LBL-35398
UC-401
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

CHEMICAL SCIENCES DIVISION

Submitted to Macromolecules

Liquid-Liquid Equilibria for Copolymer Mixtures From a Perturbed Hard-Sphere-Chain Equation of State

T. Hino, Y. Song, and J.M. Prausnitz

March 1994

REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library.
LBL-35398
Copy 1

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-35398
UC-401

Liquid-Liquid Equilibria for Copolymer Mixtures From a Perturbed Hard-Sphere-Chain Equation of State

Toshiaki Hino, Yuhua Song and John M. Prausnitz

Department of Chemical Engineering
University of California
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720, U.S.A.

March 1994

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098. Additional support was provided by E. I. du Pont de Nemours & Company (Philadelphia, PA) and by Koninklijke Shell (Amsterdam, The Netherlands).

Submitted to *Macromolecules*: March 24, 1994

LIQUID-LIQUID EQUILIBRIA FOR COPOLYMER MIXTURES FROM A PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

Toshiaki Hino, Yuhua Song, and John M. Prausnitz

Department of Chemical Engineering
University of California, Berkeley
and
Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720

ABSTRACT

A perturbed hard-sphere-chain (PHSC) equation of state for real copolymer mixtures is based on a modified form of Chiew's equation of state for athermal mixtures of heteronuclear hard-sphere chains. The PHSC equation of state includes a van-der-Waals perturbation whose parameters are related to the intermolecular potential as suggested by Song and Mason. In the present model, sequence distribution in a polymer is introduced only into the hard-sphere-chain reference state; attractive forces are averaged, independent of sequence distribution. Theoretical coexistence curves and miscibility maps were computed for binary random copolymer mixtures containing two or three kinds of segments. The PHSC equation of state can predict simultaneous occurrence of a lower critical solution temperature and an upper critical solution temperature in the temperature-composition phase diagram of high-molecular-weight copolymer blends. Theoretical and experimental coexistence curves and miscibility maps show good agreement for systems containing two kinds of segments.

(Keywords: copolymer blend; equation-of-state; lower critical solution temperature; phase equilibria;)

Correspondence concerning this paper should be addressed to J.M. Prausnitz.

INTRODUCTION

Equation-of-state theories are useful for describing the phase equilibria of solutions and blends containing copolymers. A brief review of equations of state for copolymer systems is given by Wohlfarth[1]. Equations of state based on free-volume or lattice-fluid models have an advantage over classical incompressible lattice theories such as the Flory-Huggins theory and Guggenheim's quasichemical approximation[2] because they can predict a lower critical solution temperature (LCST) at elevated temperature as well as an upper critical solution temperature (UCST). LCST behavior is a common phenomenon in polymer blends including those that copolymers. In addition, an equation of state is also able to describe the effect of pressure on phase behavior.

An equation of state applicable to polymer systems is the perturbed hard-sphere-chain (PHSC) equation recently developed by Song *et al.*[3-6]. These authors[3] first presented a hard-sphere-chain (HSC) equation of state for athermal homonuclear and heteronuclear HSC mixtures by generalizing Chiew's equation of state for mixtures of hard-sphere chains[7] through the Carnahan-Starling radial distribution function for hard-sphere mixtures at contact. Compared to Chiew's original equation of state, the new equation of state for athermal systems was expressed more succinctly. For real polymer fluids, Song *et al.*[4,5] introduced a van der Waals perturbation and the Song-Mason method to relate equation-of-state parameters to the intermolecular potential. The Song-Mason method calculates the effective van der Waals covolume, b, (i.e., second virial coefficient of hard spheres) and the attractive energy parameter, a, in terms of the well depth of the pair potential, ε, and the distance of separation at minimum potential energy, σ. In this method, the temperature dependences of parameters a and b are given by two known universal functions of a reduced temperature.

For a homopolymer, the PHSC equation of state requires three parameters: number of effective hard spheres per molecule, r; segmental diameter, σ; and non-bonded segment pair-interaction energy, ε. These parameters were regressed from available

volumetric and vapor-pressure data for a variety of normal fluids and several homopolymers; they are tabulated in Reference 3. For a homopolymer, one of the regressed characteristic quantities is r/M, where M is the molecular weight of polymer.

For mixtures, no mixing rules are required for the hard-chain-of-spheres contribution. For the perturbation term, a standard one-fluid theory was used[5,6]. For several binary mixtures including homopolymer solutions and homopolymer/homopolymer blends[6], calculated liquid-liquid coexistence curves are in good agreement with experiment.

In this paper we present an extension of the PHSC equation of state for copolymer mixtures. Theoretical coexistence curves and miscibility maps are computed for binary random copolymer mixtures containing two and three kinds of segments. These mixtures are denoted as $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ and $(A_X B_{1-X})_{r_1}/(C_Y B_{1-Y})_{r_2}$ where r_i is the number of hard spheres per molecule of component i; and X and Y are segment number fractions for segments A, B and C, in components 1 and 2, respectively.

Theoretical coexistence curves and miscibility maps are compared with experiment for mixtures of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing poly(styrene-*co*-butadiene), poly(butyl methacrylate-*co*-methyl methacrylate), and poly(styrene-*co*-methyl methacrylate) random copolymers.

THEORY

Equation of State for Pure Copolymers. Using the modified Chiew equation of state as the reference state[3], the PHSC equation of state for pure heteronuclear polymer molecules consisting of r effective hard spheres is

$$\frac{p}{\rho k_B T} = 1 + \rho \sum_{k'=1}^{r} \sum_{l'=1}^{r} b_{k'l'} g_{k'l'} - \sum_{k'=1}^{r-1} \left[g_{k',k'+1} - 1 \right] - \frac{\rho}{k_B T} \sum_{k'=1}^{r} \sum_{l'=1}^{r} a_{k'l'} \qquad (1)$$

where p is the pressure, $\rho=N/V$ (N is the number of molecules and V is the volume) is the number density, k_B is the Boltzmann constant, T is the absolute temperature, and subscripts k' and l' denote the k'-th and l'-th segments, respectively, of hard-sphere chains. In Eq. (1) $a_{k'l'}$ is a parameter which reflects the strength of attractive forces between two hard spheres; $b_{k'l'}$ represents the second virial coefficient of hard spheres; and $g_{k'l'}$ is the pair radial distribution function of hard spheres when k'-th and l'-th segments are at contact. These parameters and the pair distribution function are temperature dependent, as shown later. Eq. (1) is for hard-sphere chains consisting of an arbitrary number of chemically different segments. The segments in the chain need <u>not</u> have the same size.

We consider copolymers consisting of two types of segments α and β:

$$\left(\alpha_X \beta_{1-X}\right)_r \tag{2}$$

where X is the number fraction of segment of type α. In a polymer chain, the number of segments of type α per molecule is given by r_α and that of type β is given by r_β:

$$r_\alpha = rX \tag{3}$$

$$r_\beta = r(1-X)\ . \tag{4}$$

In the following equations, the type of segment-segment interaction is specified by subscripts k and l; these subscripts appear in parameters and pair distribution functions. For copolymers Eq. (1) reduces to

$$\frac{p}{\rho k_B T} = 1 + \rho\left(r_\alpha r_\alpha b_{\alpha\alpha} g_{\alpha\alpha} + r_\alpha r_\beta b_{\alpha\beta} g_{\alpha\beta} + r_\beta r_\alpha b_{\beta\alpha} g_{\beta\alpha} + r_\beta r_\beta b_{\beta\beta} g_{\beta\beta}\right)$$
$$-\left(n_{\alpha\alpha}[g_{\alpha\alpha} - 1] + n_{\alpha\beta}[g_{\alpha\beta} - 1] + n_{\beta\alpha}[g_{\beta\alpha} - 1] + n_{\beta\beta}[g_{\beta\beta} - 1]\right)$$
$$-\frac{\rho}{k_B T}\left(r_\alpha r_\alpha a_\alpha + r_\alpha r_\beta a_{\alpha\beta} + r_\beta r_\alpha a_{\beta\alpha} + r_\beta r_\beta a_\beta\right) \tag{5}$$

where n_{kl} ($k,l=\alpha,\beta$) is the number of k-l sequences (i.e., bonding pairs) per molecule in hard-sphere chains.

Parameters a_{kl} and b_{kl} and the radial distribution function, g_{kl}, are given by

$$a_k = \frac{2}{3}\pi\sigma_k^3 \varepsilon_k F_a(\tilde{T}_k) \tag{6}$$

$$a_{\alpha\beta} = a_{\beta\alpha} = \frac{2}{3}\pi\sigma_{\alpha\beta}^3 \varepsilon_{\alpha\beta}\sqrt{F_a(\tilde{T}_\alpha)F_a(\tilde{T}_\beta)} \tag{7}$$

$$b_k = \frac{2}{3}\pi\sigma_k^3 F_b(\tilde{T}_k) \tag{8}$$

$$b_{\alpha\beta} = b_{\beta\alpha} = \frac{1}{8}\left(b_\alpha^{1/3} + b_\beta^{1/3}\right)^3 \tag{9}$$

$$g_{kl} = g_{lk} = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{kl}}{(1-\eta)^2} + \frac{1}{2}\frac{\xi_{kl}^2}{(1-\eta)^3} \tag{10}$$

where k and l ($k,l=\alpha,\beta$) specify the type of segments and η is the packing fraction given by

$$\eta = \frac{\rho}{4}\left(r_\alpha b_\alpha + r_\beta b_\beta\right) \tag{11}$$

and

$$\xi_{kl} = \xi_{lk} = \frac{\rho}{4}\left(\frac{b_k b_l}{b_{kl}}\right)^{1/3}\left(r_\alpha b_\alpha^{2/3} + r_\beta b_\beta^{2/3}\right) . \tag{12}$$

In Eqs. (6), (7), and (8), σ_k ($k,l=\alpha,\beta$) and $\sigma_{\alpha\beta}$ are the separation distances between similar and dissimilar segments, respectively, at the minimum potential energies ε_k ($k,l=\alpha,\beta$) and $\varepsilon_{\alpha\beta}$, respectively, in the segment-segment pair potential. Eq. (9) assumes additivity of effective hard-sphere diameters of unlike segments. Eqs. (10) and (12) are the results of a generalization of the radial distribution function at contact from the Carnahan-Starling equation to copolymer systems; derivation of these equations are given in Reference 3.

In Eqs. (6), (7), and (8), F_a and F_b are known universal functions in terms of reduced temperature defined as[4]

$$\tilde{T}_k = \frac{k_B T}{\varepsilon_k s(r)} \tag{13}$$

where $s(r)$ is a scaling parameter. The universal functions are obtained from volumetric and vapor-pressure data for argon and for methane as indicated previously[4]. They are

$$F_a(\tilde{T}_k) = 0.7170 + 1.9003\exp\left(-0.5152\tilde{T}_k\right) \tag{14}$$

$$F_b(\tilde{T}_k) = 0.5849\exp\left(-0.4772\tilde{T}_k\right) + (1-0.5849\left[1-\exp\left(-1.0669\tilde{T}_k^{-1/4}\right)\right] . \tag{15}$$

The scaling parameter $s(r)$ in the reduced temperature, Eq. (13), arises from the scaling of F_a and F_b from single-sphere systems to systems containing polymer molecules. This parameter was originally introduced for homonuclear hard-sphere chains (i.e., homopolymers)[4] consisting of r tangent spheres. Although copolymers can be made of hard spheres of different sizes and interaction energies, $s(r)$ for copolymers is assumed

to be a unique function of the total number of hard spheres per molecule. The function $s(r)$ is given in Reference 4.

