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LOWER AND UPPER CRITICAL ORDERING TEMPERATURES IN COMPRESSIBLE DIBLOCK COPOLYMER MELTS FROM A PERTURBED HARD-SPHERE-CHAIN EQUATION OF STATE

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Abstract

The random-phase approximation is combined with the perturbed hard-sphere-chain (PHSC) equation of state for copolymer systems to represent the microphase separation transition in compressible diblock copolymer melts. The PHSC equation of state takes into account the equation-of-state effect that results from differences in compressibility between pairs of segments comprising a diblock copolymer; these differences favor demixing. Upon increasing the temperature of a microphase-separated diblock copolymer melt, theory first predicts an order-to-disorder transition that corresponds to the upper-critical-solution-temperature behavior in the binary blend of parent homopolymers. At conditions where the equation-of-state effect is significant, theory also predicts a disorder-to-order transition at further elevated temperature that follows closely the lower-critical-solution-temperature behavior in the binary blend containing the parent homopolymers. To compare theory with experiment, we obtain the binary interaction parameter between copolymer segments from the coexistence curve for the binary blend of parent homopolymers. Predicted microphase-separation-transition temperatures of diblock copolymer melts are compared with experiment for styrene-based diblock copolymer melts including poly(styrene-*block*-*n*-butyl methacrylate) melts that show both order-to-disorder and disorder-to-order transitions. We also discuss the pressure dependence of order-to-disorder transition temperatures of styrene-based diblock copolymer melts. Theory and experiment show semiquantitative agreement.

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I. Introduction

Because of fundamental scientific interest and possible applications of block copolymers, considerable effort has been made to examine phase equilibria for block copolymer melts and those for mixtures containing block copolymers.[1-5] A block copolymer consists of sequentially connected chemically different homopolymers. The homopolymers comprising a block copolymer are called the parent homopolymers of a block copolymer. In this work, we consider the phase behavior of a diblock copolymer melt consisting of segments A and B.

The phase behavior of an A-B diblock copolymer melt is expected to follow that of the binary blend containing parent homopolymers because both systems are characterized by the same binary interaction parameter that reflects interactions between dissimilar segments A and B. In the absence of favorable interactions such as hydrogen bonding between segments A and B, the interaction between dissimilar segments is unfavorable relative to the average of A-A and B-B interactions. Consequently, a homogeneous binary mixture of parent homopolymers exhibits upper-critical-solution-temperature (UCST) behavior upon cooling and splits into segment-A rich and segment-B rich macrophases to increase the number of contacts among similar segments.[6,7]

Disordered diblock copolymer melts also undergo phase separation with decreasing temperature. Because of the connectivity of homopolymers comprising block copolymers, however, phase separation in diblock copolymer melts leads not to ordinary large-scale phase separation but instead, to the formation of a variety of spatially ordered microstructures whose dimensions are comparable to the size of copolymers.[1-5] In diblock copolymer melts, the disorder-to-order transition upon cooling is called an upper-critical-ordering transition (UCOT).

In addition to UCST behavior, miscible polymer blends often exhibit lower-critical-solution-temperature (LCST) behavior upon heating.[6-8] In the absence of specific interactions such as hydrogen bonding between dissimilar molecules, LCST

behavior in binary polymer blends results from the equation-of-state effect, an entropic effect unfavorable to mixing. The equation-of-state effect is caused by the disparity in compressibility between the mixture's components. For polymer blends, Patterson and Robard provide a discussion on the relative importance of the equation-of-state effect and specific interactions that lead to LCST behavior.[9]

Although phase separation at elevated temperature is also expected for disordered diblock copolymer melts, the first experimental evidence of microphase separation upon heating was only recently reported by Russell *et al.*[10] for poly(styrene-*block*-*n*-butyl methacrylate)[10-12] diblock copolymer melts. This diblock copolymer also exhibits UCOT behavior. For diblock copolymer melts, the disorder-to-order transition with increasing temperature is called a lower-critical-ordering transition (LCOT).

To represent LCOT behavior in diblock copolymer melts, it is necessary to develop theories applicable to compressible diblock copolymer melts. Immediately after Russell *et al.*'s[10] discovery of both UCOT and LCOT behaviors in poly(styrene-*block*-*n*-butyl methacrylate) diblock copolymer melts, Yeung *et al.*[13] showed qualitatively that both UCOT and LCOT behaviors can be predicted by the random-phase approximation (RPA)[5,14-17] for diblock copolymer melts combined with an equation-of-state theory for polymeric fluids. The model by Yeung *et al.*[13] is based on the RPA for incompressible diblock copolymer solutions developed by Fredrickson and Leibler[16] that uses the Flory-Huggins lattice theory.[18] In lattice theories, compressible pure fluids are modeled as incompressible binary systems where vacant lattice sites (i.e., holes) are occupied by a hypothetical component whose fraction is determined by the equation of state for the system.[13]

Similarly, prior to the experiment by Russell *et al.*[10], Dudowicz and Freed[19] also combined the compressible RPA for diblock copolymer melts with the lattice-cluster theory that improves the Flory-Huggins lattice theory. Dudowicz and Freed[19] presented a semiquantitative analysis of polystyrene / poly(vinyl methyl ether) homopolymer

blends and poly(styrene-*block*-vinyl methyl ether) diblock copolymer melts. The model by Dudowicz and Freed[19] predicts phase separation upon heating in both homopolymer blends and diblock copolymer melts that contain polystyrene and poly(vinyl methyl ether). Experimental data, however, are not yet available for the phase behavior of poly(styrene-*block*-vinyl methyl ether) diblock copolymer melts.

In this work, we present a molecular-thermodynamic model to represent both UCOT and LCOT behaviors in compressible diblock copolymer melts. Our model is similar to that of Yeung *et al.*[13] because we also follow the RPA for diblock copolymer solutions presented by Fredrickson and Leibler.[16] Our model, however, is different from that by Yeung *et al.*[13] in calculating the interaction matrix required for the RPA. In addition, we present a more rigorous comparison of theory with experiment.

To calculate the interaction matrix, we use the recent perturbed-hard-sphere-chain (PHSC) equation of state[20-25] that is applicable to normal fluids, nematic liquid crystals[25], and polymers, including copolymers. Contrary to the other models for diblock copolymer melts,[13,15,16,19] however, the PHSC equation of state is an equation-of-state theory in continuous space. Therefore, we first discuss our procedure to combine the RPA with the PHSC equation of state for diblock copolymer melts.

Our main objective is to represent first, parent pure homopolymer melts; second, mixtures of parent homopolymers; and third, diblock copolymer melts using the same set of pure-component and binary parameters. We also investigate the effect of pressure on the phase behavior of diblock copolymer melts and that of mixtures containing parent homopolymers.

To present quantitative comparison of theory with experiment, we first regress the PHSC equation-of-state parameters for parent homopolymers from pressure-volume-temperature data for homopolymer melts.[24] The PHSC equation of state requires three parameters to represent thermodynamic properties of a homopolymer melt: segment diameter, number of segments per molecule, and the depth of the square-well potential

that represents the attractive interaction on a segment basis. Next, using the PHSC equation of state for binary homopolymer blends,[24] one binary interaction parameter between copolymer segments is obtained from the coexistence curve for the binary blend containing parent homopolymers at ambient pressure. Finally, we predict the pressure-dependence of microphase-separation-transition temperatures of styrene-based diblock copolymer melts.

The present work considers only the stability of homogeneous compressible diblock copolymer melts in the weak segregation limit. Equilibrium structures of microphases are not discussed.

II. Random-Phase Approximation (RPA)

The RPA for diblock copolymer melts originally developed by Leibler[15] provides a systematic procedure to calculate the Helmholtz energy density of ordered diblock copolymer melts. In this approach, the Helmholtz energy density of an ordered system is expanded around that of a disordered system in terms of the Fourier components of order parameters using the scattering functions. The scattering function matrix for real diblock copolymers consists of the scattering function matrix for ideal noninteracting Gaussian diblock chains and the interaction matrix that represents interactions among segments.[15]

In the RPA for diblock copolymer systems, the Flory-Huggins lattice theory[18] is often used to compute the interaction matrix. In this work, however, we combine the RPA with the PHSC equation of state[20-25] that is an off-lattice equation-of-state theory. In the PHSC equation of state, a polymer molecule is represented by a chain of tangent spheres that interact with spheres in another chain through repulsive and attractive interactions.

