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LIQUID-LIQUID EQUILIBRIA IN BINARY SOLVENT-COPOLYMER SOLUTIONS FROM A PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

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ABSTRACT

The perturbed hard-sphere-chain (PHSC) equation of state for copolymer systems is used to calculate liquid-liquid equilibria for binary solvent/copolymer systems that exhibit simultaneously an upper critical solution temperature (UCST) and a lower critical solution temperature. The PHSC equation of state for copolymer solutions uses those binary parameters that represent liquid-liquid equilibria for the two parent homopolymer solutions. An additional intersegmental parameter is also required to define the interaction energy between a pair of chemically dissimilar segments comprising the copolymer molecule. Theory is compared with experiment for binary copolymer solutions containing poly(styrene-co-α-methylstyrene) random copolymers. Using the same κ_{BC}, the intersegmental parameter between styrene and α-methylstyrene segments, theory and experiment show fair agreement for the copolymer-composition dependence of theta temperatures associated with UCST in cyclohexane, methyl cyclohexane, and decalin. A comparison is also made between κ_{BC} obtained from the copolymer-solution data and that obtained from the coexistence curve of homopolymer blends containing polystyrene and poly(α-methylstyrene). In copolymer solutions, theory requires a κ_{BC} that represents interactions more unfavorable than those in homopolymer blends.

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INTRODUCTION

Copolymers consist of various ratios of two chemically dissimilar comonomers. The comonomer ratio is the copolymer composition. In binary solvent/copolymer systems, solubilities of copolymers in common solvents can be larger than those of the parent homopolymers[1]. The enhancement of a copolymer's solubility occurs when the interaction between comonomers is unfavorable. In that event, the copolymer intramolecular interaction becomes more unfavorable as the copolymer composition rises. Consequently, the solvent-copolymer intermolecular interaction becomes more favorable relative to the copolymer intramolecular interaction[1,2], leading to an enhanced copolymer solubility.

Enhanced solubilities of copolymers in common solvents have been observed for poly(styrene-*co*-α-methylstyrene)[1], poly(styrene-*co*-methyl methacrylate)[3,4], and poly(styrene-*co*-methyl acrylate)[5]. Similar behavior is also observed in the homopolymer/copolymer system poly(methyl methacrylate) / poly(acrylonitrile-*co*-styrene)[6] (PMMA/AN-*co*-S). In systems containing methyl methacrylate, acrylonitrile, and styrene segments, three pairs of parent homopolymers are immiscible. The homopolymer/copolymer system PMMA/AN-*co*-S, however, is miscible and exhibits a lower critical solution temperature (LCST) when the copolymer contains about 9.5 to 35 % acrylonitrile by weight[6].

Evidence for increased solubilities of copolymers is often revealed in the effect of copolymer composition on critical solution temperatures or on theta temperatures. In binary solvent/polymer systems, the theta temperature is defined as the asymptotic critical solution temperature in the limit of infinite polymer molecular weight[7]. In the well-known Flory-Huggins theory[7], the theta temperature is also identified as that temperature where the osmotic second virial coefficient vanishes.

In earlier experimental work on copolymer solutions, theta temperatures were obtained for upper critical solution temperature (UCST) associated with phase separation

2

upon cooling. Polymer solutions, however, also exhibit phase separation at elevated temperature (i.e., LCST behavior) due to the equation-of-state effect. Simultaneous occurrence of an UCST and a LCST is a common phenomenon in many polymer solutions, including copolymer solutions. In the mixture, the equation-of-state effect is caused by the different compressibilities (i.e., densities) of components. To represent simultaneously the UCST and LCST, it is necessary to use equation-of-state theories[2,8-10] instead of dense lattice theories.

Although several equation-of-state theories are available for polymer systems[8-10], it is a challenging task to represent quantitatively liquid-liquid equilibria of polymer solutions using equation-of-state theories. When a polymer solution exhibits phase separation, one of the coexisting phases is dilute in polymer. As discussed many years ago by Flory[7], it is difficult to establish a single theory that can represent both dilute and concentrated polymer solutions. Because of chain connectivity, polymer segments in dilute solutions are localized inside spherical volume elements occupied by isolated polymer molecules. However, typical theories for polymer solutions are based on the mean-field approximation where the polymer-segment density is assumed to be uniform throughout the system at all polymer concentrations.

An equation-of-state theory applicable to copolymer systems is the perturbed hard-sphere-chain (PHSC) equation of state by Song *et al.*[2,11-16]. Because chain connectivity is neglected in the perturbation term, the PHSC equation of state overestimates the number of segment-segment contacts between a pair of polymer molecules in dilute and semidilute polymer solutions[17]. In homopolymer solutions, the PHSC equation of state predicts a LCST that is significantly lower than experiment[17]. Therefore, semiempirical adjustable parameter v was introduced into the perturbation term to represent quantitatively liquid-liquid equilibria of homopolymer solutions[17].

In this work, we use the PHSC equation of state to calculate liquid-liquid equilibria of binary copolymer solutions. First, semiempirical parameter v used in

homopolymer solutions is introduced into the PHSC theory for binary copolymer solutions. Next, theory is compared with experiment for the effect of copolymer composition on theta temperatures of binary solutions containing poly(styrene-*co-α*-methylstyrene) random copolymers[1]. The PHSC equation of state for copolymer solutions requires κ_{BC}, the intersegmental parameter that determines the interaction energy between a pair of unlike segments B and C comprising the copolymer molecule. For a pair of segments styrene and α-methylstyrene, κ_{BC} obtained from the copolymer-solution data is compared with that obtained from the coexistence curve of homopolymer blends containing polystyrene and poly(α-methylstyrene).