The effect of sequence distribution is not incorporated into the perturbation term in Eqs. (1) and (5). In principle, the effect of sequence distribution can be introduced by expanding the perturbation term by the fraction of particular sequences (e.g., dyads and triads) in place of segment fraction[8]. Such a method, however, requires additional interaction energy parameters.

Finally, in this paper we use the following combining rules to obtain parameters $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ in Eq. (7):

$$\sigma_{\alpha\beta} = \frac{1}{2}\left(\sigma_\alpha + \sigma_\beta\right) \tag{16}$$

$$\varepsilon_{\alpha\beta} = \sqrt{\varepsilon_\alpha \varepsilon_\beta}\left(1-\kappa_{\alpha\beta}\right) \tag{17}$$

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

Equation of State for Copolymer Mixtures. Eq. (1) is readily extended to mixtures of heteronuclear polymer molecules. The PHSC equation of state for mixtures of heteronuclear polymer molecules is

$$\begin{aligned}\frac{p}{\rho k_B T} &= 1 + \rho \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j \left[\sum_{k'=1}^{r_i}\sum_{l'=1}^{r_j} b_{ij,k'l'} g_{ij,k'l'}\right] \\ &\quad - \sum_{i=1}^{m} x_i \sum_{k'=1}^{r_i-1}\left[g_{ii,k',k'+1} - 1\right] - \frac{\rho}{k_B T}\sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j \left[\sum_{k'=1}^{r_i}\sum_{l'=1}^{r_j} a_{ij,k'l'}\right]\end{aligned} \tag{18}$$

where m is the number of components and x_i is the mole fraction of component i. The number of effective hard spheres per molecule of component i is designated by r_i. In Eq. (18), subscripts k' and l' denote the k'-th and l'-th segments, respectively, of hard-

sphere chains. The physical significances of parameters $a_{ij,k'l'}$ and $b_{ij,k'l'}$ and pair distribution function $g_{ij,k'l'}$ for mixtures are the same as those for pure fluids.

We consider first binary mixtures of copolymers consisting of two types of segments α and β:

$$\left(\alpha_X\beta_{1-X}\right)_{r_1}/\left(\alpha_Y\beta_{1-Y}\right)_{r_2}\ . \tag{19}$$

The number of segments of type α, $r_{1,\alpha}$, and that of β, $r_{1,\beta}$, of component 1 are given by r_1X and $r_1(1-X)$, respectively. For binary mixtures of copolymers, Eq. (18) is

$$\begin{aligned}\frac{p}{\rho k_B T} = {} & 1+\rho\sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j\Big[r_{i,\alpha}r_{j,\alpha}b_{ij,\alpha\alpha}g_{ij,\alpha\alpha} + r_{i,\alpha}r_{j,\beta}b_{ij,\alpha\beta}g_{ij,\alpha\beta} \\ & \qquad + r_{i,\beta}r_{j,\alpha}b_{ij,\beta\alpha}g_{ij,\beta\alpha} + r_{i,\beta}r_{j,\beta}b_{ij,\beta\beta}g_{ij,\beta\beta}\Big] \\ & -\sum_{i=1}^{2} x_i\Big[n_{i,\alpha\alpha}\left(g_{ii,\alpha\alpha}-1\right)+n_{i,\alpha\beta}\left(g_{ii,\alpha\beta}-1\right)+n_{i,\beta\alpha}\left(g_{ii,\beta\alpha}-1\right)+n_{i,\beta\beta}\left(g_{ii,\beta\beta}-1\right)\Big] \\ & -\frac{\rho}{k_B T}\sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j\Big[r_{i,\alpha}r_{j,\alpha}a_{ij,\alpha\alpha} + r_{i,\alpha}r_{j,\beta}a_{ij,\alpha\beta} + r_{i,\beta}r_{j,\alpha}a_{ij,\beta\alpha} + r_{i,\beta}r_{j,\beta}a_{ij,\beta\beta}\Big]\end{aligned} \tag{20}$$

where $n_{i,kl}$ (i=1,2; k,l=α,β) is the number of k-l sequences per molecule in component i. In the following equations, indices k and l are used to specify the type of segment. With a substitution of appropriate segments into segments α and β, Eq. (20) is applicable to mixtures of type $\left(A_XB_{1-X}\right)_{r_1}/\left(A_YB_{1-Y}\right)_{r_2}$, $\left(A_XB_{1-X}\right)_{r_1}/\left(C_YB_{1-Y}\right)_{r_2}$, and $\left(A_XB_{1-X}\right)_{r_1}/\left(C_YD_{1-Y}\right)_{r_2}$. For example, for mixtures of type $\left(A_XB_{1-X}\right)_{r_1}/\left(C_YB_{1-Y}\right)_{r_2}$ we replace segments α and β of component 1 by segments A and B, respectively. Similarly, we replace segments α and β of component 2 by segments C and B, respectively.

In this type of mixture, parameters $a_{ij,kl}$ and $b_{ij,kl}$ and the radial distribution function $g_{ij,kl}$ are given by

$$a_{ii,kk} = \frac{2}{3}\pi\sigma_{i,k}^{3}\,\varepsilon_{i,k}F_{\mathrm{a}}\left(\widetilde{T}_{i,k}\right) \tag{21}$$

$$a_{ij,kl} = a_{ji,lk} = \frac{2}{3}\pi\sigma_{ij,kl}^{3}\,\varepsilon_{ij,kl}\sqrt{F_{\mathrm{a}}\left(\widetilde{T}_{i,k}\right)F_{\mathrm{a}}\left(\widetilde{T}_{j,l}\right)} \tag{22}$$

$$b_{ii,kk} = b_{i,k} = \frac{2}{3}\pi\sigma_{i,k}^{3}F_{\mathrm{b}}\left(\widetilde{T}_{i,k}\right) \tag{23}$$

$$b_{ij,kl} = b_{ji,lk} = \frac{1}{8}\left(b_{i,k}^{1/3} + b_{j,l}^{1/3}\right)^{3} \tag{24}$$

$$g_{ij,kl} = g_{ji,lk} = \frac{1}{1-\eta} + \frac{3}{2}\frac{\xi_{ij,kl}}{(1-\eta)^{2}} + \frac{1}{2}\frac{\xi_{ij,kl}^{2}}{(1-\eta)^{3}} \tag{25}$$

where η is the packing fraction given by

$$\eta = \frac{\rho}{4}\sum_{i=1}^{2} x_i\left(r_{i,\alpha}b_{i,\alpha} + r_{i,\beta}b_{i,\beta}\right) \tag{26}$$

and

$$\xi_{ij,kl} = \xi_{ji,lk} = \frac{\rho}{4}\left[\frac{b_{i,k}b_{j,l}}{b_{ij,kl}}\right]^{1/3}\sum_{i=1}^{2} x_i\left(r_{i,\alpha}b_{i,\alpha}^{2/3} + r_{i,\beta}b_{i,\beta}^{2/3}\right) \tag{27}$$

$$\widetilde{T}_{i,k} = \frac{k_{\mathrm{B}}T}{\varepsilon_{i,k}s(r_i)}\ . \tag{28}$$

In Eqs. (21) to (28), subscripts i and j (i,j=1,2) and k and l (k,l=α,β) specify the component and type of segment, respectively. The scaling parameter, $s(r_i)$, in Eq. (28) is assumed to be a unique function of the total number of hard spheres of component i per molecule.

We use combining rules similar to Eqs. (16) and (17) to define $\sigma_{ij,kl}$ and $\varepsilon_{ij,kl}$, respectively:

$$\sigma_{ij,kl} = \sigma_{ji,lk} = \frac{1}{2}(\sigma_{i,k} + \sigma_{j,l}) \tag{29}$$

$$\varepsilon_{ij,kl} = \varepsilon_{ji,lk} = \sqrt{\varepsilon_{i,k}\varepsilon_{j,l}}(1-\kappa_{ij,kl}) \tag{30}$$

where $\kappa_{ij,kl}$ is an adjustable intersegmental parameter whenever $k \neq l$ and

$$\sigma_{ii,kk} = \sigma_{i,k} \tag{31}$$

$$\varepsilon_{ii,kk} = \varepsilon_{i,k} \quad . \tag{32}$$

Critical Condition and Coexistence Curve. The critical points and coexistence curves of mixtures can be found from the Helmholtz energy of the mixture, $A(T,x_i,\rho)$, which should not be confused with segment type A. The Helmholtz energy of the mixture is calculated from Eq. (18); it is[9]

$$\begin{aligned}\frac{A}{Nk_BT} &= \sum_{i=1}^{m} x_i \frac{A_i^{\circ}}{Nk_BT} + \int_0^{\rho}\left(\frac{p}{\rho k_BT} - 1\right)\frac{d\rho}{\rho} + \sum_{i=1}^{m} x_i \ln(x_i \rho k_BT) \\ &= \sum_{i=1}^{m} x_i \frac{A_i^{\circ}}{Nk_BT} + \rho \sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j \left[\sum_{k'=1}^{r_i}\sum_{l'=1}^{r_j} b_{ij,k'l'} W_{ij,k'l'}\right] - \sum_{i=1}^{m} x_i \sum_{k'=1}^{r_i-1} Q_{ii,k',k'+1} \\ &\quad - \frac{\rho}{k_BT}\sum_{i=1}^{m}\sum_{j=1}^{m} x_i x_j \left[\sum_{k'=1}^{r_i}\sum_{l'=1}^{r_j} a_{ij,k'l'}\right] + \sum_{i=1}^{m} x_i \ln(x_i \rho k_BT)\end{aligned} \tag{33}$$

where A_i° is the Helmholtz energy of component i in the reference state and

$$W_{ij,k'l'} = \frac{1}{\rho}\int_0^{\rho} g_{ij,k'l'}\,\mathrm{d}\rho \tag{34}$$

$$Q_{ii,k',k'+1} = \int_0^{\rho} \left[g_{ii,k',k'+1} - 1\right]\frac{\mathrm{d}\rho}{\rho}\ . \tag{35}$$

The reference state is taken to be the pure ideal gas at unit pressure and at the temperature of the mixture containing the same number of molecules as the total number of molecules in the mixture.

