters between segments A and C are then regressed such that the temperature dependence of the miscibility−immiscibility boundary at $\omega_{1,A} = 1$ is correctly predicted by the model. In the mixture of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ shown in Figure 5, the system at $\omega_{1,A} = 1$ corresponds to the homopolymer/copolymer mixture polystyrene/poly(styrene-*co*-methyl methacrylate).

Intersegmental parameters between segments A and C obtained in this manner are not sensitive to initial guesses for those between segments B and C because the miscibility−immiscibility boundary at $\omega_{1,A} = 1$ lies in the region where copolymers are rich in segment A. In the segment A-rich region of a miscibility map, interactions between segments B and C do not contribute significantly to the phase equilibrium calculation.

After the intersegmental parameters between segments A and C are obtained, those between segments B and C are then regressed such that the temperature dependence of the miscibility−immiscibility boundary at $\omega_{2,A} = 0$ is correctly predicted by the model. The system at $\omega_{2,A} = 0$ corresponds to the homopolymer/copolymer mixtures poly(methyl methacrylate)/poly(styrene-*co*-methyl methacrylate).

In this fitting procedure, agreement between theory and experiment at intermediate copolymer compositions

Table 3. Intersegmental Parameters for Figure 5

diad pair[a]	segment pair	κ	ζ
SS–MMAMMA	A–B	−0.0241	−0.02
SS–SMMA	A–C	−0.00884	−0.008
MMAMMA–SMMA	B–C	−0.00094	−0.0003

[a] S = styrene; MMA = methyl methacrylate.

is determined by initial guesses for the intersegmental parameters between segments A and B. This procedure is appropriate because the numbers of segments A and B in terpolymers that represent AA and BB diads of copolymers, respectively, are highest near the equimolar copolymer composition.

By considering diad interactions, theory and experiment show good agreement at two different temperatures using the same set of intersegmental parameters. Theory is able to represent immiscibility caused by LCST behavior where the miscible area decreases with temperature. Table 3 gives the intersegmental parameters used in Figure 5.

A remaining question is whether the screening effect is observed in mixtures of a S-*co*-MMA random copolymer with another copolymer such as poly(acrylonitrile-*co*-styrene). For copolymer mixtures containing more than three kinds of segments, it is not practical to represent copolymers by terpolymers because many sets of intersegmental parameters are required. In these systems, however, the simple model used in Figures 1–4 is readily employed to examine the screening effect at constant temperature. The screening effect in systems containing three kinds of segments is discussed in the subsequent article using the model presented here.

Conclusions

Reactivity ratios of copolymerization kinets are used to introduce the screening effect into the perturbed hard-sphere-chain equation of state for copolymer systems. The theory with screening effect is able to explain the strong dependence of the critical copolymer composition difference on the copolymer compositions in the system where immiscibility is caused by phase behavior due to a lower critical solution temperature.

For a mixture containing poly(styrene-*co*-methyl methacrylate) random copolymers differing in copolymer compositions, the theory with screening effect and parameter φ shows good agreement with the experimental miscibility map at constant temperature. Although the theory is able to predict immiscibility due to LCST behavior in the system poly(styrene-*co*-methyl methacrylate), the temperature dependence of the miscibility map is not predicted using a temperature-independent set of intersegmental parameters. In this system, it is necessary to consider diad interactions to represent the temperature dependence of the miscibility map. Representation is then achieved using one set of temperature-independent intersegmental parameters.

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