EQUATION-OF-STATE FOR BINARY SOLVENT/COPOLYMER SYSTEMS

The PHSC equation of state uses the modified Chiew equation of state for athermal mixtures of hard-sphere chains[11] as the reference state and a van der Waals-type perturbation term[12,13]. The reference equation of state and perturbation term represent repulsive and attractive interactions, respectively. The PHSC equation of state is expressed in terms of the pair radial distribution function at contact prior forming the hard-sphere chain[11]. The equation of state uses parameters that represent attractive and repulsive interactions on a segment basis as given by the Song-Mason method[12]. Details of the PHSC equation of state are given in References 2 and 12 to 17.

Consider a binary solvent/copolymer system where the solvent consists of segments A and the copolymer consists of segments B and C:

$$A_{r_1}/(C_Y B_{1-Y})_{r_2} \tag{1}$$

where r_i is the total number of segments per molecule of component i and Y is the number fraction of segment type C in the copolymer. For mixtures of type $A_{r_1}/(C_Y B_{1-Y})_{r_2}$, the PHSC equation of state is given by[2,16]

4

$$\frac{p}{\rho k_B T} = 1 + \rho \left\{ x_1^2 r_1^2 b_{AA} g_{AA} + 2x_1 x_2 r_1 r_2 [Y b_{AC} g_{AC} + (1-Y) b_{AB} g_{AB}] \right.$$

$$\left. + x_2^2 r_2^2 [Y^2 b_{CC} g_{CC} + 2Y(1-Y) b_{BC} g_{BC} + (1-Y)^2 b_{BB} g_{BB}] \right\}$$

$$- \left\{ x_1(r_1 - 1)(g_{AA} - 1) + x_2(r_2 - 1) [Y^2(g_{CC} - 1) \right.$$

$$\left. + 2Y(1-Y)(g_{BC} - 1) + (1-Y)^2(g_{BB} - 1)] \right\}$$

$$- \frac{\rho}{k_B T} \left(x_1^2 \tilde{a}_{11} + 2x_1 x_2 \tilde{a}_{12} + x_2^2 \tilde{a}_{22} \right) \tag{2}$$

where p is the pressure, $\rho \equiv N/V$ (N is the total number of molecules and V is the volume) is the number density, k_B is the Boltzmann constant, T is the absolute temperature, and x_i is the mole fraction of component i.

In Eq. (2), $g_{\alpha\beta} (\alpha,\beta\text{=A,B,C})$ is the pair radial distribution function at contact prior to bonding and $b_{\alpha\beta}$ is the van der Waals covolume of effective hard spheres that represents the repulsive interaction on a segment basis; subscript $\alpha\beta$ denotes a pair of segments type α and β. The Boublik-Mansoori-Carnahan-Starling expression is used for the pair radial distribution function at contact[2,11,16].

The last term in Eq. (2) is the perturbation term that accounts for attractive interactions. The parameter $\tilde{a}_{ij}$ represents the attractive interaction between a pair of molecules of components i and j. In Eq. (2), the term second to last is the bonding term that accounts for the chain connectivity in the reference equation of state. The bonding term depends on the sequence distribution of segments C and B which is assumed to be that of a truly random copolymer.

Perturbation Term. The PHSC theory expresses $\tilde{a}_{ij}$ in terms of parameter $a_{\alpha\beta}$ $(\alpha,\beta\text{=A,B,C})$ that represents the attractive interaction on a segment basis:

$$\tilde{a}_{11} = r_1^2 a_{AA} \tag{3}$$

$$\tilde{a}_{12} = r_1 r_C a_{AC} + r_1 r_B a_{AB} \tag{4}$$

$$\tilde{a}_{22} = r_C^2 a_{CC} + 2 r_B r_C a_{BC} + r_B^2 a_{BB} \tag{5}$$

where r_C and r_B are the numbers of segments C and B, respectively, per copolymer molecule:

$$r_C = Y r_2, \qquad r_B = (1-Y) r_2 . \tag{6}$$

As discussed in Reference 17, Eqs. (2) to (5) neglect chain connectivity in the perturbation term. The PHSC theory approximates the perturbation term of a hard-sphere-chain system by that of a hard-sphere system obtained by first breaking the bonds between bonded hard spheres and then randomly mixing non-bonded hard spheres. In that event, the segment-number density of a particular segment is uniform throughout the system. For copolymer systems, such an approximation also results in the neglect of sequence distribution in the copolymer molecule.

Parameters a and b. Consider parameters $a_{\alpha\alpha}$ and $b_{\alpha\alpha}$ (α=A,B,C) for pure fluids consisting of segment type α. In the PHSC theory, these parameters are scaled in terms of the minimum of the segmental pair potential ε_α at the center to center distance σ_α:

$$a_{\alpha\alpha} = \frac{2}{3} \pi \sigma_\alpha^3 \varepsilon_\alpha F_a(k_B T / \varepsilon_\alpha) \qquad (\alpha\text{=A,B,C}) \tag{7}$$

$$b_{\alpha\alpha} = \frac{2}{3} \pi \sigma_\alpha^3 F_b(k_B T / \varepsilon_\alpha) \tag{8}$$

where F_a and F_b are universal functions of reduced temperature $k_B T / \varepsilon_\alpha$ as given by the Song-Mason method[12]. The essential roles of universal functions F_a and F_b are to

provide temperature dependences to parameters a and b, respectively. For segments B and C comprising the copolymer, parameters $a_{\alpha\alpha}$ and $b_{\alpha\alpha}$ are equal to those of the homopolymer comprising segment type α.