For binary mixtures, the critical conditions are given by

$$\rho^2\left(\frac{\partial^2 A}{\partial x^2}\right)_{T,\rho}\left(\frac{\partial p}{\partial \rho}\right)_{T,x} - \left(\frac{\partial p}{\partial x}\right)^2_{T,\rho} = 0 \tag{36}$$

$$\begin{aligned}\rho^3\left(\frac{\partial^3 A}{\partial x^3}\right)_{T,\rho}\left(\frac{\partial p}{\partial \rho}\right)^3_{T,x} - 3\rho\left(\frac{\partial p}{\partial x}\right)_{T,\rho}\left(\frac{\partial^2 p}{\partial x^2}\right)_{T,\rho}\left(\frac{\partial p}{\partial \rho}\right)^2_{T,x} \\ + 3\rho\left(\frac{\partial p}{\partial x}\right)^2_{T,\rho}\left(\frac{\partial^2 p}{\partial x \partial \rho}\right)_{T}\left(\frac{\partial p}{\partial \rho}\right)_{T,x} - \left[2\left(\frac{\partial p}{\partial \rho}\right)_{T,x} + \rho\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,x}\right]\left(\frac{\partial p}{\partial x}\right)^3_{T,\rho} = 0\end{aligned} \tag{37}$$

where x is the mole fraction of component 1 or 2.

The chemical potential per molecule of component i, μ_i, is found from Eq. (33):

$$\mu_i = \left(\frac{\partial A}{\partial N_i}\right)_{T,\rho,N_{j\neq i}} \tag{38}$$

where N_i is the number of molecules of component i. The expression for the chemical potential is given in Appendix I. For a fixed temperature, the coexistence curve is calculated by equating the pressure and chemical potentials of coexisting phases:

$$p'(T,x',\rho') = p''(T,x'',\rho'') \tag{39}$$

$$\mu_1'(T,x',\rho') = \mu_1''(T,x'',\rho'') \tag{40}$$

$$\mu_2'(T,x',\rho') = \mu_2''(T,x'',\rho'') \tag{41}$$

where superscripts $'$ and $''$ denote the coexisting phases.

RESULTS AND DISCUSSION

Theoretical Coexistence Curves and Miscibility Maps. We first consider random copolymer mixtures of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing two kinds of segments. For these systems the characteristic parameters in Eqs. (29) to (32) are:

$$\sigma_{i,\alpha} = \sigma_A,\ \sigma_{i,\beta} = \sigma_B,\ \varepsilon_{i,\alpha} = \varepsilon_A,\ \varepsilon_{i,\beta} = \varepsilon_B$$
$$\varepsilon_{ij,\alpha\beta} = \varepsilon_{ij,\beta\alpha} = \varepsilon_{AB}\ ,\ \kappa_{ij,\alpha\beta} = \kappa_{ij,\beta\alpha} = \kappa_{AB} \quad (i,j=1,2) \tag{42}$$

where

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}(1-\kappa_{AB})\ . \tag{43}$$

In addition, for random copolymers the number of k-l sequences (i.e., bonding pairs) of component 1, $n_{1,kl}$ (k,l=A,B) , may be calculated from a statistical average as

$$n_{1,AA} = X^2(r_1-1),\ n_{1,AB} = n_{1,BA} = X(1-X)(r_1-1),\ n_{1,BB} = (1-X)^2(r_1-1)\ . \tag{44}$$

Similar expressions for $n_{2,kl}$ are obtained by replacing X and subscript 1 by Y and 2, respectively, in the above equation. Here we consider only mixtures of random copolymers.

Figure 1 shows theoretical coexistence curves for mixtures of random copolymers of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ ($r_1 = r_2 = 10000$) with different copolymer compositions X and Y. Since the total number of hard spheres per molecule is the same for both components, the only difference between components 1 and 2 is the copolymer composition. In this system, the miscibility of the mixture is expected to be enhanced as the difference in the copolymer compositions, |X–Y|, decreases. When X=Y, there is complete miscibility because, in that event, components 1 and 2 are identical.

The PHSC equation of state can produce both a lower critical solution temperature (LCST) and an upper critical solution temperature (UCST) in the temperature-composition phase diagram of high-molecular-weight copolymer blends. Figure 1 shows that the miscible temperature range (i.e., temperatures between LCST and UCST) increases as the difference in copolymer compositions declines.

Figure 2 shows theoretical coexistence curves of mixtures of random copolymers of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ ($r_1 = r_2 = 10000$, X=0.8, Y=0.3) with different values of intersegmental parameter κ_{AB}. Calculated coexistence curves are very sensitive to κ_{AB}. When the theory is applied to real systems, this parameter must be obtained by comparing the theoretical prediction with experiment.

Figure 3 shows miscibility maps of mixtures of random copolymers of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ at four reduced temperatures, $\tilde{T}_A = k_BT/\varepsilon_A$. 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 phase diagram of the system shown in Figure 3 is similar to that shown in Figures 1 and 2, exhibiting both a LCST and an UCST. Therefore, the mixture of copolymers is completely miscible if the temperature of interest is between LCST and UCST. At temperatures in Figure 3a, immiscibility is caused by

LCST behavior and the miscible area decreases as the temperature rises; however, at temperatures in Figure 3b, immiscibility is caused by UCST behavior and the miscible area increases as the temperature rises.

Next, we consider mixtures of random copolymers of type $(A_X B_{1-X})_{r_1}/(C_Y B_{1-Y})_{r_2}$ containing three kinds of segments. The characteristic parameters for these systems are:

$$\sigma_{1,\alpha} = \sigma_A,\ \sigma_{i,\beta} = \sigma_B,\ \sigma_{2,\alpha} = \sigma_C,\ \varepsilon_{1,\alpha} = \varepsilon_A,\ \varepsilon_{i,\beta} = \varepsilon_{12,\beta\beta} = \varepsilon_B,\ \varepsilon_{2,\alpha} = \varepsilon_C$$
$$\varepsilon_{11,\alpha\beta} = \varepsilon_{12,\alpha\beta} = \varepsilon_{AB},\ \varepsilon_{12,\alpha\alpha} = \varepsilon_{AC},\ \varepsilon_{12,\beta\alpha} = \varepsilon_{22,\beta\alpha} = \varepsilon_{BC}$$
$$\kappa_{11,\alpha\beta} = \kappa_{12,\alpha\beta} = \kappa_{AB},\ \kappa_{12,\alpha\alpha} = \kappa_{AC},\ \kappa_{12,\beta\alpha} = \kappa_{22,\beta\alpha} = \kappa_{BC} \quad (i,j=1,2) \tag{45}$$

where

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}(1-\kappa_{AB}),\ \varepsilon_{AC} = \sqrt{\varepsilon_A \varepsilon_C}(1-\kappa_{AC}),\ \varepsilon_{BC} = \sqrt{\varepsilon_B \varepsilon_C}(1-\kappa_{BC})\ . \tag{46}$$

An important system of this type is the mixture $A_{r_1}/(C_Y B_{1-Y})_{r_2}$ which corresponds to copolymer-solvent solutions and to homopolymer/copolymer blends. In these systems the interesting question is how the miscibility of copolymer in solvents or homopolymers varies with the copolymer composition. Figure 4a shows coexistence curves of three binary systems of type A_1/B_{500}, A_1/C_{500}, and B_{20}/C_{20}. The segment fraction of component 2 is defined as $x_2 r_2/(x_1 r_1 + x_2 r_2)$ where x_i and r_i are the mole fraction and the number of hard spheres per molecule of component i, respectively. The systems A_1/B_{500} and A_1/C_{500} represent homopolymer-solvent solutions which exhibit both a LCST and an UCST. For simplicity, let these two systems be identical. The system B_{20}/C_{20} is a homopolymer blend which is essentially immiscible in the temperature range shown in Figure 4a.

Copolymer solutions of type $A_1/(C_Y B_{1-Y})_{500}$ also exhibit both a LCST and an UCST. Figure 4b shows the copolymer composition dependence of reduced LCST and

UCST, $k_B T_c/\varepsilon_A$; parameters are the same as those used in Figure 4a. The miscible temperature range increases as the copolymer composition rises, i.e., the solubility of homopolymer B_{500} is enhanced by making a copolymer with segments of type C which has unfavorable interaction with segments of type B.

Similar results can be obtained for the homopolymer/copolymer blend of type $A_{r_1}/(C_Y B_{1-Y})_{r_2}$. Figure 5a shows the coexistence curves of three binary systems of type A_{10000}/B_{10000}, A_{10000}/C_{10000}, and B_{1000}/C_{1000}. Systems A_{10000}/B_{10000} and A_{10000}/C_{10000} represent homopolymer blends which exhibit both a LCST and an UCST. For simplicity, these two systems are assumed to be identical. The system B_{1000}/C_{1000} is a homopolymer blend which is essentially immiscible. The homopolymer/copolymer blend of type $A_{10000}/(C_Y B_{1-Y})_{10000}$ also exhibits both a LCST and an UCST. Figure 5b shows the copolymer composition dependence of LCST and UCST. The miscible temperature range increases as the copolymer composition rises.

The enhanced solubility of copolymer can be explained as follows. Since the parameters are chosen such that the interactions between segments B and C are unfavorable, the presence of segment C among segment B in copolymers gives interactions that are less favorable between the copolymers than those between homopolymers consisting of segment B only. Therefore, interactions between copolymer and solvent relative to those between copolymers become more favorable, resulting in increased solubility of copolymer in solvent A or homopolymer consisting of segments of type A. These results imply that a copolymer and a homopolymer can be miscible even though the corresponding three binary mixtures of homopolymers are immiscible[10].

Figure 6a shows the miscibility map for mixtures of random copolymers of type $(A_X B_{1-X})_{r_1}/(C_Y B_{1-Y})_{r_2}$ at three reduced temperatures, $\tilde{T}_A = k_B T/\varepsilon_A$. The theoretical coexistence curves of two pairs of copolymers, X=0.1; Y=0.56 and X=0.4; Y=0.1, are also shown in Figure 6b. While for small values of Y the miscible area monotonically decreases, for large values of Y the miscible area first increases and then decreases as $\tilde{T}_A$

rises from 1.0 to 1.4. This behavior occurs because immiscibility is caused by LCST behavior for small values of Y at $\tilde{T}_A$ above 1.0. On the other hand, immiscibility is caused by UCST behavior for large values of Y at $\tilde{T}_A$=1.0. If a pair of copolymers are immiscible due to UCST behavior, the mixture becomes miscible as the temperature starts to exceed the UCST of the mixture. As the temperature rises further, however, the mixture eventually becomes immiscible because of the presence of a LCST at elevated temperature.

Comparison with experiment. In comparing the theory with experiment, theoretical calculations were performed at the zero pressure limit, an excellent approximation if the experimental data are at atmospheric pressure. The equation-of-state parameters for copolymer mixtures are obtained as follows. Consider component 1, a copolymer of type $(A_X B_{1-X})_{r_1}$. We use the regressed parameters ε_A, σ_A, and r/M of homopolymer consisting of segment A reported in Reference 3 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 data. When the copolymer composition in weight fraction and the number 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 homopolymer consisting of segment A to obtain the number of effective hard spheres of type A, $r_{1,A}$. A similar calculation is performed to obtain $r_{1,B}$ the number of effective hard spheres of type B.