1. Helmholtz Energy and Stability Limit. In continuous space of volume V, we consider a diblock copolymer melt containing N molecules of type

$$(A_X B_{1-X})_r \tag{1}$$

where A and B are the segments comprising a diblock copolymer with diameters σ_A and σ_B, respectively; X is the number fraction of segment A; and r is the total number of segments per molecule. The number of segment A and that of segment B per molecule are $r_A = rX$ and $r_B = r(1-X)$, respectively. For a diblock copolymer, the numbers of α–β $(\alpha, \beta = \mathrm{A}, \mathrm{B})$ sequences per molecule are given by

$$r_{AA} = r_A - 1, \quad r_{BB} = r_B - 1, \quad r_{AB} = 1 \ . \tag{2}$$

Figure 1 shows a schematic of a diblock copolymer melt in continuous space. The average packing fraction of segment A is η_A and that of segment B is η_B; they are given by

$$\eta_\alpha = \frac{\rho}{6} r_\alpha \pi \sigma_\alpha^3 \quad (\alpha = \mathrm{A}, \mathrm{B}) \tag{3}$$

where $\rho \equiv N/V$ is the number density. The average total packing fraction η is given by

$$\eta = \eta_A + \eta_B \ . \tag{4}$$

We follow closely the theory for incompressible diblock copolymer solutions developed by Fredrickson and Leibler[16] that uses the Flory-Huggins lattice theory. The model by Fredrickson and Leibler[16] reduces to Leibler's original model for incompressible diblock copolymer melts[15] by setting the number of lattice sites occupied by solvent molecules equal to zero. For a compressible melt, the lattice sites occupied by solvent molecules are replaced by vacancies. The fraction of sites that is vacant is determined by the system's equation of state.[13]

In the lattice theory of Fredrickson and Leibler,[16] the average volume fraction of segment A and that of segment B are denoted as ϕ_A and ϕ_B, respectively. In the present theory, packing fractions η_A and η_B correspond to volume fractions ϕ_A and ϕ_B in Reference 16. Therefore, the independent fluctuating fields in our model are $\delta\eta_A(\mathbf{x})$ and $\delta\eta_B(\mathbf{x})$ that correspond to $\delta\phi_A(\mathbf{x})$ and $\delta\phi_B(\mathbf{x})$, respectively, in Reference 16. Parameters $\delta\eta_A(\mathbf{x})$ and $\delta\eta_B(\mathbf{x})$ represent the fluctuation in the packing fraction of segment A and that of segment B, respectively, at point $\mathbf{x}$.

We also define order parameters ψ_1 and ψ_2 by

$$\begin{pmatrix} \psi_1(\mathbf{x}) \\ \psi_2(\mathbf{x}) \end{pmatrix} = \mathbf{M} \begin{pmatrix} \langle \delta\eta_A(\mathbf{x}) \rangle \\ \langle \delta\eta_B(\mathbf{x}) \rangle \end{pmatrix} \tag{5}$$

where the angular brackets denote the thermodynamic average and

$$\mathbf{M} = \eta^{-1} \begin{pmatrix} 1-f & -f \\ \eta & \eta \end{pmatrix} \tag{6}$$

where f is the volume fraction of segment A per chain given by

$$f = \frac{r_A \sigma_A^3}{r_A \sigma_A^3 + r_B \sigma_B^3} \ . \tag{7}$$

Order parameter ψ_1 describes the composition fluctuation of segment A for a fixed total packing fraction. Order parameter ψ_2 represents the deviation of the total packing fraction from its average value.

In this work, we consider only the stability of homogeneous diblock copolymer melts in the weak segregation limit where the order parameters are small. In that event, it is sufficient to retain only the second-order term in the expansion of the Helmholtz

energy density in the order parameters.[13,16] The Helmholtz energy density is given by[13,16]

$$\frac{A}{Vk_{\mathrm{B}}T} = \left(\frac{A}{Vk_{\mathrm{B}}T}\right)_{\mathrm{dis}} + \frac{1}{2V}\sum_{i,j}\int \frac{d\,\mathbf{q}}{(2\pi)^3}\,\Gamma_{ij}^{(2)}(q)\psi_i(\mathbf{q})\psi_j(-\mathbf{q}) \tag{8}$$

where A is the Helmholtz energy; k_{B} is the Boltzmann constant; T is the absolute temperature; $\mathbf{q}$ is the scattering vector of magnitude q; $\Gamma_{ij}^{(2)}(q)$ is the second-order vertex function; and $\psi_i(\mathbf{q})$ is the Fourier transform of $\psi_i(\mathbf{x})$. The first term in the right-hand side of Eq. (8) is the Helmholtz energy density of a disordered system.

The matrix for the second-order vertex function is a function of **M** given by Eq. (6) and the scattering-function matrix defined by[16]

$$\widetilde{\mathbf{S}}(q) = \left[\eta^{-1}\mathbf{S}^{-1}(q) + \mathbf{W}\right]^{-1} \tag{9}$$

where **S** is the scattering-function matrix for the noninteracting Gaussian diblock chains and **W** is the interaction matrix defined later. These matrices are 2×2 matrices and the indices ij (i, j=1, 2) of their elements denote segment type with i=1 and 2 referring to segments A and B, respectively.

The elements of matrix **S** are functions of the modified Debye function as given by Leibler.[15,16] Although the PHSC equation of state uses different segment diameters for chemically different segments, in calculating the scattering functions for noninteracting Gaussian diblock chains, we use the expressions for the diblock chain consisting of a uniform segment size. The elements of matrix **S** are given by[15,16]

$$S_{11}(q) = rv\,g_1(f, x) \tag{10}$$

$$S_{22}(q) = rv\, g_1(1-f, x) \tag{11}$$

$$S_{12}(q) = S_{21}(q) = \frac{1}{2} rv\,[g_1(1, x) - g_1(f, x) - g_1(1-f, x)] \tag{12}$$

where v is the average segment volume given by

$$v = \frac{\pi}{6r}\left(r_A\sigma_A^3 + r_B\sigma_B^3\right) . \tag{13}$$

In Eqs. (10) to (12), $g_1(f, x)$ is the modified Debye function given by[15,16]

$$g_1(f, x) = \frac{2}{x^2}[fx + exp(-fx) - 1] \tag{14}$$

where f is the volume fraction of segment A per chain given by Eq. (7) and

$$x \equiv q^2 nl^2/6 \tag{15}$$

where n is the number of the statistical segments of (Kuhn) length l. The pair of parameters n and l models the chain statistics of a real diblock copolymer by that of an ideal Gaussian chain. Segments A and B are assumed to have the same statistical segment length. In principle, as discussed by Tanaka *et al.*,[26] a unique pair of segment diameter and statistical segment length can be assigned to each segment to compute the scattering functions for noninteracting Gaussian diblock chains. For parent polymers studied in this work, segment diameters regressed by the PHSC equation of state are close to each other. Therefore, we use the scattering functions for the diblock chain consisting of a uniform segment size. We assume that n and l are given, respectively, by r (number of segments per molecule) and the average hard-sphere diameter.

In matrix notation, the second-order vertex function is given by

$$\Gamma(q) = \left(\mathbf{M}^{-1}\right)^{\mathrm{T}} \tilde{\mathbf{S}}^{-1}(q) \mathbf{M}^{-1} \tag{16}$$

where matrices $\mathbf{M}$ and $\tilde{\mathbf{S}}$ are given by Eqs. (6) and (9), respectively. A disordered block copolymer melt becomes unstable against vanishingly small fluctuation in order parameters when the smallest eigenvalue of the matrix Γ becomes negative[13]; the condition for stability of a disordered system is given in terms of the function $F(q)$ defined by[13]

$$F(q) \equiv \Gamma_{11}^{(2)} \Gamma_{22}^{(2)} - \Gamma_{12}^{(2)} \Gamma_{21}^{(2)} > 0 \quad \text{(for any } q\text{)} \ . \tag{17}$$

The essential step in combining the RPA with the PHSC equation of state is the calculation of the interaction matrix $\mathbf{W}$ in Eq. (9). In theories based on the Flory-Huggins lattice theory, the elements of the interaction matrix are usually obtained by solving the RPA equations as shown by Fredrickson and Leibler[16] for diblock copolymer solutions. In terms of the Fourier transform, the RPA equations calculate the composition changes induced by the external potentials using the scattering functions for noninteracting Gaussian chains.

In this work, we use an alternate procedure to obtain the interaction matrix. This procedure follows a thermodynamic relation between the scattering-function matrix and the Helmholtz energy density for multicomponent systems. The derivation of interaction matrix used here, however, is not discussed by Fredrickson and Leibler[16] and by Yeung *et al.*[13] for diblock copolymer solutions and melts. Therefore, we first propose a systematic procedure for computing the interaction matrix by reviewing the RPA combined with the Flory-Huggins theory for homopolymer blends and that for diblock copolymer melts.