For a pair of unlike segments α and $\beta(\alpha\neq\beta)$, parameters a and b are given by

$$a_{\alpha\beta} = \frac{2}{3}\pi\sigma_{\alpha\beta}^3\varepsilon_{\alpha\beta}\sqrt{F_a(k_BT/\varepsilon_\alpha)F_a(k_BT/\varepsilon_\beta)} \qquad (\alpha\neq\beta) \qquad (9)$$

$$b_{\alpha\beta} = \frac{1}{8}\left(b_{\alpha\alpha}^{1/3} + b_{\beta\beta}^{1/3}\right)^3 \qquad (10)$$

$$\sigma_{\alpha\beta} = \frac{1}{2}\left(\sigma_\alpha + \sigma_\beta\right) \qquad (11)$$

$$\varepsilon_{\alpha\beta} = \left(1 - \kappa_{\alpha\beta}\right)\sqrt{\varepsilon_\alpha\varepsilon_\beta} \qquad (12)$$

where $\kappa_{\alpha\beta}$ is an adjustable intersegmental parameter. Equation (10) follows the additivity of effective hard-sphere diameters of unlike segments.

This work uses a simplified version of the universal functions F_a and F_b[14,15,17]. These functions were determined from configurational thermodynamic properties of methane and argon[12]; they are given by[14,15,17]

$$F_a(k_BT/\varepsilon_\alpha) = 1.8681\exp[-0.0619(k_BT/\varepsilon_\alpha)] + 0.6715\exp\left[-1.7317(k_BT/\varepsilon_\alpha)^{3/2}\right] \qquad (13)$$

$$F_b(k_BT/\varepsilon_\alpha) = 0.7303\exp\left[-0.1649(k_BT/\varepsilon_\alpha)^{1/2}\right] + (1 - 0.7303)\exp\left[-2.3973(k_BT/\varepsilon_\alpha)^{3/2}\right]. \qquad (14)$$

Table I gives the PHSC equation-of-state parameters for solvents and homopolymers.

PHASE EQUILIBRIUM CALCULATION

To perform phase equilibrium calculations, expressions for the critical points of mixtures and chemical potentials are required; they are given in References 2 and 16. For a fixed temperature, the coexistence curve is calculated by equating the pressure and the chemical potentials of components in the coexisting phases. For solvent/polymer systems, the pressure of the mixture is computed by equating the chemical potential of a solvent molecule in the vapor phase to that in the liquid phase; the vapor phase is pure solvent. For polymer/polymer systems, calculations are made at zero pressure, an excellent approximation for polymer blends at pressures near atmospheric.

RESULTS AND DISCUSSION

Introduction of Parameter v. The critical solution temperature of a polymer solution lies in a dilute or semidilute polymer concentration range. As discussed in Reference 17, the PHSC equation of state overestimates the equation-of-state effect in dilute and semidilute polymer solutions. The equation-of-state effect provides an unfavorable entropic effect responsible for lower-critical-solution-temperature (LCST) behavior at elevated temperature. In polymer solutions, the equation-of-state effect is caused by the difference between the segment density of expanded solvent and that of relatively dense polymer. The PHSC equation of state predicts an LCST significantly lower than experiment[17]. Theory requires a semiempirical adjustable parameter to represent quantitatively liquid-liquid equilibria of homopolymer solutions.[17]

Consider a binary solvent/homopolymer system denoted by A_{r_1}/B_{r_2}. For this system, Eqs. (4) and (5) are

$$\tilde{a}_{12} = r_1 r_2 a_{AB} \tag{15}$$

$$\tilde{a}_{22} = r_2^2 a_{BB} \ . \tag{16}$$

In polymer solutions, overestimation of the equation-of-state effect is caused by the overestimated contribution of $\tilde{a}_{22}$ in the perturbation term[17]. Equation-of-state parameters for homopolymers are regressed from the volumetric properties of pure polymer melts where polymers interpenetrate significantly. The PHSC theory assumes that the number of segment-segment contacts between a pair of polymers in a pure polymer melt is equal to that in a polymer solution. Because of the excluded volume effect, however, polymer molecules in dilute and semidilute solutions cannot interpenetrate significantly[17-19]. Consequently, in dilute and semidilute polymer solutions, fewer polymer segments of a polymer molecule may be interacting with those of another polymer molecule. The extent of interpenetration could depend on solvent quality and mixture composition.

In Reference 17, we proposed to introduce semiempirical parameter ν_B (≤ 1) into the perturbation term by replacing r_2 by $\nu_B r_2$ in parameters $\tilde{a}_{12}$ and $\tilde{a}_{22}$. As a first approximation, ν_B was found to be constant, independent of the mixture composition, polymer molecular weight, and temperature[17]. The primary role of parameter ν_B is to decrease parameter $\tilde{a}_{22}$ that represents the attractive interaction between a pair of polymer molecules. Essentially, parameter ν_B decreases the density of polymer in solutions and hence decreases the difference between the density of solvent and that of polymer. Because the equation-of-state effect is caused by the different densities of components, parameter ν_B effectively reduces the unfavorable equation-of-state effect which causes LCST behavior at elevated temperature.