When the miscibility map at constant chain volume, v_1^*, is reported as a function of the volume fraction of segment A, $\phi_{1,A}$, we assume that these parameters are related to the equation-of-state parameters by

$$r_{1,A}=\frac{\phi_{1,A} v_1^*}{1/6\pi\sigma_{1,A}^3} \quad . \tag{47}$$

Eq. (47) assumes that the measured chain volume is equal to the hard-core volume of hard-sphere chains. A similar equation for $r_{1,B}$ is obtained by replacing subscript A by B in Eq. (47). The total number of effective hard spheres per molecule, r_1, is therefore given by $r_{1,A} + r_{1,B}$. The number fraction of segment A, X, is then computed as $X = r_{1,A}/r_1$.

In addition to the intersegmental parameter κ_{AB}, for the mixture of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ we introduce an additional adjustable intersegmental parameter ζ_{AB} such that

$$b_{ij,AB}^{1/3} = \frac{\left(b_{i,A}^{1/3} + b_{j,B}^{1/3}\right)}{2}\left(1-\zeta_{AB}\right) \quad (i,j=1,2) \tag{48}$$

ζ_{AB} therefore relaxes the additivity of effective hard-sphere diameters of unlike segments. When the experimental coexistence curve is available, these parameters can be obtained from the critical point of homopolymer blends of type A_{r_1}/B_{r_2}.

Eq. (48) is different from the combining rule used in Reference 6. In the present paper we use Eq. (48) because, when the molecular-weight dependence of the critical temperature is compared with experiment, the combining rule given by Eq. (48) gives better agreement with experiment.

We first compare theory with experiment for systems containing butadiene and styrene segments. Several experimental cloud-point curves of these systems are reported by Roe and Zin[11] and Park and Roe[12]. Tables I and II give characterizations of the polymer samples used by these authors and the PHSC equation-of-state parameters of polystyrene and polybutadiene homopolymers.

Intersegmental parameters, κ_{AB} and ζ_{AB}, are obtained from the observed critical point of the (PBD-PS1) system[12]. The experimental critical point, however, is very difficult to determine. In this paper we obtain two sets of intersegmental parameters by assuming two different critical points. We show calculated results based on each set.

Figure 7a shows a comparison of theoretical coexistence curves with experiment for (PBD-PS1) system[12]. Two sets of intersegmental parameters obtained from the critical point are given in Table III. Parameter sets 1 and 2 are obtained by assuming that the critical polystyrene weight fractions are 0.59 and 0.585, respectively. In both calculations the critical temperature is assumed to be 122°C. The theoretical curve with parameter set 2 is slightly wider than that with parameter set 2. The width of the coexistence curve, however, is narrower than that from experiment. Next, we predict the coexistence curves of other systems containing styrene and butadiene segments, including random copolymers, using the binary parameters obtained above.

Figure 7b compares predicted coexistence curves with experiment for the systems (PBD-PS2) and (PBD-PS3)[11]. The critical temperatures predicted by the theory with parameter set 1 agree well with experiment. The critical temperatures predicted by the theory with parameter set 2, however, are slightly lower than the experimental critical temperatures.

Figures 8a and 8b compare predicted coexistence curves with experiment for the systems (PS4-R50/50) and (PS2-R25/75), respectively[11]. In these systems one component is a random copolymer. In both systems the theoretical coexistence curves with parameter set 2 gives slightly better agreement with experiment than those with parameter set 1.

Figure 9 compares theoretical miscibility maps at two temperatures with experimental data by Braun *et al.*[13] for a mixture of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing poly(butyl methacrylate-*co*-methyl methacrylate) random copolymers. Braun *et al.* carried out experiments at constant chain volume v_1^* of 130 $(\mathrm{nm})^3$. We assume that the chain volume is equal to the hard-core volume of hard-sphere chains, that is,

$$v_1^* = r_{1,A}\frac{\pi\sigma_{1,A}^3}{6} + r_{1,B}\frac{\pi\sigma_{1,B}^3}{6} \tag{49}$$

where subscripts A and B denote the butyl methacrylate and methyl methacrylate segments, respectively. For a given volume fraction of segment A, $\phi_{1,A}$, the number of segments A per molecule, $r_{1,A}$, is calculated by Eq. (47). Eq. (49) then gives the number of segments of type B per molecule, $r_{1,B}$.

The intersegmental parameters were obtained as follows. We first assume a reasonable value of ζ_{AB} (for example ζ_{AB}=1.000), and then compute κ_{AB} assuming that at 25°C the boundary between miscible and immiscible regions at $\phi_{1,A}$=1.0 lies at $\phi_{2,A}$=0.74. The best fit was obtained with ζ_{AB}=1.001. Table III gives the values of intersegmental parameters. The theory predicts that the immiscibility in this system is caused by LCST behavior. Also shown in Figure 9 is the miscibility map at 180°C. The theoretical miscibility map was computed using parameters obtained at 25°C. Although the choice of ζ_{AB} is somewhat arbitrary, the agreement of predicted miscibility map with experiment at 180°C is good.

Classical incompressible lattice theory such as the Flory-Huggins theory[14] predicts that for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ a pair of copolymers is miscible if the copolymer composition difference $|X-Y|$ is smaller than a critical value $|X-Y|_c$ which is independent of the copolymer compositions. The miscibility of the system shown in Figure 9 follows the prediction of Flory-Huggins theory. The temperature dependence of miscibility maps, however, cannot be explained by the Flory-Huggins theory which can predict an UCST only. The Flory-Huggins theory predicts that the miscible area increases as the temperature rises. Equation-of-state theory is necessary to explain the immiscibility caused by LCST behavior[15-18].

Figure 10 compares theoretical miscibility maps with experiment obtained by Braun *et al.*[13] for mixtures of type $(A_XB_{1-X})_{r_1}/(A_YB_{1-Y})_{r_2}$ containing poly(styrene-*co*-butyl methacrylate) random copolymers. The average chain volume v_1^* is reported to be 230 $(nm)^3$. We first assume a value of ζ_{AB} and then solve for κ_{AB} assuming that at 25°C the boundary between miscible and immiscible regions at $\phi_{1,A}$=1.0 lies at $\phi_{2,A}$=0.70; here

subscripts A and B denote styrene and butyl methacrylate segments, respectively. The best fit was obtained with ζ_{AB}=1.002. Table III gives intersegmental parameters. These parameters are used to predict the miscibility map at 180°C. The theory predicts that immiscibility is caused by LCST behavior. The miscible area therefore decreases as the temperature rises.

In the system shown in Figure 10, the critical composition difference $|X-Y|_c$ strongly depends on the copolymer compositions. Although the theory can qualitatively describe the dependence of critical composition difference on copolymer compositions and temperature, agreement with experiment is not as good as that for the system shown in Figure 9. Better agreement would be obtained by considering the dyad interactions as proposed by Braun *et al.*[13]. The effect of dyad interactions can be introduced into the equation of state by expanding the perturbation term by dyad fraction. In this model the interaction energy between segments *A* belonging to different *AA* dyads is assumed to be different from the interaction energy between segment *A* in an *AA* dyad and segment *A* of an *AB* dyad. The physical interpretation of this assumption is that the presence of segment *B* in *AB* dyads produces a screening effect on the interaction of segment *A* of *AB* dyads with segment *A* of *AA* dyads.

CONCLUSIONS

A perturbed hard-sphere-chain (PHSC) equation of state for copolymer systems is presented. PHSC uses the modified Chiew equation of state for athermal mixtures of heteronuclear hard-sphere chains by Song *et al.* and a van der Waals perturbation. The Song-Mason method relates equation-of-state parameters to the segment-segment intermolecular potential. The PHSC equation of state can explain immiscibility due to lower critical solution temperature behavior in binary polymer blends containing copolymers. Theoretical coexistence curves and miscibility maps are compared with experiment for binary systems containing two kinds of segments. Theoretical miscibility

maps are in good agreement with experiment for the system containing poly(butyl methacrylate-*co*-methyl methacrylate) random copolymers. The theory also gives semi-quantitative agreement with experiment for systems containing poly(styrene-*co*-butadiene) and poly(styrene-*co*-methyl methacrylate) random copolymers.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE–AC03–76SF0098. Additional funding was provided by E.I. du Pont de Nemours & Co. (Philadelphia, PA) and Koninklijke Shell (Amsterdam, The Netherlands). The authors thank S.M. Lambert for useful discussions concerning the pure-component parameters of homopolymers.

Appendix A. Chemical Potential

Consider mixtures of heteronuclear hard-sphere chains. The chemical potential of component n, μ_n, is given by

$$
\begin{aligned}
\frac{\mu_n}{k_B T} &= \frac{\mu_n^o}{k_B T} + \int_0^\rho \left[\frac{V}{k_B T}\left(\frac{\partial p}{\partial N_n}\right)_{T,V,N} - 1\right]\frac{d\rho}{\rho} + \ln(x_n \rho k_B T) + 1 \\
&= \frac{\mu_n^o}{k_B T} + 2\rho \sum_{i=1}^{m} x_i \left[\sum_{k'=1}^{r_i} \sum_{l'=1}^{r_n} b_{in,k'l'} W_{in,k'l'}\right] \\
&+ \frac{\rho^2}{4} \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \left\{\sum_{k'=1}^{r_i} \sum_{l'=1}^{r_j} b_{ij,k'l'} \left[\left(\sum_{k'=1}^{r_n} b_{n,k'}\right) X_{ij,k'l'} + \left(\sum_{k'=1}^{r_n} b_{n,k'}^{2/3}\right)\left(\frac{b_{i,k'} b_{j,l'}}{b_{ij,k'l'}}\right) Y_{ij,k'l'}\right]\right\} \\
&- \sum_{k'=1}^{r_n - 1} Q_{nn,k',k'+1} - \frac{\rho}{4} \sum_{i=1}^{m} x_i \sum_{k'=1}^{r_i - 1} \left[\left(\sum_{k'=1}^{r_n} b_{n,k'}\right) g_{ii,k',k'+1} + \left(\sum_{k'=1}^{r_n} b_{n,k'}^{2/3}\right)\left(\frac{b_{i,k'} b_{i,k'+1}}{b_{ii,k',k'+1}}\right) H_{ii,k',k'+1}\right] \\
&- \frac{2\rho}{k_B T} \sum_{i=1}^{m} x_i \left[\sum_{k'=1}^{r_i} \sum_{l'=1}^{r_n} a_{in,k'l'}\right] + \ln(x_n \rho k_B T) + 1 \qquad \text{(A.1)}
\end{aligned}
$$

where μ_n° is the chemical potential per molecule of component i in the reference state, $W_{in,k'l'}$ and $Q_{nn,k',k'+1}$ are given by Eqs. (34) and (35), respectively, and

$$X_{ij,k'l'} = \left(\frac{1}{\rho^2}\right)\int_0^{\rho}\left(\frac{\partial g_{ij,k'l'}}{\partial \eta}\right)\rho d\rho \tag{A.2}$$

$$Y_{ij,k'l'} = \left(\frac{1}{\rho^2}\right)\int_0^{\rho}\left(\frac{\partial g_{ij,k'l'}}{\partial \xi_{ij,k'l'}}\right)\rho d\rho \tag{A.3}$$

$$H_{ii,k',k'+1} = \frac{1}{\rho}\int_0^{\rho}\frac{\partial g_{ii,k',k'+1}}{\partial \xi_{ii,k',k'+1}} d\rho \ . \tag{A.4}$$

The reference state is taken to be the pure ideal gas at unit pressure and at the temperature of the mixture containing the same number of molecules as the total number of molecules in the mixture.