2. Definition of the Interaction Matrix

Our approach is based on the thermodynamic relation between the Helmholtz energy density for homopolymer blends and $\tilde{\mathbf{S}}^{-1}(0)$, the inverse of the scattering-function matrix in the limit $q \rightarrow 0$. In homopolymer blends, the elements of matrix $\tilde{\mathbf{S}}^{-1}(0)$ are equal to the second derivatives of the Helmholtz energy density with respect to the segment volume fractions.[27]

Consider first the RPA for compressible binary homopolymer blends combined with the Flory-Huggins theory.[27] The RPA for compressible homopolymer blends was recently discussed by Bidkar and Sanchez[27] using the lattice-fluid equation of state (i.e., a compressible Flory-Huggins theory). Bidkar and Sanchez[27], however, did not apply their theory to compressible diblock copolymer melts. In the RPA for homopolymer blends, the scattering function matrix is also expressed by Eq. (9) with $\mathbf{S}(q)$ representing the scattering-function matrix for noninteracting Gaussian homopolymer chains.

In the Flory-Huggins theory for binary homopolymer blends, the Helmholtz energy consists of two contributions:[27] the ideal Helmholtz energy that represents the translational entropy of polymers and the nonideal Helmholtz energy that describes interactions among segments. The second derivatives of the ideal Helmholtz energy with respect to the segment volume fractions are identical to the elements of matrix $\mathbf{S}^{-1}(0)$, the inverse of the scattering-function matrix for noninteracting Gaussian homopolymer chains in the limit $q \rightarrow 0$. Therefore, by assuming that the elements of the interaction matrix $\mathbf{W}$ are independent of q, these elements are identified as the second composition derivatives of the nonideal Helmholtz energy density.

We now consider the Flory-Huggins theory for incompressible diblock copolymer solutions developed by Fredrickson and Leibler[16] and that for compressible diblock copolymer melts by Yeung *et al.*[13] In these systems, the Helmholtz energy density is also separated into the ideal and nonideal Helmholtz energies that, respectively, represent the translational entropy of diblock copolymers and interactions among segments. The

nonideal Helmholtz energy density is next expressed in terms of ϕ_A and ϕ_B, the volume fraction of segment A and that of segment B, respectively.

Although not shown here, the interaction matrix derived by Fredrickson and Leibler[16] and that by Yeung *et al.*[13] are identical to the matrices whose elements are the second derivatives of the relevant nonideal Helmholtz energy density with respect to ϕ_A and ϕ_B. These derivatives are taken by considering ϕ_A and ϕ_B to be independent variables. Based on this general relationship between the interaction matrix and the nonideal Helmholtz energy density in the Flory-Huggins theory, the RPA for A-B diblock copolymer melts may also be combined with the PHSC equation of state by the following procedure.

Consistent with earlier studies, in the PHSC equation of state the Helmholtz energy density is also separated into two contributions: the ideal Helmholtz energy that is identical to the contribution from the translational entropy of polymers in the Flory-Huggins theory and the nonideal Helmholtz energy that represents interactions among segments. The nonideal Helmholtz energy is then expressed in terms of η_A and η_B by considering these variables as independent composition variables. The interaction matrix is the matrix whose elements are the second composition derivatives of the nonideal Helmholtz energy density.

3. Interaction Matrix for the PHSC Equation of State

Details of the PHSC equation of state are given in References 20 to 24. In the PHSC equation of state, ΔA, the Helmholtz energy with respect to that in the standard state, is given by

$$\frac{\Delta A}{Nk_BT} = \ln(\rho k_BT) + \left(\frac{A}{Nk_BT}\right)_{\text{ref}} + \left(\frac{A}{Nk_BT}\right)_{\text{pert}} . \tag{18}$$

The standard state is the ideal gas at system temperature and unit pressure. The leading term in the right-hand side of Eq. (18) is the configurational Helmholtz energy of an ideal gas. The terms denoted by subscripts ref and pert are the reference and perturbation terms, respectively; these terms represent repulsive and attractive interactions, respectively. The equation of state is obtained from the Helmholtz energy by

$$p = \rho^2 \left(\frac{\partial \frac{\Delta A}{N}}{\partial \rho} \right)_{T,N} \tag{19}$$

where p is the pressure.

There are two versions of the PHSC equation of state reported in the literature: the original model[21-23] that uses a van der Waals-type perturbation term and the more recent model that uses the perturbation theory for the square-well fluid of variable well width.[24,25] In this work, we use the latter version of the PHSC theory because that model provides significant improvement in correlating thermodynamic properties of pure fluids and mixtures[22,23].

In the PHSC equation of state, parameter b represents the excluded volume on a segment basis. For diblock copolymers consisting of two types of segments A and B, parameter b is given by

$$b_\alpha = b_{\alpha\alpha} = \frac{2}{3}\pi\sigma_\alpha^3 \quad (\alpha = \mathrm{A, B}) \tag{20}$$

$$b_{\mathrm{AB}} = b_{\mathrm{BA}} = \frac{1}{8}\left(b_{\mathrm{A}}^{1/3} + b_{\mathrm{B}}^{1/3}\right)^3 . \tag{21}$$

In terms of parameter b, the reference Helmholtz energy is given by

$$\left(\frac{A}{Nk_BT}\right)_{\text{ref}} = \rho\left(r_A^2 b_A Z_{AA} + 2r_A r_B b_{AB} Z_{AB} + r_B^2 b_B Z_{BB}\right)$$
$$-\left[r_{AA}Q_{AA} + r_{AB}Q_{AB} + r_{BB}Q_{BB}\right] \tag{22}$$

where the first term in the right-hand side of Eq. (22) represents the Helmholtz energy of hard-sphere mixtures prior to bonding to form a hard-sphere chain and the second term represents chain connectivity with $r_{\alpha\beta}(\alpha, \beta = \text{A, B})$ given by Eq. (2). In Eq. (22), functions Z and Q are given by

$$Z_{\alpha\beta} = \frac{1}{\eta} I_1 + \frac{3}{2}\frac{\xi_{\alpha\beta}}{\eta^2} I_2 + \frac{1}{2}\frac{\xi_{\alpha\beta}^2}{\eta^3} I_3 \quad (\alpha, \beta = \text{A, B}) \tag{23}$$

$$Q_{\alpha\beta} = -\ln(1-\eta) + \frac{3}{2}\frac{\xi_{\alpha\beta}}{1-\eta} + \frac{1}{4}\frac{\xi_{\alpha\beta}^2}{(1-\eta)^2} \tag{24}$$

where

$$\xi_{\alpha\beta} = \frac{\rho}{4}\left(\frac{b_\alpha b_\beta}{b_{\alpha\beta}}\right)^{1/3}\left(r_A b_A^{2/3} + r_B b_B^{2/3}\right) \tag{25}$$

$$I_1 = -\ln(1-\eta) \tag{26}$$

$$I_n = -I_{n-1} + \frac{1}{n-1}\frac{\eta^{n-1}}{(1-\eta)^{n-1}} \quad (n > 2)\ . \tag{27}$$

The perturbation term is based on the second-order perturbation theory for the square-well fluid of variable well width presented in Reference 24. The square-well potential is defined by

$$u(R) = \begin{cases} \infty & R < \sigma \\ -\varepsilon & \sigma \le R < \lambda\sigma \\ 0 & R \ge \lambda\sigma \end{cases} \tag{28}$$

where $u(R)$ is the pair potential; R is the intersegmental center-to-center distance between nonbonded segments; σ is the hard-sphere diameter; ε is the depth of the well; and λ is the reduced well width. Although Reference 24 considers only homogeneous molecules consisting of one kind of segment (e.g., homopolymers), we also apply the perturbation terms given in Reference 24 to copolymers consisting of two kinds of segments by replacing parameters for homogeneous molecules by those for copolymers averaged over the copolymer composition.