In a binary homopolymer solution which shows a LCST only, the theoretical LCST is raised to the experimental LCST by adjusting ν_B alone; κ_{AB} is set to zero. For systems exhibiting simultaneously an UCST and a LCST, both ν_B and κ_{AB} are necessary. Essentially, parameters ν_B and κ_{AB} determine LCST and UCST, respectively.

In copolymer systems of type $A_{r_1}/(C_Y B_{1-Y})_{r_2}$, we also require parameter ν_C associated with the solvent/homopolymer system A_{r_1}/C_{r_2}. For copolymer systems, we

propose to introduce parameters v_B and v_C by replacing r_B and r_C by $v_B r_B$ and $v_C r_C$, respectively, in $\tilde{a}_{12}$ and $\tilde{a}_{22}$:

$$\tilde{a}_{12} = r_1(v_C r_C)a_{AC} + r_1(v_B r_B)a_{AB} \tag{17}$$

$$\tilde{a}_{22} = (v_C r_C)^2 a_{CC} + 2(v_B r_B)(v_C r_C)a_{BC} + (v_B r_B)^2 a_{BB} . \tag{18}$$

Parameters v_B and v_C are readily introduced into the previously given equation of state and Helmholtz energy of the mixture[2,12-16]; we replace $a_{\alpha\beta}$ by $v_\beta a_{\alpha\beta}$ $(\alpha=A,B,C; \beta=B,C)$. The reference equation of state remains unchanged.

Comparison with Experiment. We compare theory with experiment for the copolymer-composition dependence of theta temperatures of binary solvent/copolymer systems containing poly(styrene-co-α-methylstyrene) (PSMS) random copolymers. For PSMS solutions, Goldwasser and Williams[1] obtained the copolymer-composition dependence of theta temperatures associated with UCST in cyclohexane, methyl cyclohexane, and decalin. PSMS solutions, however, also exhibit LCST behavior at elevated temperature. We choose the systems studied by Goldwasser and Williams[1] because the solvents used by these authors are nonpolar which do not exhibit specific interactions such as hydrogen bonding. Other copolymer systems reported in the literature contain polar solvents[4,5]. In principle, specific interactions can be incorporated into the PHSC equation of state[20]. In that event, however, theory requires additional parameters.

Goldwasser and Williams[1] obtained theta temperatures from Shultz-Flory plots[21] using UCSTs determined by cloud-point measurements. The Shultz-Flory plot is based on the equation[21]

$$\frac{1}{T_c} = \frac{1}{\Theta}\left\{1 + \frac{1}{\psi}\left(\frac{1}{r^{1/2}} + \frac{1}{2r}\right)\right\} \tag{19}$$

where T_c is the critical solution temperature, Θ is the theta temperature, ψ is Flory's entropy parameter, and r is the ratio of the molar volume of polymer to that of solvent. The Shultz-Flory plot gives the reciprocal of T_c as a function of $(1/\sqrt{r} + 1/2r)$. From Eq. (19), the theta temperature is the critical temperature in the limit of infinite polymer molecular weight when $r \to \infty$. In systems exhibiting both an UCST and a LCST, there are two theta temperatures; Θ_{UCST}, the theta temperature associated with UCST and Θ_{LCST}, the theta temperature associated with LCST.

We consider the system solvent/PSMS denoted by $A_{r_1}/(C_Y B_{1-Y})_{r_2}$ where segments C and B represent styrene and α-methylstyrene comonomers, respectively. The parent homopolymer solutions are polystyrene (PS) and poly(α-methylstyrene) (PMS) solutions; they are denoted by A_{r_1}/C_{r_2} and A_{r_1}/B_{r_2}, respectively. These systems exhibit simultaneously an UCST and a LCST. To apply PHSC theory to the system solvent/PSMS, we first need a set of parameters κ_{AC} and v_C that represent PS solutions and another set of parameters κ_{AB} and v_B for PMS solutions. We also require parameter κ_{BC} that determines the interaction energy between styrene and α-methylstyrene segments comprising the copolymer molecule.

Polystyrene and Poly(α-methylstyrene) Solutions. To obtain parameters κ and v from parent homopolymer solutions, we need a complete phase diagram containing both the LCST and UCST branches of a phase diagram. In Reference 17, parameters κ_{AC} and v_C for PS solutions were determined for several solvents including cyclohexane, methyl cyclohexane, and *trans*-decalin. For these solvents, parameter $v_C (=0.771)$ was essentially constant. Relatively few experimental phase diagrams are available for PMS solutions. Recently, Pfohl *et al.*[22] obtained cloud-point curves for several PMS solutions and those for solutions containing the PSMS random copolymer having 20 mol% styrene in the copolymer.

We obtain parameter v_B for PMS from the theta temperatures of the system cyclohexane/PMS; $\Theta_{UCST}=32.2$ and $\Theta_{LCST}\approx186.7$ °C. In this system, Θ_{LCST} was obtained from Shultz-Flory plots[21], Eq. (19), using LCSTs reported by Pfohl et al.[22]; Θ_{UCST} is taken from Reference 1. In Eq. (19), r was calculated using the molar volumes of polymer and solvent calculated from measured densities. Pfohl et al.[22] report only the critical temperatures for two molecular weights of PMS. Therefore, Θ_{LCST} for the system cyclohexane/PMS used here is approximate.