The chemical potentials are related to Gibbs energy, G, by

$$G = \sum_{i=1}^{m} N_i \mu_i \tag{A.5}$$

where

$$\frac{G}{Nk_BT} = \frac{A}{Nk_BT} + \frac{p}{\rho k_BT} \tag{A.6}$$

where A is the Helmholtz energy given by Eq. (33).

References

1 Wohlfarth, C. *Makromol. Chem., Theory Simul.* **1993**, *2*, 605.

2 Guggenheim, E.A. "Mixtures", Clarendon Press: Oxford, 1952.

3. Song, Y.; Lambert, S.M.; Prausnitz, J.M. *Macromolecules* **1994**, 27, 441.

4. Song, Y.; Lambert, S.M.; Prausnitz, J.M. *Ind. Eng. Chem. Res.* **1994** in press.

5. Song, Y.; Lambert, S.M.; Prausnitz, J.M. *Chem. Eng. Sci.* **1994** in press.

6. Song, Y.; Lambert, S.M.; Prausnitz, J.M. submitted to *Ind. Eng. Chem. Res.* **1994**.

7. Chiew, Y.C. *Mol. Phys.* **1990**, *70*, 129.

8. Balazs, A.C.; DeMeuse, M.T. *Macromolecules* **1989**, *22*, 4260.

9. Prausnitz, J.M.; Lichtenthaler, R.N.; de Azevedo, E.G. "Molecular Thermodynamics of Fluid-Phase Equilibria", 2nd ed.; Prentice-Hall Inc.: Englewood Cliffs, N.J., 1986; Chapter 3.

10. Paul, D.R.; Barlow, J.W. *Polymer* **1984**, *25*, 487.

11. Roe, R.J.; Zin, W.C. *Macromolecules* **1980**, *13*, 1221.

12. Park, D.W.; Roe, R.J. *Macromolecules* **1991**, *24*, 5324.

13. Braun, D.; Yu, D.; Kohl, P.R., Gao, X.; Andradi, L.N., Manger, E.; Hellmann, G.P. J. *of Poly. Sci. B. Poly. Phys. Ed.* **1992**, 30, 577.

14. Hino, T.; Lambert, S.M.; Soane, D.S.; Prausnitz, J.M. *Polymer* **1993**, *34*, 4756.

15. Shiomi, T.; Ishimatsu, H.; Eguchi, T.; Imai, K. *Macromolecules* **1990**, *23*, 4970.

16. Shiomi, T.; Eguchi, T.; Ishimatsu, H.; Imai, K. *Macromolecules* **1990**, *23*, 4978.

17. Kim, C.K.; Paul, D.R. *Polymer* **1992**, *33*, 1630.

18. Kim, C.K.; Paul, D.R. *Polymer* **1992**, *33*, 2089.

TABLE I. Characterization of Polymer Samples Used in References 11 and 12

sample designation	polymer type	styrene content (wt%)	mol wt (Mn)	Mw/Mn
PBD	polybutadiene	0	2350	1.13
PS1	polystyrene	100	1900	1.06
PS2	polystyrene	100	2220	1.08
PS3	polystyrene	100	3302	1.06
PS4	polystyrene	100	5200	1.10-1.14
R50/50	poly(styrene-co-butadiene) random copolymer	50	24000	1.00
R25/75	poly(styrene-co-butadiene) random copolymer	25	27000	1.07

Mn = number average molecular weight (g/mol)

Mw = weight average molecular weight (g/mol)

TABLE II. PHSC Equation-of-State Parameters for Homopolymers[3]

polymer	r/M (mol/g)	σ (Å)	ε/k_B (K)
cis-1,4–polybutadiene	0.01499	5.264	611.8
polystyrene	0.01117	5.534	724.7
poly(methyl methacrylate)	0.01432	4.850	655.9
poly(butyl methacrylate)	0.01899	4.550	510.8

M = molecular weight (g/mol)

TABLE III. Intersegmental Parameters

binary pair	κ_{AB}	ζ_{AB}
butadiene–styrene (parameter set 1)	0.00412	0.00026
butadiene–styrene (parameter set 2)	0.00544	0.00117
butyl methacrylate–methyl methacrylate	–0.00158	–0.001
styrene–butyl methacrylate	0.01085	–0.002

Figure Captions

Figure 1. Theoretical coexistence curves for mixtures of random copolymers of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ with different copolymer compositions: $r_1 = r_2 = 10000$, σ_B/σ_A=1.1, $\varepsilon_B/\varepsilon_A$=1.2, κ_{AB}=0.00336, p=0.

Figure 2. Theoretical coexistence curves of mixtures of random copolymers of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ ($r_1 = r_2 = 10000$, X=0.8, Y=0.3) with different values of intersegmental parameters κ_{AB}: σ_B/σ_A=1.2, $\varepsilon_B/\varepsilon_A$=1.4, p=0.

Figure 3. Miscibility maps of mixtures of random copolymers of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ at four reduced temperatures: $r_1 = r_2 = 10000$, σ_B/σ_A=1.1, $\varepsilon_B/\varepsilon_A$=1.2, κ_{AB}=0.00335, p=0; (a) Immiscibility due to LCST behavior, (b) Immiscibility due to UCST behavior.

Figure 4. (a) Coexistence curves of three binary systems of type A_1/B_{500}, A_1/C_{500}, and B_{20}/C_{20}: $\sigma_B/\sigma_A=\sigma_C/\sigma_A$=1.1, $\varepsilon_B/\varepsilon_A=\varepsilon_C/\varepsilon_A$=1.2, $\kappa_{AB}=\kappa_{AC}=\kappa_{BC}$=0.01, p=0; (b) Copolymer composition dependence of reduced LCST and UCST of copolymer solutions of type $A_1/(C_Y B_{1-Y})_{500}$.

Figure 5. (a) Coexistence curves of three binary systems of type A_{10000}/B_{10000}, A_{10000}/C_{10000}, and B_{1000}/C_{1000}: $\sigma_B/\sigma_A=\sigma_C/\sigma_A$=1.1, $\varepsilon_B/\varepsilon_A=\varepsilon_C/\varepsilon_A$=1.2, $\kappa_{AB}=\kappa_{AC}$=0.00332, κ_{BC}=0.0002, p=0; (b) Copolymer composition dependence of reduced LCST and UCST of homopolymer/copolymer blends of type $A_{10000}/(C_Y B_{1-Y})_{10000}$.

Figure 6. (a) Temperature dependence of the miscibility map for mixtures of random copolymers of type $(A_X B_{1-X})_{r_1}/(C_Y B_{1-Y})_{r_2}$: σ_B/σ_A=1.1, σ_C/σ_A=1.2, $\varepsilon_B/\varepsilon_A$=1.2, σ_C/σ_A=1.4, κ_{AB}=0.00332, κ_{AC}=0.0122, κ_{BC}=0.00276, p=0. (b) Theoretical coexistence curves of copolymer mixtures corresponding to two pairs of copolymers denoted in Figure 6a.

Figure 7. Comparison of theoretical coexistence curves with experiment for polybutadiene/polystyrene mixtures: (a) (PBD-PS1) system, (b) (PBD-PS2) and (PBD-PS3) systems. The curves in (b) are predictions.

Figure 8. Comparison of predicted coexistence curves with experiment for polystyrene/poly(styrene-*co*-butadiene) mixtures: (a) (PS4-R50/50) system, (b) (PS2-R25/75) system.

Figure 9. Comparison of theoretical miscibility maps with experiment for a mixture of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing poly(butyl methacrylate-*co*-methyl methacrylate) random copolymers. The theory predicts that immiscibility is caused by LCST behavior. Data are from Braun *et al.*[13]: o miscible at 25 and 180 °C, Δ miscible at 25 °C but immiscible at 180 °C, ∘ immiscible at 25 and 180 °C.

Figure 10. Comparison of theoretical miscibility maps with experiment for mixtures of type $(A_X B_{1-X})_{r_1}/(A_Y B_{1-Y})_{r_2}$ containing poly(styrene-*co*-butyl methacrylate) random copolymers. The theory predicts that immiscibility is caused by LCST behavior. Data are from Braun *et al.*[13]: o miscible at 25 and 180 °C, Δ miscible at 25 °C but immiscible at 180 °C, ∘ immiscible at 25 and 180 °C.

Figure 1

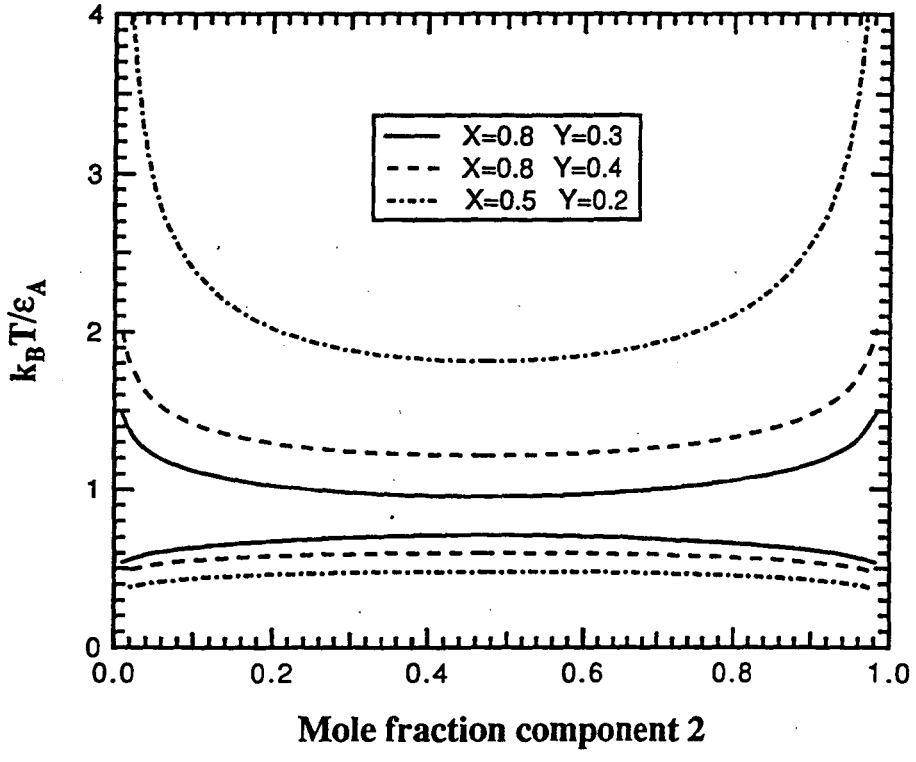

X=0.8 Y=0.3
X=0.8 Y=0.4
X=0.5 Y=0.2
k_BT/ε_A
0
1
2
3
4
0.0
0.2
0.4
0.6
0.8
1.0
Mole fraction component 2