The perturbation term is given by

$$\left(\frac{A}{Nk_{\mathrm{B}}T}\right)_{\mathrm{pert}} = \left(\frac{A_1}{Nk_{\mathrm{B}}T}\right)_{\mathrm{pert}} + \left(\frac{A_2}{Nk_{\mathrm{B}}T}\right)_{\mathrm{pert}} \tag{29}$$

where A_1 and A_2 are the first- and second-order perturbation terms, respectively, for the Helmholtz energy given by[24]

$$\left(\frac{A_1}{Nk_{\mathrm{B}}T}\right)_{\mathrm{pert}} = -\frac{\langle r^2 b\varepsilon\rangle}{k_{\mathrm{B}}T}\rho\Psi \tag{30}$$

$$\left(\frac{A_2}{Nk_{\mathrm{B}}T}\right)_{\mathrm{pert}} = -\frac{1}{2}\frac{\langle r^2 b\varepsilon^2\rangle}{(k_{\mathrm{B}}T)^2}\rho\frac{(1-\eta)^4}{\left(1+4\eta+4\eta^2\right)}\left(\Psi + \eta\frac{\partial\Psi}{\partial\eta}\right) \tag{31}$$

where

$$\langle r^2 b\,\varepsilon^m\rangle = r_{\mathrm{A}}^2 b_{\mathrm{A}}\varepsilon_{\mathrm{A}}^m + 2r_{\mathrm{A}}r_{\mathrm{B}}b_{\mathrm{AB}}\varepsilon_{\mathrm{AB}}^m + r_{\mathrm{B}}^2 b_{\mathrm{B}}\varepsilon_{\mathrm{B}}^m \quad (m=1,2) \tag{32}$$

$$\varepsilon_{AB} = (1 - \kappa_{AB})\sqrt{\varepsilon_A \varepsilon_B} \tag{33}$$

where κ_{AB} is an adjustable binary parameter. Equation (33) is used only to introduce an adjustable binary parameter. As shown later, the theoretical phase diagrams of polymer blends and those of diblock copolymer melts are very sensitive to κ_{AB}. The geometric mean of ε_A and ε_B cannot be used to predict ε_{AB}. The interaction parameter between segments A and B must be obtained by correlating thermodynamic properties of systems containing both segments A and B.

In Eqs. (30) and (31), Ψ is a function of η and λ resulting from integration of the radial distribution function for hard spheres over the width of the well. In this work, the reduced well width λ is 1.455 for all fluids; λ=1.455 is the optimum value for methane with r=1.[24] Function Ψ is obtained by fitting[24] the analytic equation for Ψ in the range of $1<\lambda\leq 2$ given by Chang and Sandler[28] to a polynomial function of η:

$$\Psi(\eta) = 3\sum_{k=1}^{10} c_k \eta^{k-1} \quad . \tag{34}$$

For λ=1.455, Table 1 gives numerical coefficients c_k. As shown in Reference 24, the optimum reduced well width (here λ=1.455) can be assigned to each segment combined with appropriate mixing rules for the perturbation term.

As discussed in Reference 24, the quality of fits is sensitive to λ when the equation-of-state parameters of a normal fluid are obtained from the saturated vapor pressure and liquid density of the saturated liquid. The PHSC equation of state, however, provides excellent correlations of homopolymer pVT data for several values of λ including λ=1.455. It is not possible to obtain the optimum reduced well width based solely on the quality of fits of homopolymer pVT data. Therefore, we use the PHSC

equation of state with λ=1.455 that correlates very well both the thermodynamic properties of saturated liquids and pVT data of homopolymer melts.

To calculate the interaction matrix for the RPA, the Helmholtz energy density is required. From Eq. (18), the Helmholtz energy density is given by

$$\frac{\Delta A}{Vk_BT} = \frac{\eta}{rv}\ln\left(\frac{\eta k_BT}{rv}\right) + \left(\frac{A}{Vk_BT}\right)_{\text{ref}} + \left(\frac{A}{Vk_BT}\right)_{\text{pert}} \tag{35}$$

where r is the number of segments per molecule; v is the average segment volume given by Eq. (13); and η is the packing fraction given by Eq. (4). The leading term in the right-hand side of Eq. (35) resembles the translational entropy of polymers in the Flory-Huggins theory.[13,16,18] Therefore, the sum of the reference and perturbation terms in Eq. (35) are identified as the nonideal Helmholtz energy density for the PHSC theory. This nonideal Helmholtz energy is used to obtain the interaction matrix for the RPA.

The next step is to express the nonideal Helmholtz energy density in terms of η_A and η_B, the packing fractions of segments A and B. Using Eqs. (22), (30), and (31), the nonideal Helmholtz energy density is given by

$$\begin{aligned}\left(\frac{\Delta A}{Vk_BT}\right)_{\text{ref+pert}} &= \frac{16}{b_Ab_B}\left(\eta_A^2b_BZ_{AA} + 2\eta_A\eta_Bb_{AB}Z_{AB} + \eta_B^2b_AZ_{BB}\right) \\ &\quad - 4\left[\frac{\eta_A}{b_A}Q_{AA} + \frac{\eta_B}{b_B}Q_{BB}\right] - \frac{\eta}{rv}\left[-Q_{AA} + Q_{AB} - Q_{BB}\right] \\ &\quad + \left(\frac{A_1}{Vk_BT}\right)_{\text{pert}} + \left(\frac{A_2}{Vk_BT}\right)_{\text{pert}}\end{aligned} \tag{36}$$

where the subscript ref+per denotes the nonideal Helmholtz energy density consisting of the reference and perturbation terms for the PHSC theory and

$$\left(\frac{A_1}{Vk_BT}\right)_{\text{pert}} = -\frac{16}{b_Ab_B}\left[\eta_A^2 b_B\left(\frac{\varepsilon_A}{k_BT}\right) + 2\eta_A\eta_B b_{AB}\left(\frac{\varepsilon_{AB}}{k_BT}\right) + \eta_B^2 b_A\left(\frac{\varepsilon_B}{k_BT}\right)\right]\Psi \tag{37}$$

$$\left(\frac{A_2}{Vk_BT}\right)_{\text{pert}} = -\frac{8}{b_Ab_B}\left[\eta_A^2 b_B\left(\frac{\varepsilon_A}{k_BT}\right)^2 + 2\eta_A\eta_B b_{AB}\left(\frac{\varepsilon_{AB}}{k_BT}\right)^2 + \eta_B^2 b_A\left(\frac{\varepsilon_B}{k_BT}\right)^2\right]\frac{(1-\eta)^4}{\left(1+4\eta+4\eta^2\right)}\left(\Psi + \eta\frac{\partial\Psi}{\partial\eta}\right). \tag{38}$$

In terms of η_A and η_B, $\xi_{\alpha\beta}$ in functions Q and Z are given by

$$\xi_{AA} = \eta_A + \eta_B\left(\frac{b_A}{b_B}\right)^{1/3},\ \xi_{BB} = \eta_A\left(\frac{b_B}{b_A}\right)^{1/3} + \eta_B,\ \xi_{AB} = \eta_A\left(\frac{b_B}{b_{AB}}\right)^{1/3} + \eta_B\left(\frac{b_A}{b_{AB}}\right)^{1/3}. \tag{39}$$

Finally, the elements of the interaction matrix are given by

$$W_{ij} = \left[\frac{\partial^2\left(\frac{\Delta A}{Vk_BT}\right)_{\text{ref+pert}}}{\partial\eta_i\partial\eta_j}\right]_{V,T,\eta_k} \quad (i,j=1,2) \tag{40}$$

where subscripts 1 and 2 denote segments A and B, respectively. Subscript η_k denotes that the derivative with respect to η_i is taken while the other $\eta_{k\neq i}$ is held constant.

III. Results and Discussion

We first note common shortcomings of molecular thermodynamic models, including the PHSC equation of state, that become apparent when models are applied to fit experimental data for real systems. Although theories for polymeric fluids use molecular parameters that are independent of temperature and polymer molecular weight, the theoretical phase diagrams of mixtures do not always show quantitative agreement with experiment over the entire range of polymer molecular weight and temperature. In

addition, it is a challenging task to correlate both UCST and LCST behaviors of polymer solutions and blends using only one adjustable binary parameter. To correlate quantitatively the phase diagrams of mixtures, it is often necessary to introduce a temperature dependence in the binary adjustable parameter or to use several binary parameters.

In equation-of-state theories for polymer blends, the theoretical phase diagrams are also sensitive to pure-component parameters. To achieve quantitative correlations of the phase diagrams of mixtures by equation-of-state theories, the pure-component parameters of one polymer may be slightly adjusted from those that give the optimum correlations of pure-component data.

1. Computation Procedure. To apply the PHSC equation of state to real diblock copolymer melts, theory requires three equation-of-state parameters for each of the parent homopolymers. The PHSC equation of state can then describe thermodynamic properties of a homopolymer melt: segment diameter σ, well depth ε, and r/M where r is the number of segments per molecule and M is the molecular weight of polymer. To compute r for a given polymer, we use the weight-average molecular weight of polymer M_w.