Because experimental pressure-volume-temperature data are not available for poly(α-methylstyrene), equation-of-state parameters for poly(o-methylstyrene) are used as those for poly(α-methylstyrene). The calculated critical solution temperature for the polymer of effectively infinite molecular weight is assumed to be the theta temperature. We obtain $v_B=0.778$ and $\kappa_{AB}=0.02034$ by using the theta temperatures of the system cyclohexane/poly(α-methylstyrene).

Poly(styrene-*co*-α-methylstyrene) Solutions. Figures 1 and 2 show the effect of copolymer-composition on theta temperatures associated with UCST and that associated with LCST, respectively, for systems methyl cyclohexane/PSMS, cyclohexane/PSMS, and decalin/PSMS[1,22,23]. The equation-of-state parameters for *trans*-decalin are used as those for decalin. Theoretical curves show critical solution temperatures for the polymer with effectively infinite molecular weight.

Parameters $v_B=0.778$ and $v_C=0.771$ are independent of the solvent. For systems not studied in Reference 17, intersegmental parameters κ_{AB} and κ_{AC} were adjusted to match the theta temperatures associated with UCST of parent homopolymer solutions. In decalin, the predicted LCSTs lie above 350 °C.

Parameter κ_{BC} determines the interaction energy between styrene and α-methylstyrene in the copolymer; κ_{BC} was determined such that theory agrees with experiment for the system cyclohexane/PMSM. Although theory slightly underestimates

12

the UCST in the system methyl cyclohexane/PSMS, theory and experiment show fair agreement using the same intersegmental parameter κ_{BC}.

The measured critical temperatures of a copolymer solution deviate from the calculated critical temperatures obtained by linearly interpolating between the measured critical temperatures of two parent homopolymer solutions. In the system PSMS/cyclohexane, the PSMS copolymer is more soluble than the parent PS and PMS homopolymers because of the intramolecular repulsion effect in the copolymer molecule. If the interaction between segments comprising the copolymer molecule is unfavorable, the copolymer intramolecular interaction becomes more unfavorable as the copolymer composition varies from $Y=0$ or 1. Consequently, the solvent-copolymer intermolecular interaction becomes more favorable relative to the copolymer intramolecular interaction, leading to an enhanced solubility of copolymers. In that event, the UCST and LCST of a copolymer can be lower and higher, respectively, than the calculated critical temperatures obtained by linearly interpolating between the measured critical temperatures of parent homopolymer solutions.

In the PHSC theory, the intramolecular repulsion effect is explained in terms of the magnitude of parameter $\tilde{a}_{22}$ given by Eq. (18). Parameter $\tilde{a}_{22}$ represents the attractive interaction between a pair of copolymer molecules. The intramolecular repulsion effect results from a decrease in $\tilde{a}_{22}$ due to an unfavorable interaction between segments B and C represented by the intersegmental parameter κ_{BC} in Eq. (12).

Consider a hypothetical copolymer system $A_{r_1}/(C_Y B_{1-Y})_{r_2}$ where $a_{BB}=a_{CC}$, $a_{AB}=a_{AC}$, and $v_B=v_C$. The solvent molecule cannot distinguish between segments B and C. When κ_{BC} is zero, a_{BC} is given by the geometric mean of a_{BB} and a_{CC} and parameter $\tilde{a}_{22}$ is independent of copolymer composition. In that event, the critical temperature is also independent of the copolymer composition. If κ_{BC} is positive, a_{BC} is smaller than the geometric mean of a_{BB} and a_{CC} and hence parameter $\tilde{a}_{22}$ of a copolymer becomes smaller than that of a parent homopolymer. The copolymer intramolecular interaction becomes

energetically more unfavorable as the copolymer composition rises up to an equimolar copolymer composition because a smaller $\tilde{a}_{22}$ represents energetically more unfavorable interactions between a pair of copolymer molecules.

The intramolecular repulsion effect may also have the following entropic origin. LCST behavior in polymer solutions is due to the entropic equation-of-state effect caused by the different densities of components. At elevated temperature, solvent is more expanded than relatively dense polymer. In equation-of-state theories for polymer solutions, a decrease in $\tilde{a}_{22}$ also results in a decrease in the density of polymer. Therefore, a decrease in $\tilde{a}_{22}$ may also raise the LCST because of the decreased equation-of-state effect which is entropically unfavorable. The energetic and entropic effects dominate at low and high temperatures, respectively.

Although experimental data are not available for the copolymer-composition dependence of Θ_{LCST}, theoretical curves shown in Figures 1 and 2 indicate that the intramolecular repulsion effect is more apparent in the copolymer-composition dependence of Θ_{UCST} than that of Θ_{LCST}. This observation agrees with the measurements by Pfohl et al.[22] who obtained cloud-point curves associated with both UCST and LCST for solutions containing the PSMS random copolymer having 20 mol% styrene in the copolymer. The noticeable intramolecular repulsion effect in Θ_{UCST} probably follows because the energetic nature of the intramolecular repulsion effect is dominant in the systems shown in Figures 1 and 2.

Intersegmental Parameter Between Styrene and α-Methylstyrene. Finally, we discuss the magnitude of κ_{BC}, the intersegmental parameter between styrene and α-methylstyrene segments. An interesting question is whether κ_{BC}=0.00337 used in PSMS solutions is comparable to that obtained from the homopolymer blend containing poly(α-methylstyrene) (PMS) and polystyrene (PS). The system PMS/PS exhibits UCST behavior; cloud-point curves are reported by Lin and Roe[24].