Figure 2

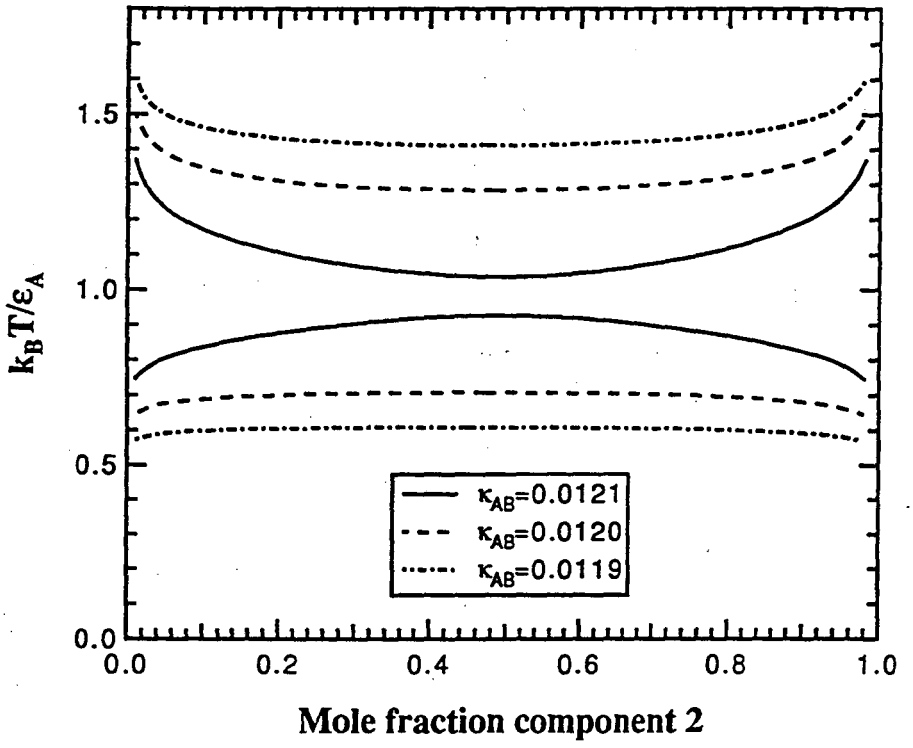

1.5
1.0
0.5
0.0
$k_B T/\varepsilon_A$
0.0
0.2
0.4
0.6
0.8
1.0
Mole fraction component 2
κ_{AB}=0.0121
κ_{AB}=0.0120
κ_{AB}=0.0119

Figure 3

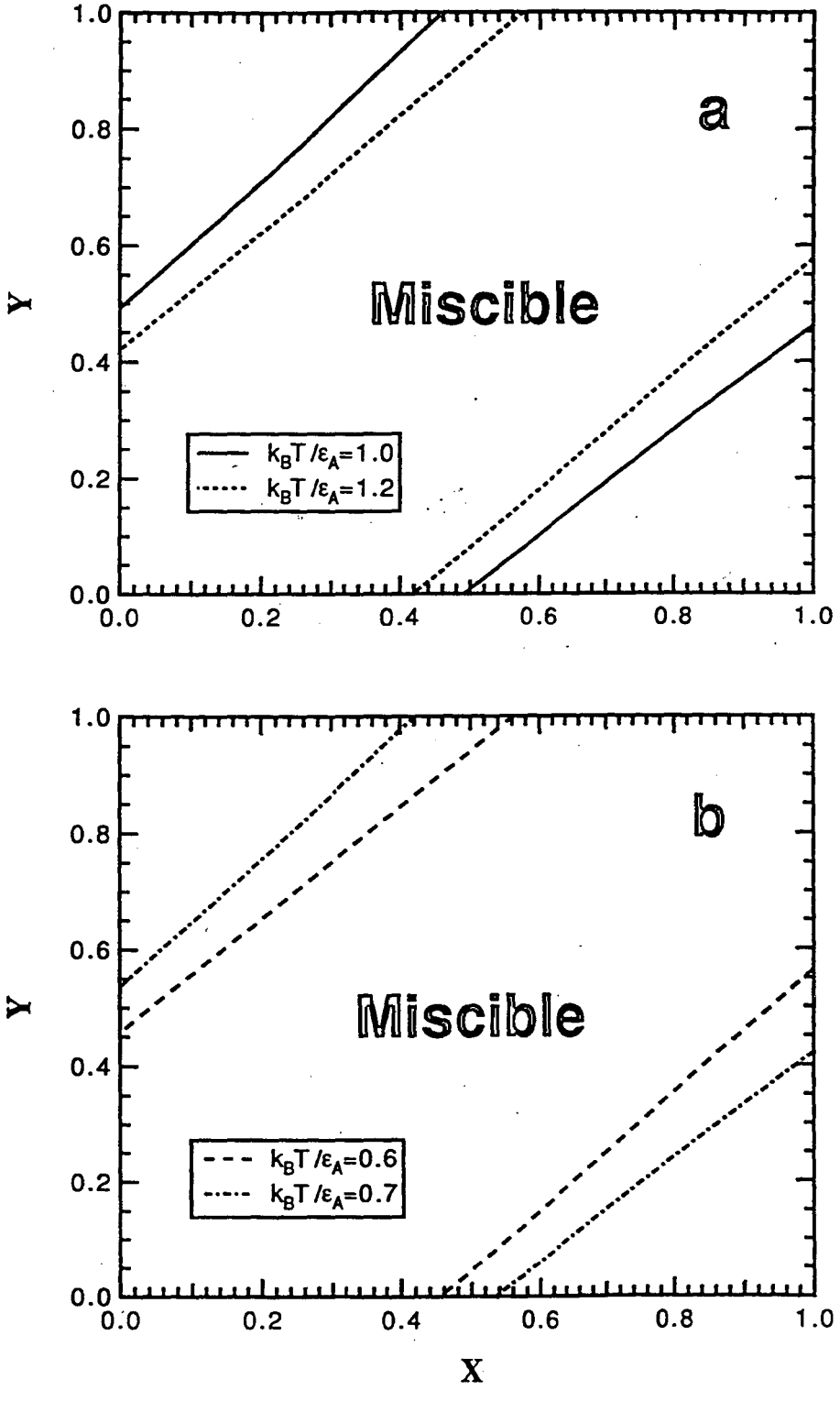

a
Miscible
k_BT/ε_A=1.0
k_BT/ε_A=1.2
b
Miscible
k_BT/ε_A=0.6
k_BT/ε_A=0.7
Y
X
0.0
0.2
0.4
0.6
0.8
1.0

Figure 4

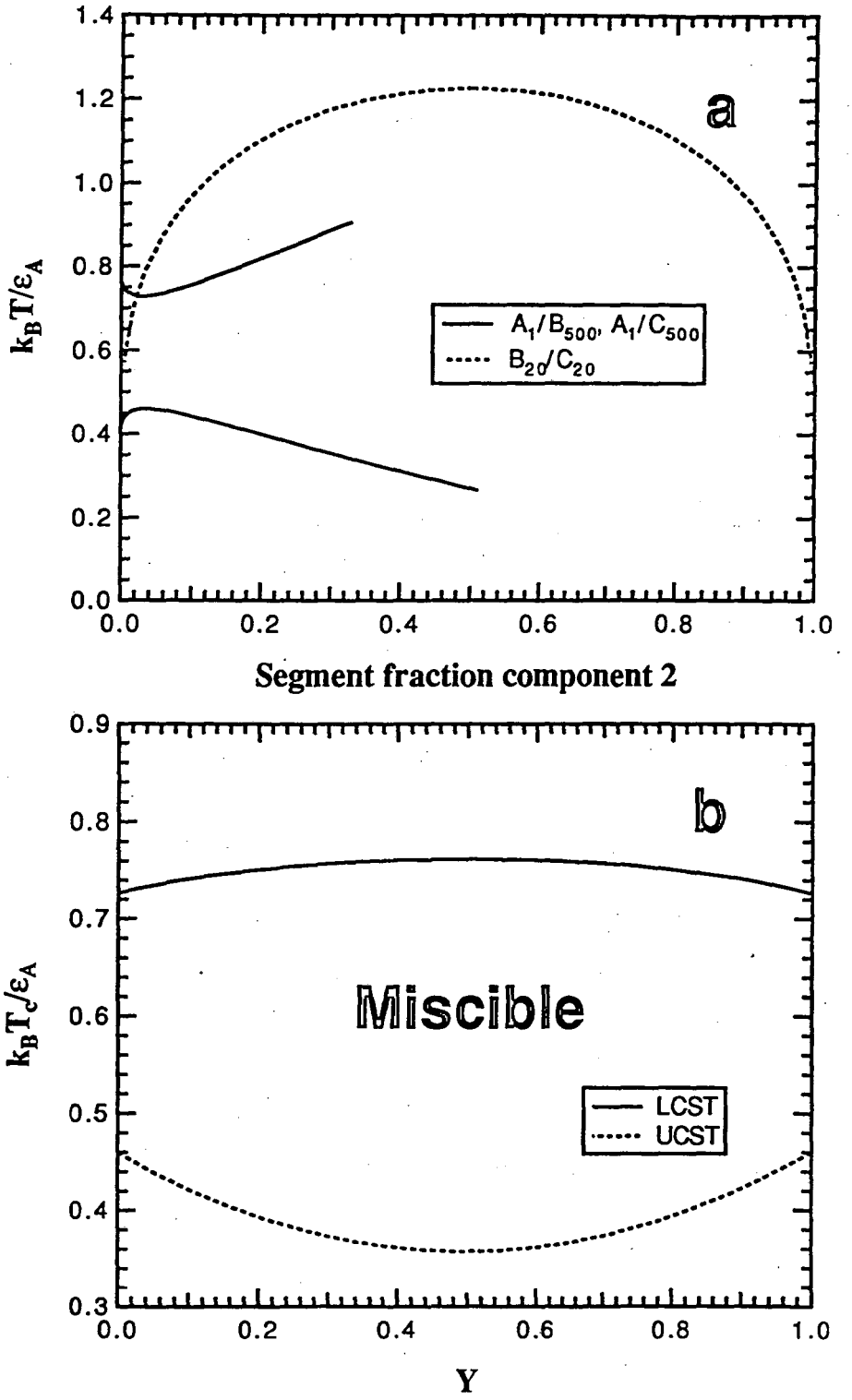

a
k_BT/ε_A
A_1/B_{500}, A_1/C_{500}
B_{20}/C_{20}
Segment fraction component 2
b
k_BT_c/ε_A
Miscible
LCST
UCST
Y