For homopolymers, the equation-of-state parameters are regressed from pure-component pressure-volume-temperature (pVT) data[29-32] in the liquid state. Table 2 gives the PHSC equation-of-state parameters with λ=1.455 for common polymers studied in this work. For each homopolymer, these parameters were regressed from the pVT data over the entire liquid range reported in the literature. Experimental pVT data are usually collected to about 2000 bar. Except for poly(α-methylstyrene), the equation-of-state parameters given in Table 2 are those that give the optimum correlations of pVT data.

In the present theory, we use the optimum set of equation-of-state parameters regressed from experimental pVT data because there is no physical basis for representing the repeat unit of homopolymer by a single sphere. It is possible to establish correlations

between the chemical structure of homopolymer and the equation-of-state parameters that give the optimum correlations of homopolymer pVT data.[33]

For poly(α-methylstyrene), we use another set of equation-of-state parameters because theory with these parameters correlates better the dependence of coexistence curves on the molecular weight of polymer in the blend polystyrene/poly(α-methylstyrene). The equation-of-state parameters for poly(α-methylstyrene) were obtained by first presetting σ to a reasonable value and then regressing for ε and r/M. For all homopolymers including poly(α-methylstyrene), the PHSC equation of state provides excellent correlations of pure-component pVT data.

The PHSC equation of state also requires adjustable binary parameter κ_{AB} (in Eq. (33)) that reflects the strength of attractive interaction between a pair of unlike segments A and B. In this work, parameter κ_{AB} is obtained from the coexistence curve for the binary blend containing parent homopolymers. Details of the PHSC equation of state for homopolymer blends are given in Reference 24.

With κ_{AB} obtained in this manner, the function $F(q)$ defined by Eq. (17) is used to predict the stability limit for a disordered diblock copolymer melt. The stability limit is defined as the extreme temperature when the temperature that satisfies $F(q) = 0$ is plotted against q. This extreme temperature is the order-to-disorder transition temperature of a diblock copolymer melt. Equation (17) expresses $F(q)$ in terms of the second-order vertex functions defined by Eq. (16). In this work, the packing fraction of a disordered system is used as the packing fraction in the second-order vertex functions. The packing fraction of a disordered system is calculated through Eq. (19) using Eqs. (22) and (29) as the reference and perturbation terms, respectively, for the Helmholtz energy. Unless otherwise specified, all calculations are made at zero pressure, an excellent approximation for diblock copolymer melts and homopolymer blends near atmospheric pressure.

2. Poly(styrene-*block*-α-methylstyrene). We first apply the model to poly(styrene-*block*-α-methylstyrene) (PS-PMS) diblock copolymer melts. Because the chemical structure of polystyrene (PS) is similar to that of poly(α-methylstyrene) (PMS), the homopolymer blend PS/PMS is one of few nearly compatible polymer blends that exhibit UCST behavior in the temperature range accessible by standard experiments. The miscible blend of PS with PMS, however, does not exhibit LCST behavior at elevated temperature, probably because the disparity in compressibility between PS and PMS is not strong enough to induce phase separation at elevated temperature. All experimental data used here are those obtained with nearly monodisperse polymers having polydispersity indices of less than 1.09.

Binary parameter κ_{AB} between styrene and α-methylstyrene segments is obtained from coexistence curves for the homopolymer blend PS/PMS reported by Lin and Roe.[34] Figure 2a compares the theoretical coexistence curves with experiment for the system PS(M_w=49000) / PMS(M_w=56100) and system PS(M_w=58400) / PMS(M_w=62100). The PHSC equation of state for binary homopolymer blends is given in Reference 24. Theory and experiment show good agreement using κ_{AB}=–0.000207. Consistent with experiment, theory predicts only UCST behavior in the system shown in Figure 1a.

Using binary parameter κ_{AB}=–0.000207, we are ready to predict the order-to-disorder transition temperature T_{ODT} for PS-PMS diblock copolymer melts that show UCOT behavior. Although precise measurements of T_{ODT} are not reported for PS-PMS diblock copolymers, there are several PS-PMS diblock copolymers having different molecular weights and copolymer compositions that are known to be either in the disordered or in the ordered state at a given temperature[34].

Figure 2b shows the locus of temperatures that satisfies $F(q)$=0 for PS(M_w=120000)-PMS(M_w=135000) and PS(M_w=130000)-PMS(M_w=50000) diblock copolymer melts studied by Kim and Han.[35,36] The abscissa of Figure 2b is x and depends on the wave number q as defined by Eq. (15). The maximum temperature on the

curve is the order-to-disorder transition temperature; above that temperature, a disordered system is stable. In Figure 2b, the maximum temperature occurs at x=3.8 and 4.1 for the solid and broken curves, respectively. Using differential scanning calorimetry and rheological measurements, Kim and Han report that the order-to-disorder transition temperatures for the copolymers shown in Figure 2b should lie below the glass transition temperature for PMS, about 170 °C.[35,36]

Similar to other equation-of-state theories, our theoretical phase diagrams of polymer blends are also sensitive to binary parameter κ_{AB}. For the system PS(M_w=58400) / PMS(M_w=62100) shown in Figure 2a, the theoretical UCST with κ_{AB}=–0.000107 is about 140 °C higher than that with κ_{AB}=–0.000207. Similarly, for the diblock copolymer PS(M_w=120000)-PMS(M_w=135000) shown in Figure 2b, the theoretical UCOT with κ_{AB}=–0.000107 is about 120 °C higher than that with κ_{AB}=–0.000207.

The present model slightly overestimates T_{ODT} for PS-PMS diblock copolymer melts. Kim and Han[35] mention that when the RPA is combined with incompressible Flory-Huggins theory, the prediction also overestimates T_{ODT} for PS-PMS diblock copolymer melts when the binary parameter is obtained from the phase diagrams shown in Figure 2a. As discussed by Fredrickson and Helfand[37], a possible explanation for this behavior is the fluctuation effect that is not considered in the present model. For a given binary parameter between copolymer segments, the theory by Fredrickson and Helfand[37] (that includes the fluctuation effect) predicts T_{ODT} associated with UCOT at a temperature lower than the T_{ODT} predicted by the theory that neglects the fluctuation effect. The fluctuation effect is negligible only in the limit of infinite molecular weight of diblock copolymers.[37] Because the RPA calculation is a total prediction, agreement of theoretical prediction with experiment is encouraging.

3. Poly(styrene-*block*-butadiene). The order-to-disorder transition temperature associated with UCOT is also reported for a poly(styrene-*block*-butadiene) (PS-PBD) diblock copolymer melt by Zin and Roe.[38,39] For PS-PBD diblock copolymer melts, the binary parameter κ_{AB} between styrene and butadiene segments is obtained from the cloud-point curves for the homopolymer blend PS/PBD reported by Roe and Zin.[40] Figure 3a compares the theoretical coexistence curves with experiment for the system PS(M_w=3500)/PBD(M_w=2660) and system PS(M_w=2400)/PBD(M_w=2660). Although theory quantitatively represents the dependence of UCST on the molecular weight of PS, the theoretical coexistence curves are narrow compared to experiment.

Using κ_{AB}=0.00917 obtained from Figure 3a, Figure 3b shows the locus of temperatures that satisfies $F(q)$=0 for the PS(M_w=7600)-PBD(M_w=20400) diblock copolymer melt studied by Roe and Zin.[38,39] In Figure 3b, the maximum temperature occurs at x=4.2. The theoretical T_{ODT} is 215 °C that is about 70 °C higher than the measured T_{ODT}. For the PS-PBD diblock copolymer shown in Figure 3b, Han *et al.*[41] also report that the RPA combined with the incompressible Flory-Huggins theory predicts T_{ODT} at 221 °C. Similarly, for the same diblock copolymer, the analysis based on the Hong-Noolandi theory by Baek et al.[42] predicts T_{ODT} at about 215 °C.

In addition to the fluctuation effect,[37] for PS-PBD diblock copolymer melts, the discrepancy between theoretical prediction and measured T_{ODT} may be caused by the uncertainty in binary parameter κ_{AB} because κ_{AB} between styrene and butadiene segments is obtained from the mixtures of oligomers shown in Figure 3a. Furthermore, this discrepancy may also be due to the difference between the microstructure of PBD homopolymer used in Reference 40 and that of PBD block in the PS-PBD diblock copolymer studied in Reference 38 and 39. All polymers considered in Figures 3a and 3b are essentially monodisperse having polydispersity indices less than 1.13.