Figure 3 compares theoretical coexistence curves with experiment for the system PMS/PS. To represent the dependence of UCST on polymer molecular weight, additional parameter ζ_{BC} was introduced to relax slightly the additivity of hard-sphere diameters of unlike segments:

$$b_{BC}^{1/3} = \frac{\left(b_{BB}^{1/3} + b_{CC}^{1/3}\right)}{2}\left(1-\zeta_{BC}\right) \; . \tag{20}$$

Intersegmental parameters, κ_{BC}=0.0001881 and ζ_{BC}=0.0000807, were obtained such that theory is able to represent the dependence of UCST on polymer molecular weight. In the system PMS/PS, the calculated UCST is sensitive to intersegmental parameters. Theory predicts that the systems shown in Figure 3 exhibit only UCST behavior at temperatures below ~1600°C.

The intersegmental parameter κ_{BC}=0.00337 used to represent the copolymer-solution data is too large for systems shown in Figure 3. If we use κ_{BC}=0.00337 and ζ_{BC}=0, theory predicts that systems shown in Figure 3 are completely immiscible in the liquid region. Conversely, κ_{BC}=0.0001881 is too small to represent the effect of copolymer composition on theta temperatures shown in Figures 1 and 2. If κ_{BC}=0.0001881 and ζ_{BC}=0.0000807 are used in the system cyclohexane/PSMS, the calculated Θ_{UCST} almost lies on the straight line between the theta temperatures of the two parent homopolymer solutions. Theory for copolymer solutions requires a κ_{BC} that represents interactions more unfavorable than those for the system PMS/PS.

One possible explanation for this observation is the effect of sequence distribution. In the present model, the effect of sequence distribution is not included in the perturbation term. When a pair of copolymer molecules interacts with each other, Eq. (5) assumes that the contact frequency between a pair of particular segments depends only on the copolymer composition; this assumption is reasonable only for truly random copolymers.

15

Depending on reactivity ratios, the sequence distribution of real copolymers deviates from that of truly random copolymers. Kotaka *et al.*[25] showed that in the system solvent/poly(styrene-*co*-methyl methacrylate), the intramolecular repulsion effect decreases in the order alternating, random, and tri-block copolymers. The theta temperature of a tri-block copolymer lies on the straight line between the critical temperatures of the parent-homopolymer systems. It is also possible that the magnitude of the intramolecular repulsion effect depends on the sequence distribution in the PSMS copolymer.

For a given segment type, the present model also assumes that the shortest hard-sphere sequence is unity in the copolymer, even though comonomers are represented by more than one hard sphere. Strictly speaking, the shortest hard-sphere sequence of a particular segment in the copolymer should be the number of hard spheres comprising the relevant comonomer.

It may also be an oversimplification to assume that parameters v_C and v_B are independent of the copolymer composition. Because the interaction between styrene and α-methylstyrene is unfavorable, when a pair of PSMS copolymer molecules interacts, the number of interacting segments may be smaller than that of hypothetical PSMS copolymers which do not exhibit the intramolecular repulsion effect. In the present model, this effect can be represented by allowing parameters v_C and v_B to be slightly copolymer-composition dependent in $\tilde{a}_{22}$, decreasing with the copolymer composition up to approximately equimolar copolymer composition. A decrease in v_C and v_B results in a decrease in $\tilde{a}_{22}$ which leads to an enhancement in the intramolecular repulsion effect.

CONCLUSIONS

The perturbed hard-sphere-chain (PHSC) equation of state was used to calculate liquid-liquid equilibria of binary solvent/copolymer solutions denoted by the system $A_{r_1}/(C_Y B_{1-Y})_{r_2}$. The previously proposed semiempirical parameter v^{17} for homopolymer

solutions was introduced into the PHSC equation of state for binary copolymer solutions. Theory requires two pairs of parameters κ_{AC} and v_C and κ_{AB} and v_B that represent liquid-liquid equilibria of the parent homopolymer solutions A_{r_1}/C_{r_2} and A_{r_1}/B_{r_2}, respectively. Theory also requires parameter κ_{BC} that determines the interaction energy between segments B and C comprising the copolymer molecule.

Comparison with experiment is made for binary copolymer solutions containing poly(styrene-co-α-methylstyrene) random copolymers. The intersegmental parameter between styrene and α-methylstyrene segments (κ_{BC}) was obtained from the copolymer-solution data; κ_{BC} is independent of solvent. Theory and experiment show fair agreement for the effect of copolymer composition on theta temperatures associated with upper critical solution temperature in cyclohexane, methyl cyclohexane, and decalin.

Intersegmental parameter κ_{BC} was also obtained from the coexistence curve of homopolymer blends containing polystyrene and poly(α-methylstyrene). Compared to κ_{BC} obtained from the homopolymer blend, theory requires κ_{BC} that represents more unfavorable interactions between styrene and α-methylstyrene segments in copolymer solutions.

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TABLE I. PHSC Equation-of-State Parameters[15,17]

Solvent and homopolymer		σ (Å)	ε/k_B (K)
cyclohexane	$r = 2.723$	4.215	286.7
methyl cyclohexane	$r = 2.968$	4.336	283.7
decalin [a]	$r = 3.160$	4.657	333.8
polystyrene	$r/M = 0.03834$	3.899	385.4
poly(α-methylstyrene) [b]	$r/M = 0.03925$	3.893	393.5

M = molecular weight (g/mol); [a] parameters for *trans*-decalin; [b] parameters for poly(*o*-methylstyrene).