Figure 5

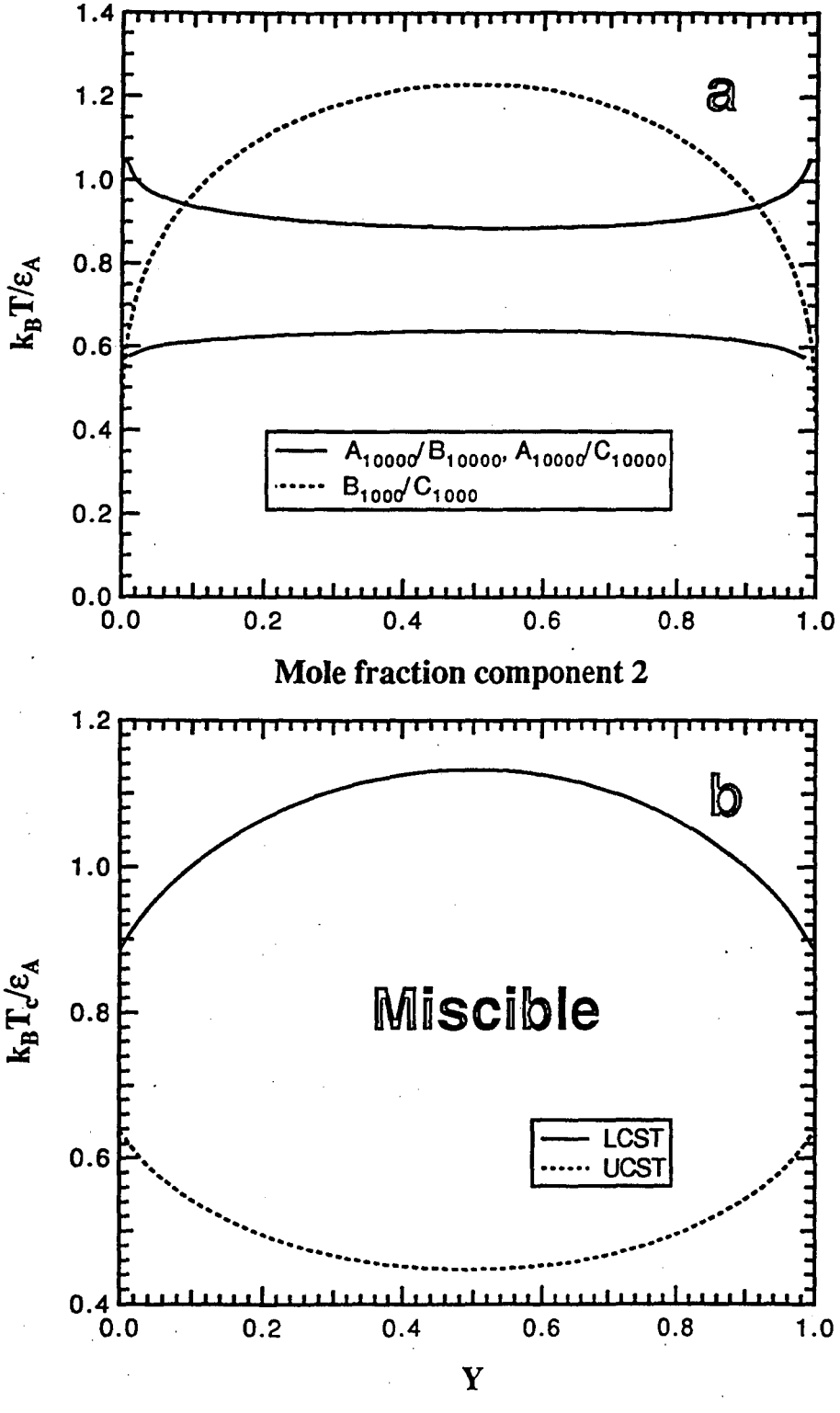
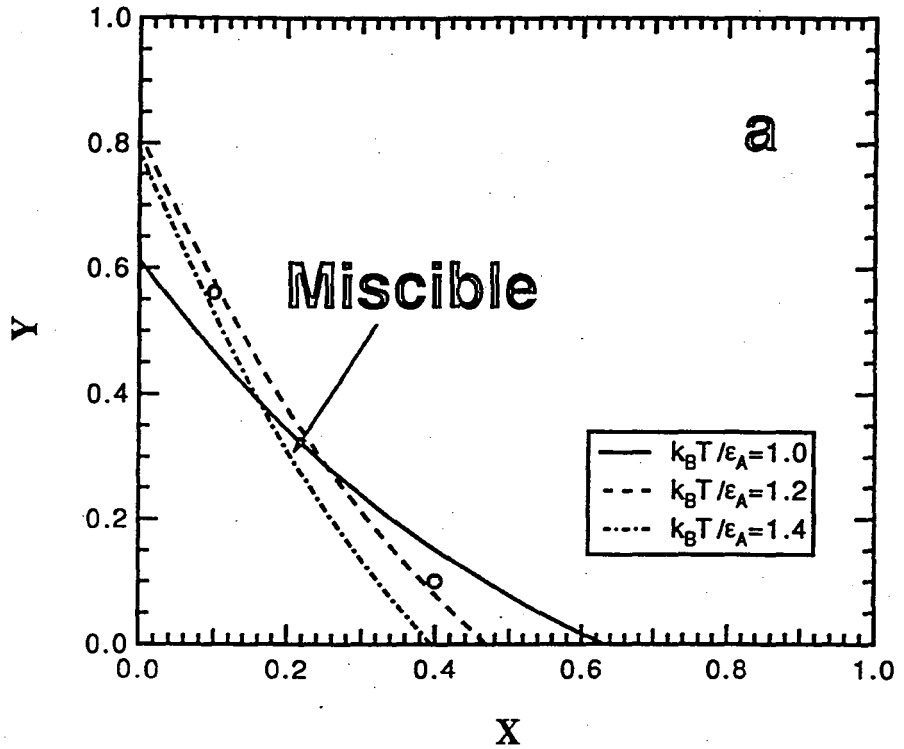

a
k_BT/ε_A
A_{10000}/B_{10000}, A_{10000}/C_{10000}
B_{1000}/C_{1000}
Mole fraction component 2
b
k_BT_c/ε_A
Miscible
LCST
UCST
Y

Figure 6


a
Miscible
Y
X
k_BT/ε_A=1.0
k_BT/ε_A=1.2
k_BT/ε_A=1.4
0.0
0.2
0.4
0.6
0.8
1.0

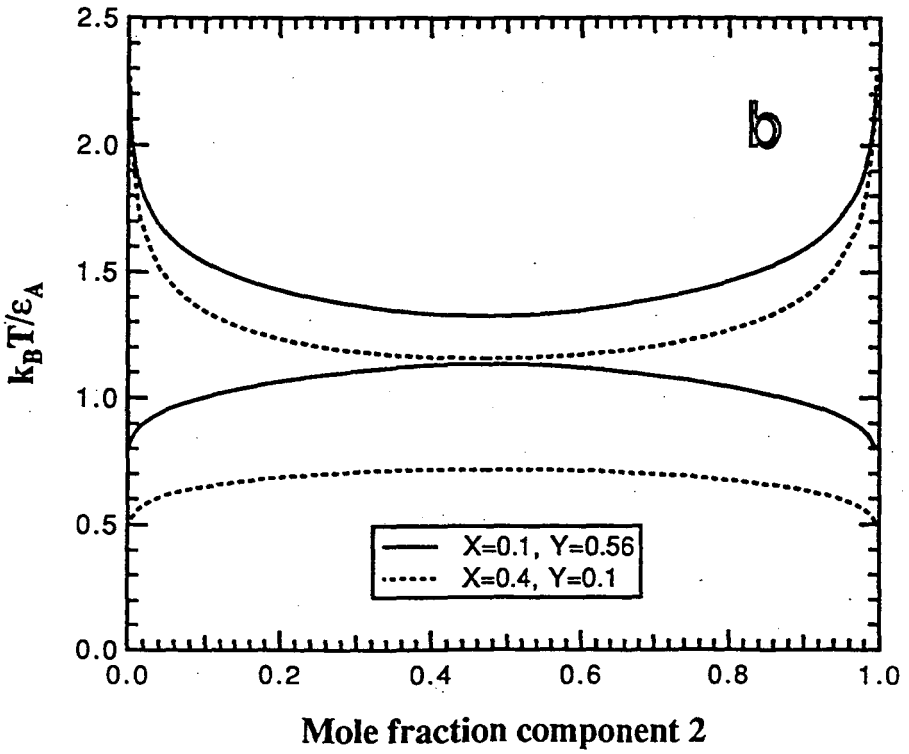

b
k_BT/ε_A
X=0.1, Y=0.56
X=0.4, Y=0.1
0.0
0.5
1.0
1.5
2.0
2.5
0.2
0.4
0.6
0.8
1.0
Mole fraction component 2