For systems such as PS-PMS and PS-PBD diblock copolymer melts that show only UCOT behavior, predicted order-to-disorder transition temperatures by the present

model may be close to those predicted by the RPA combined with the incompressible Flory-Huggins theory.[15,18,35]

4. Poly(styrene-*block*-*n*-butyl methacrylate). Next, we consider the poly(styrene-*block*-*n*-butyl methacrylate) diblock copolymer melt that has recently been found to exhibit both an UCOT and a LCOT by Russell *et al.*[10-12] All experimental data in this section use deuterated polystyrene (PSD); the diblock copolymer consisting of PSD and poly(*n*-butyl methacrylate) (PBMA) is denoted as PSD-PBMA. Phase equilibrium calculations, however, are performed using the equation-of-state parameters for normal polystyrene. For theoretical calculations, the poly(styrene-*block*-*n*-butyl methacrylate) diblock copolymer is denoted as PS-PBMA.

Shortly after the discovery of both UCOT and LCOT behaviors in PSD-PBMA diblock copolymer melts, Hammouda *et al.*[11] used small-angle neutron scattering to show that the parent homopolymer blend PSD/PBMA exhibits both an UCST and a LCST in a temperature-composition diagram. These experiments on the system containing PSD and PBMA indicate that the phase behavior of a diblock copolymer melt that exhibits both an UCOT and a LCOT also follows closely the phase behavior of the binary blend containing parent homopolymers.

Using the PHSC equation of state, our main objective here is to establish a quantitative relation between the phase behavior of PS-PBMA diblock copolymer melts and that of binary homopolymer blends containing PS and PBMA. To perform quantitative analysis, it is necessary to use a unique set of binary and equation-of-state parameters for diblock copolymer melts as well as for parent homopolymer blends.

Consistent with experiment, the PHSC equation of state predicts both an UCST and a LCST in a temperature-composition diagram for homopolymer blends containing PS and PBMA. Theory also predicts UCOT behavior as well as LCOT behavior in PS-PBMA diblock copolymer melts. Parts a and b of Figure 4 show, respectively, the

theoretical coexistence curves for the blend PS/PBMA and the locus of temperatures that satisfies $F(q)=0$ for PS-PBMA diblock copolymer melts with $\kappa_{AB}=0.00782$. In Figure 4b, the maximum temperature occurs at $x=3.8$ for both diblock copolymers. The numbers in these figures are the molecular weights of homopolymers and the molecular weights of blocks comprising diblock copolymers in g/mol. Binary parameter κ_{AB} was adjusted such that theory roughly agrees with experiment for both homopolymer blends[9] and diblock copolymer melts[10,12] for the molecular weights shown in Figure 4.

For the homopolymer blend PS/PBMA shown in Figure 4a, precise comparison of theory with experiment by Hammouda *et al.*[11] is difficult because the exact locations of cloud-point temperatures are not reported. In addition, the polymers used by Hammouda *et al.*[11] are polydisperse with polydispersity indices of about 2.0. Nevertheless, theoretical UCSTs and LCSTs are at least in semiquantitative agreement with experiment for the molecular weights shown in Figure 4a.[11]

The PSD-PBMA diblock copolymers studied by Russell *et al.*[10,12] are nearly monodisperse with polydispersity indices of less than 1.04. For the system 47000-*block*-52000 in Figure 4b, theoretical UCOT and LCOT are about 20 °C lower than those determined by rheological measurements.[12] The rheological measurements[12] on the sample 34500-*block*-33500 also indicate that this copolymer is in the disordered state from 100 to 275 °C. Therefore, theory with $\kappa_{AB}=0.00782$ may slightly underestimate LCOT and UCOT for PS-PBMA diblock copolymer melts.

Figure 5 shows the theoretical T_{ODT} for PS-PBMA diblock copolymer melts as functions of polymer molecular weight and copolymer composition. The shape of curves in this figure resemble the coexistence curves for blends of parent homopolymers shown in Figure 4a. However, the ordered region in Figure 5 is narrow compared to the two-phase region in Figure 4a.

Overall agreement of theory with experiment is encouraging for the system containing PS and PBMA. Using the same set of binary and equation-of-state

parameters, the PHSC equation of state shows semiquantitative agreement with experiment for the phase behavior of diblock copolymer melts as well as that for parent homopolymer blends. We conclude that within the prediction by the PHSC equation of state combined with the RPA, the LCOT and UCOT behavior for PS-PBMA diblock copolymer melts follows closely the LCST and UCST behavior for PS/PBMA homopolymer blends.

For PS-PBMA diblock copolymer melts that exhibit both UCOT and LCOT behaviors, the RPA combined with the compressible lattice-cluster theory[19] and that combined with the lattice-fluid equation of state[27] (i.e., a compressible Flory-Huggins theory) may also predict the results similar to those obtained with the PHSC equation of state. Although the PHSC equation of state correlates pVT data of homopolymer melts slightly better than the lattice-fluid equation of state and the compressible lattice-cluster theory,[24,33] the latter theories are also capable of predicting both UCST and LCST behaviors in homopolymer blends. However, to provide a fair comparison of the PHSC equation of state with the above-mentioned compressible lattice theories, it would be necessary to perform consistent fitting procedures to obtain both the pure-component and binary parameters.

5. Effect of Pressure. Finally, we consider the effect of pressure on the phase behavior of diblock copolymer melts and that of the binary blends containing parent homopolymers studied in this work.

For diblock copolymer melts that exhibit UCOT behavior, the pressure dependence of T_{ODT} was recently measured for styrene-isoprene (SI),[44] (ethylene-propylene)-ethylethylene (PEP-PEE),[45] and (ethylene-propylene)-dimethylsiloxane (PEP-PDMS)[46] diblock copolymers. The measured T_{ODT} shows complicated dependence on the pressure. While T_{ODT} for SI diblock copolymers rises with increasing pressure at a rate of about +20 °C/kbar over the range 0 to 0.6 kbar,[44] T_{ODT} for PEP-PEE

diblock copolymers decreases with increasing pressure at a rate of about –20 °C/kbar for pressures up to 1 kbar.[45] On the other hand, T_{ODT} for PEP-PDMS diblock copolymers first decreases and then rises with increasing pressure over the range 0 to 1.5 kbar.[46]

A theoretical study by Dudowicz and Freed[19,47] investigated the effect of pressure on the phase behavior of diblock copolymer melts and that of binary blends containing parent homopolymers. Using the compressible lattice-cluster theory, Dudowicz and Freed[19] presented a semiquantitative analysis of systems containing PS and poly(vinyl methyl ether) (PVME). Both experiment and theory show that the homopolymer blend of PS and PVME exhibits LCST behavior. Although the phase behavior of PS-PVME diblock copolymer melts has not yet measured, the theory by Dudowicz and Freed[19] predicts that a disordered PS-PVME diblock copolymer melt exhibits disorder-to-order transition upon heating. Recently, Dudowicz and Freed[47] also presented a more rigorous analysis of the homopolymer blend of PS and PVME by the compressible lattice-cluster theory.

We now discuss the predicted pressure dependence of T_{ODT} by the PHSC equation of state. In the plot of temperature that satisfies $F(q)=0$, shown in Figures 2b, 3b, and 4b, the extreme temperature (i.e., T_{ODT}) occurs at x^* that is nearly independent of pressure. (x^* is related to the wave number q^* by Eq. (15).) Therefore, for each system, T_{ODT} is computed as a function of pressure from the condition $F(q^*)=0$ using q^* at zero pressure. We assume that binary parameter κ_{AB} is independent of pressure.

For systems containing PS and PMS discussed in Figure 2, part a of Figure 6 shows the predicted pressure dependence of critical solution temperature (T_C) for a PS/PMS blend and that of T_{ODT} for a PS-PMS diblock copolymer melt. These systems show UCOT behavior in the diblock copolymer melt and UCST behavior in the binary blend of parent homopolymers. As the pressure rises, the predicted T_C and T_{ODT} first decrease and then become almost independent of pressure.

For systems containing PS and PBD discussed in Figure 3, part b of Figure 6 shows the pressure dependence of predicted T_C for a PS/PBD blend and that of T_{ODT} for a PS-PBD diblock copolymer melt. These systems also show UCST and UCOT behavior. For the PS-PBD diblock copolymer shown in Figure 6b, the predicted T_{ODT} rises with increasing pressure. Recent experiment by Hadjuk *et al.*[44] shows that for styrene-isoprene diblock copolymers that exhibit UCOT behavior, the measured T_{ODT} also rises with increasing pressure at a rate of about +20 °C/kbar over the range 0 to 0.6 kbar. Because the structure of isoprene is similar to that of butadiene, for styrene-diene diblock copolymers, there may be a general trend that T_{ODT} associated with UCOT behavior rises with increasing pressure.