FIGURE CAPTIONS

Figure 1. Copolymer-composition dependence of theta temperature associated with UCST for systems methyl cyclohexane/PSMS[1] (κ_{AB}=0.02034, κ_{AC}=0.0216), cyclohexane/PSMS (κ_{AB}=0.02276, κ_{AC}=0.02456), and decalin/PS (κ_{AB}=0.02413, κ_{AC}=0.02575). In all systems v_B=0.778, v_C=0.771, and κ_{BC}=0.00337. The calculated critical solution temperature for the polymer of effectively infinite molecular weight is assumed to be the theta temperature.

Figure 2. Copolymer-composition dependence of theta temperature associated with LCST for systems methyl cyclohexane/PSMS[22] and cyclohexane/PSMS[23]. In decalin, the predicted LCSTs lie above 350 °C. Intersegmental parameters are the same as those used in Figure 1. The calculated critical solution temperature for the polymer of effectively infinite molecular weight is assumed to be the theta temperature.

Figure 3. Coexistence curves for the system poly(α-methylstyrene)/polystyrene (PMS/PS)[2 4] : κ_{BC}=0.0001881, ζ_{BC}=0.0000807. M_w=weight-average molecular weight.
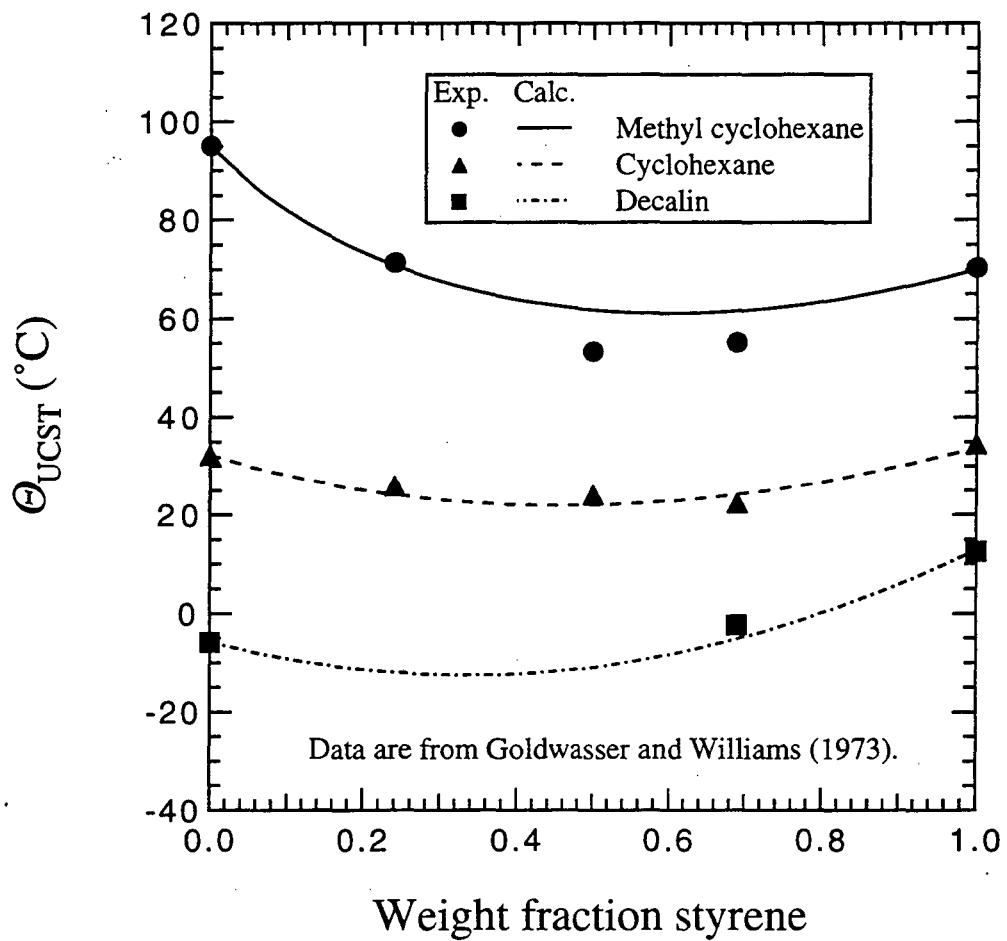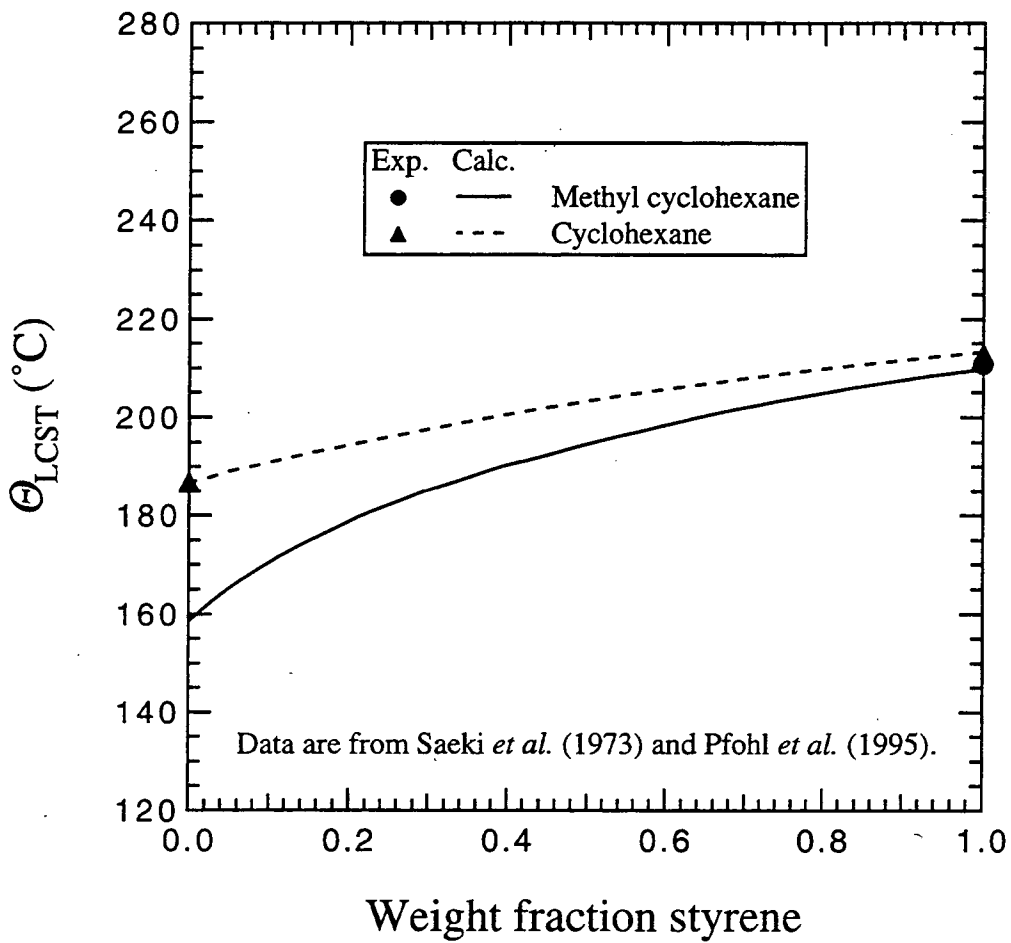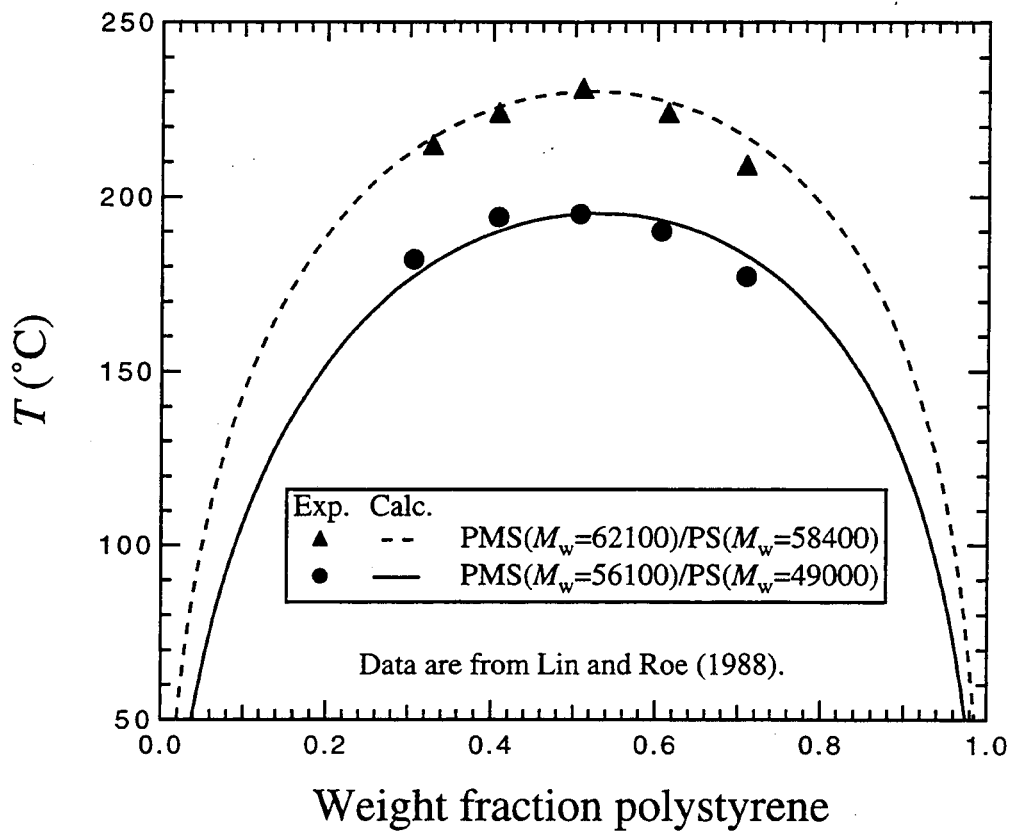
Figure 1

Figure 2

Figure 3

Figure 3

Legend (within plot):

Exp.	Calc.	
▲	- -	PMS(M_w=62100)/PS(M_w=58400)
●	——	PMS(M_w=56100)/PS(M_w=49000)

Data are from Lin and Roe (1988).

Axes: T (°C) versus Weight fraction polystyrene