Figure 7

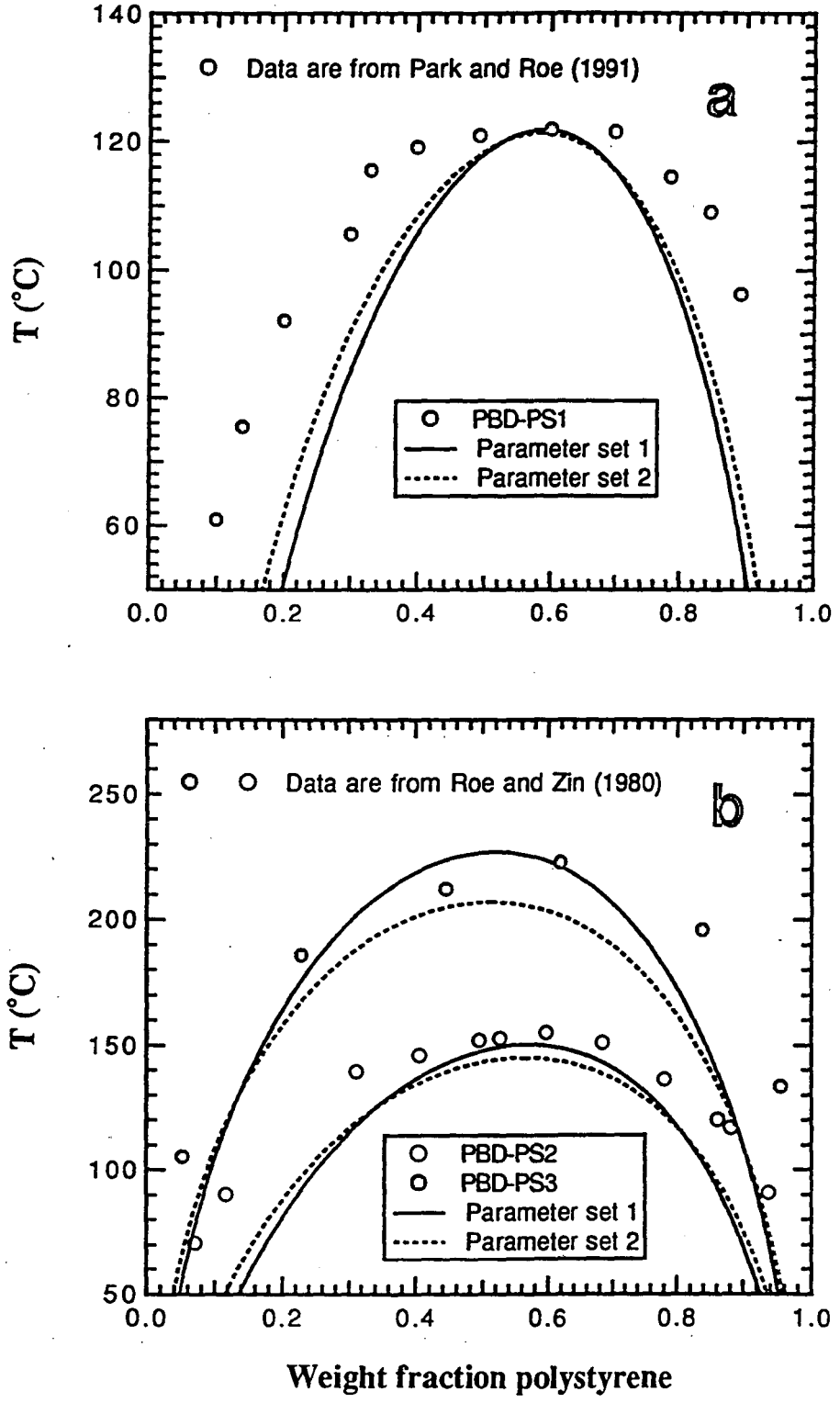

Data are from Park and Roe (1991)
a
PBD-PS1
Parameter set 1
Parameter set 2
T (°C)
140
120
100
80
60
0.0
0.2
0.4
0.6
0.8
1.0
Data are from Roe and Zin (1980)
b
PBD-PS2
PBD-PS3
Parameter set 1
Parameter set 2
T (°C)
250
200
150
100
50
0.0
0.2
0.4
0.6
0.8
1.0
Weight fraction polystyrene

Figure 8

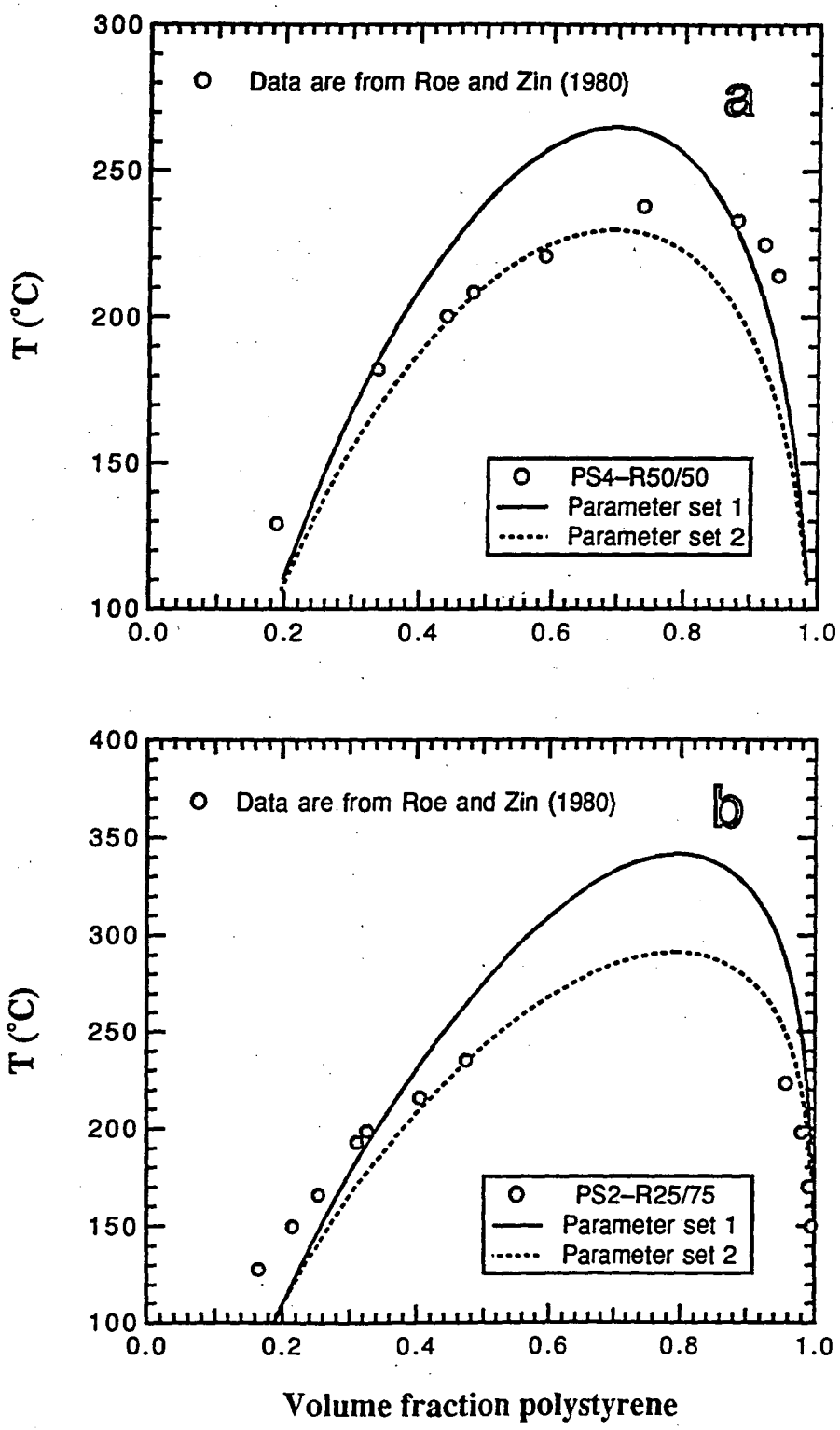

Data are from Roe and Zin (1980)
a
PS4–R50/50
Parameter set 1
Parameter set 2
T (°C)
300
250
200
150
100
0.0
0.2
0.4
0.6
0.8
1.0
Data are from Roe and Zin (1980)
b
PS2–R25/75
Parameter set 1
Parameter set 2
T (°C)
400
350
300
250
200
150
100
0.0
0.2
0.4
0.6
0.8
1.0
Volume fraction polystyrene

Figure 9

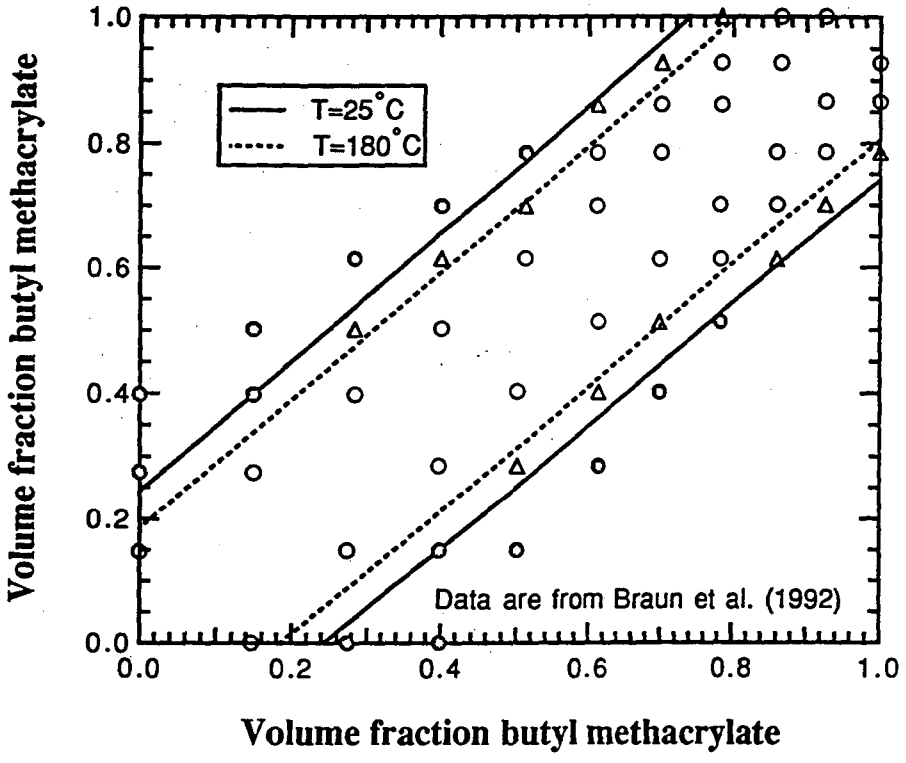
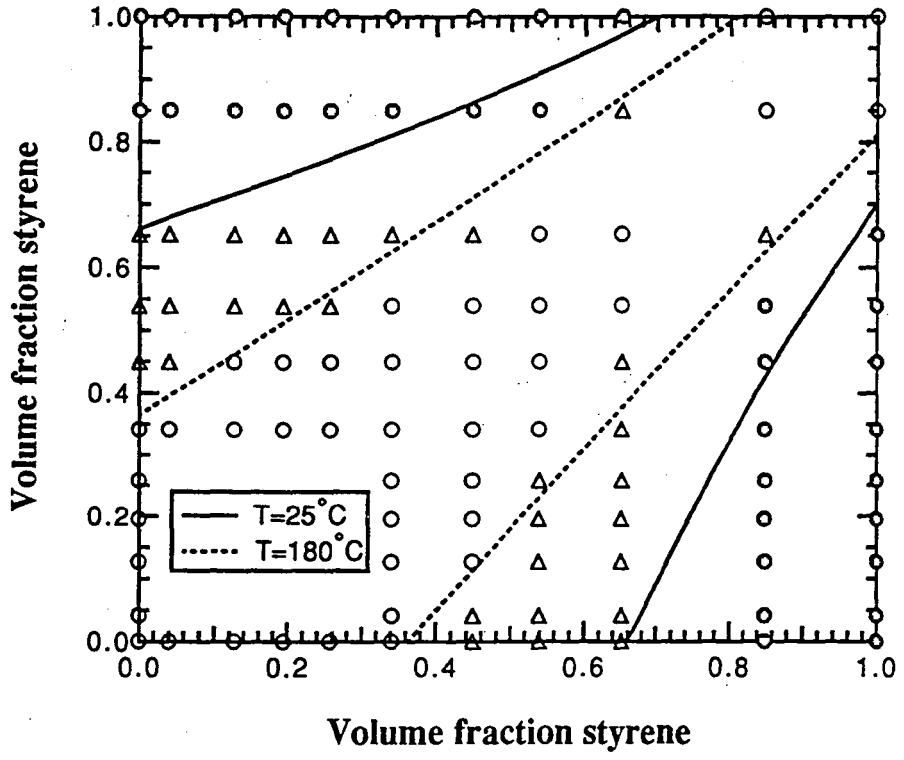

T=25°C
T=180°C
Data are from Braun et al. (1992)
Volume fraction butyl methacrylate
Volume fraction butyl methacrylate
0.0
0.2
0.4
0.6
0.8
1.0

Figure 10


1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
Volume fraction styrene
Volume fraction styrene
T=25°C
T=180°C

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720