For systems containing PS and PBMA shown in Figure 4, Figure 7a shows the predicted pressure dependence of T_C for a PS/PBMA blend (exhibiting both UCST and LCST behavior) and that of T_{ODT} for a PS-PBMA diblock copolymer melt (exhibiting both UCOT and LCOT behavior). Figure 7b shows the predicted T_{ODT} as functions of pressure and copolymer composition for a PS-PBMA diblock copolymer with M_w=99000. In these systems, miscibility is enhanced by raising the pressure. There is a similar dependence on the pressure between the predicted T_{ODT} for a PS-PBMA diblock copolymer melt and the predicted T_C for a blend of parent homopolymers PS and PBMA.

For systems containing PS and PBMA, the predicted LCST and T_{ODT} associated with LCOT behavior are very sensitive to the pressure. Our theory predicts that for a PS/PBMA blend, LCST rises with increasing pressure at a rate about +200 °C/kbar that is one order of magnitude larger than the measured rates for mixtures of ethylene-vinyl acetate copolymer with a chlorinated polyethylene[48] and for the blend of PSD and PVME[49] that also exhibit LCST behavior. Similarly, the analysis by Rudolf and Cantow shows that the lattice-fluid theory and the equation-of-state theory by Patterson also predicts a very large pressure dependence of LCST in polymer blends.[50,51]

Conclusions

The PHSC equation of state[20-24] is combined with the RPA[5,14-17] for diblock copolymer melts to represent UCOT behavior as well as LCOT behavior in compressible diblock copolymer melts. The present model follows closely the RPA for incompressible diblock copolymer solutions by Fredrickson and Leibler[17] based on the Flory-Huggins lattice theory.[18]

However, contrary to other models for diblock copolymer melts and solutions,[12,15,16] we use an equation-of-state theory in continuous space. To demonstrate that off-lattice equation-of-state theories can also be combined with the RPA, a systematic procedure is first presented to combine the RPA with the PHSC equation of state for diblock copolymer melts. This procedure identifies the elements of the interaction matrix in the RPA as the second derivatives of the nonideal Helmholtz energy density with respect to the packing fractions of segments comprising a diblock copolymer.

Theory is compared with experiment for several styrene-based diblock copolymer melts using the binary parameters obtained from the coexistence curve for the binary blend of relevant parent homopolymers. Using the binary parameter obtained in this manner, the order-to-disorder transition temperature of a diblock copolymer melt is predicted. For PS-PMS and PS-PBD diblock copolymer melts that show only UCOT behavior, the predicted order-to-disorder transition temperatures by the present model are close to those predicted by the RPA combined with the incompressible Flory-Huggins theory.[15,18,35]

The advantage of the present model lies in its applicability to systems that exhibit LCOT behavior at elevated temperature due to the equation-of-state effect. Our model is also capable of predicting the effect of pressure on the order-to-disorder transition temperatures of diblock copolymer melts.

To demonstrate the present model's capabilities for representing LCOT behavior, our theory is applied to the PS-PBMA diblock copolymer melt that was recently found to show both LCOT and UCOT behavior.[10-12] The phase behavior of PS-PBMA diblock copolymer melts follows closely that of PS/PBMA homopolymer blends that exhibit both UCST and LCST behaviors in temperature-composition diagrams. Using the same set of binary and equation-of-state parameters, the PHSC equation of state, combined with the RPA, shows semiquantitative agreement with experiment for PS-PBMA diblock copolymer melts as well as for PS/PBMA homopolymer blends.

Our model predicts that for a PS-PMS diblock copolymer melt, the theoretical T_{ODT} decreases with increasing pressure. Conversely, theory predicts that for a PS-PBD diblock copolymer melt, T_{ODT} rises with increasing pressure. For a PS-PBMA diblock copolymer melt, the theoretical T_{ODT} associated with LCOT behavior and that associated with UCOT behavior rises and decreases, respectively, with increasing pressure. The predicted T_{ODT} associated with LCOT behavior shows a strong dependence on the pressure that does not agree with limited experimental data concerning the pressure dependence of LCST behavior in polymer blends.

For a given pair of homopolymers, it may be possible to predict the type of phase behavior (e.g., UCST or LCST behavior) by the present theory with $\kappa_{AB}=0$. However, quantitative predictions of phase separation temperatures require additional information to determine binary parameter κ_{AB} because phase separation temperatures in polymer blends and diblock copolymer melts are highly sensitive to κ_{AB}.

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Table 1. Coefficients c_k for Function Ψ with λ=1.455

c_1	0.6934288007E+00
c_2	0.1031329977E+01
c_3	0.3231430915E+00
c_4	−0.7601028313E+00
c_5	−0.1898718617E+01
c_6	−0.1129836508E+01
c_7	−0.5829453430E+00
c_8	−0.4161049123E+01
c_9	−0.8040279885E+01
c_{10}	0.2470320458E+02

Table 2. Equation-of-State Parameters for Homopolymers with λ=1.445

				% rms [a] deviation	
Polymer	r/M (mol/g)	σ (Å)	ε/k_B (K)	ρ_{liq}	ref [b]
poly(*cis*-1,4-butadiene)	0.03382	3.631	329.2	0.07	29 (63)[c]
polystyrene	0.02123	4.059	409.9	0.09	30 (69)
poly(α-methylstyrene)	0.02188	3.965	414.5	0.15	31 (86)
poly(*n*-buthyl methacrylate)	0.02942	3.595	311.5	0.24	32 (168)

[a] root-mean-square relative deviations. [b] Reference. [c] Numbers in parentheses indicate numbers of data points used in the correlations.

Figure Captions

Figure 1. Schematic of a diblock copolymer melt consisting of segments A and B represented by filled and open spheres, respectively, in continuous space.

Figure 2. (a) Comparison of theoretical coexistence curves with experiment for the system polystyrene/poly(α-methylstyrene)[34] (PS/PMS,κ_{AB}=–0.000207). (b) Predicted locus of temperatures that satisfies $F(q)$=0 for poly(styrene-*block*-α-methylstyrene) (PS-PMS) diblock copolymer melts[35] as a function of x defined by Eq. (15). The maximum on the curve shown in part b is the predicted order-to-disorder transition temperature T_{ODT} associated with UCOT. The diblock copolymers shown here have T_{ODT} below the glass-transition temperature of PMS, about 170 °C.

Figure 3. (a) Comparison of theoretical coexistence curves with experiment for the system polystyrene/polybutadiene[40] (PS/PBD, κ_{AB}=0.00917). (b) Predicted locus of temperatures that satisfies $F(q)$=0 for a poly(styrene-*block*-butadiene) (PS-PBD) diblock copolymer melt[35] as a function of x defined by Eq. (15). The maximum on the curve shown in part b is the predicted order-to-disorder transition temperature associated with UCOT, about 70 °C higher than the measurement by Zin and Roe.[38,39]

Figure 4. Theoretical phase diagrams for systems containing polystyrene (PS) and poly(n-butyl methacrylate) (PBMA) with κ_{AB}=0.00782. (a) Coexistence curves for the homopolymer blend PS/PBMA. (b) Predicted locus of temperatures that satisfies $F(q)$=0 for PS-PBMA diblock copolymer melts. The maximum and minimum on the curve shown in part b are the predicted

UCOT and LCOT, respectively. For the 47000-*block*-52000 diblock copolymer in part b, theoretical UCOT and LCOT are about 20 °C lower than those determined by rheological measurements.[12] The numbers in these figures denote the molecular weights of parent homopolymers and those of blocks comprising diblock copolymers in g/mol.

Figure 5. Theoretical T_{ODT} for PS-PBMA diblock copolymer melts as functions of polymer molecular weight and copolymer composition.

Figure 6. Predicted pressure dependence of critical solution temperature (T_C) for a parent homopolymer blend and that of the order-to-disorder transition temperature (T_{ODT}) for a diblock copolymer melt: (a) Systems containing PS and PMS shown in Figure 2, (b) Systems containing PS and PBD shown in Figure 3. These systems exhibit UCST and UCOT behavior. κ_{AB} is independent of pressure.

Figure 7. (a) Predicted pressure dependence of critical solution temperature (T_C) for a PS/PBMA blend and that of the order-to-disorder transition temperature (T_{ODT}) for a PS-PBMA diblock copolymer melt shown in Figure 4. (b) Theoretical T_{ODT} as functions of pressure and copolymer composition for a PS-PBMA diblock copolymer with M_w=99000. κ_{AB} is independent of pressure.

Figure 1

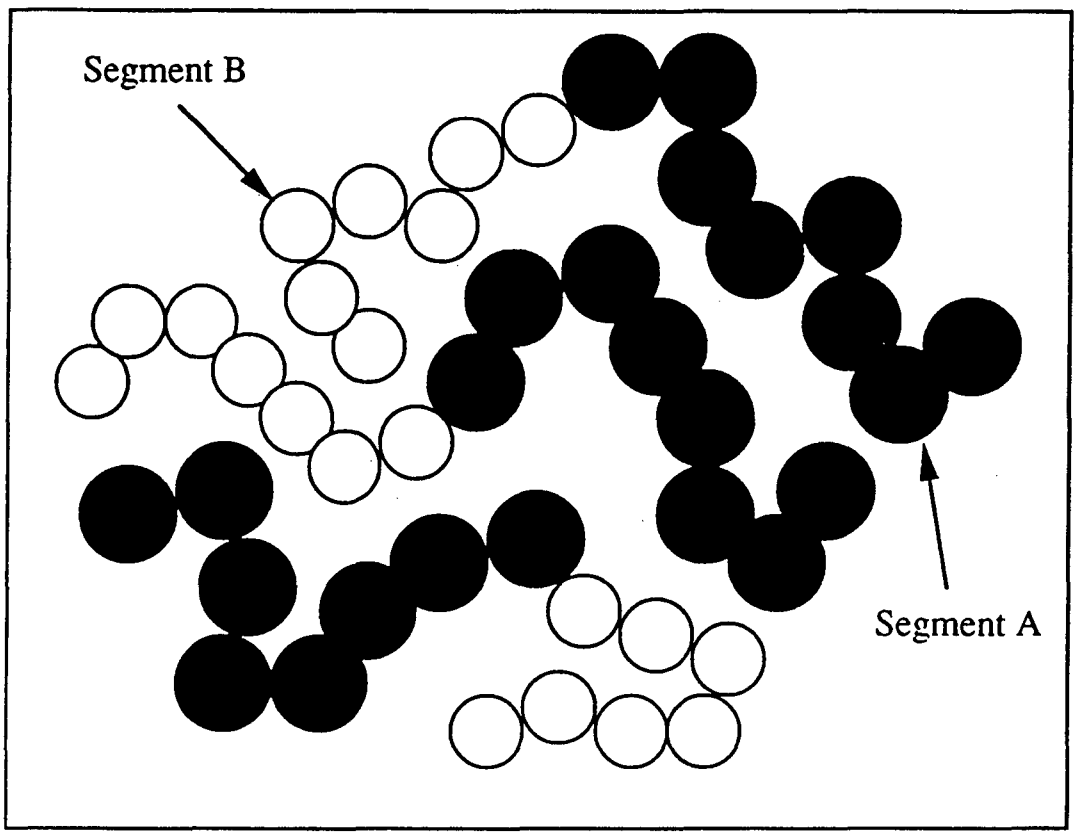
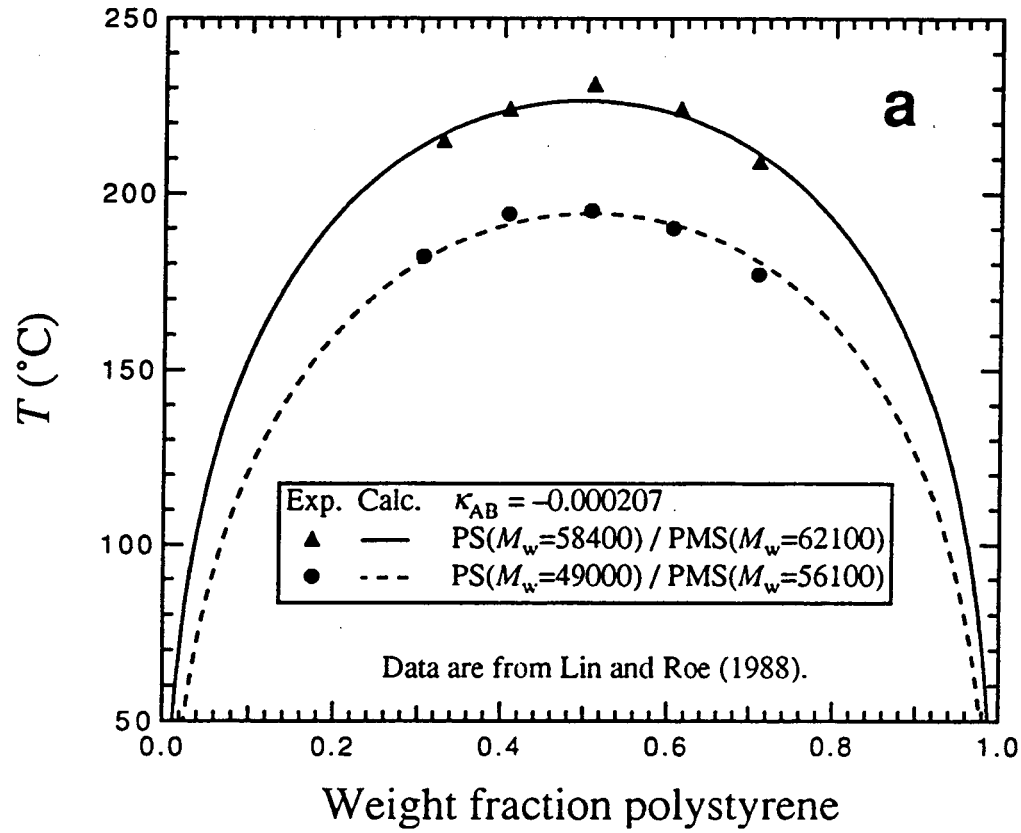


Figure 2


a
T (°C)
250
200
150
100
50
0.0
0.2
0.4
0.6
0.8
1.0
Exp. Calc. κ_{AB} = –0.000207
PS(M_w=58400) / PMS(M_w=62100)
PS(M_w=49000) / PMS(M_w=56100)
Data are from Lin and Roe (1988).
Weight fraction polystyrene

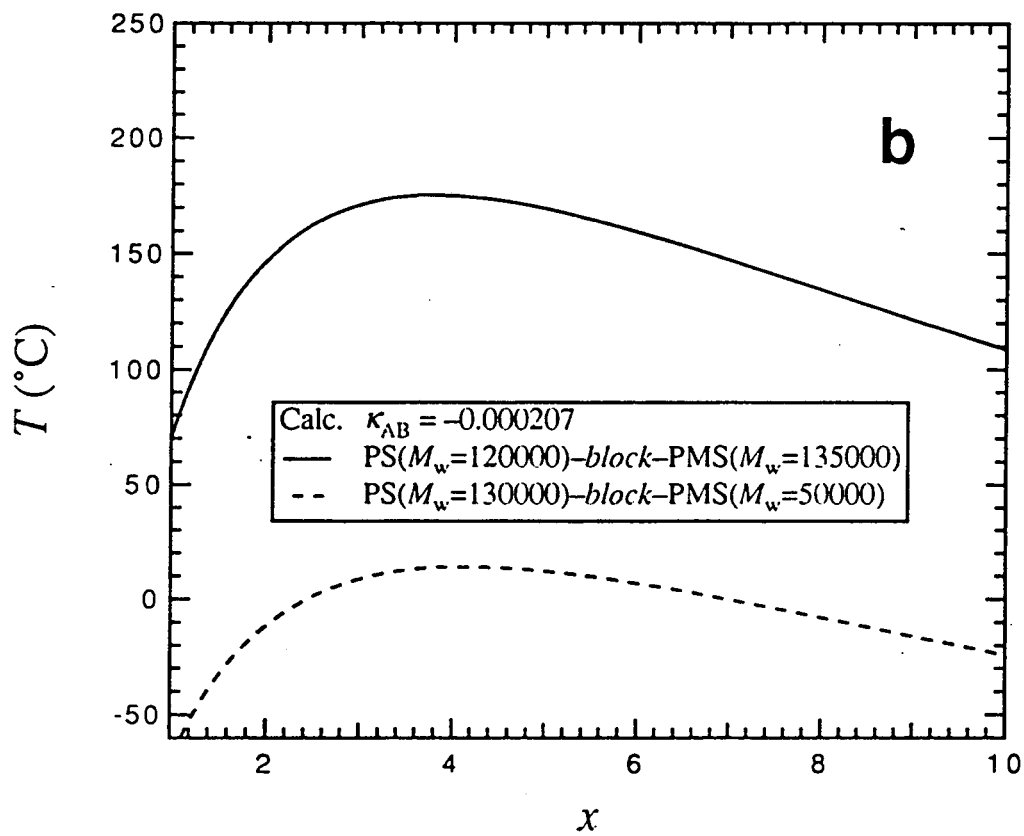
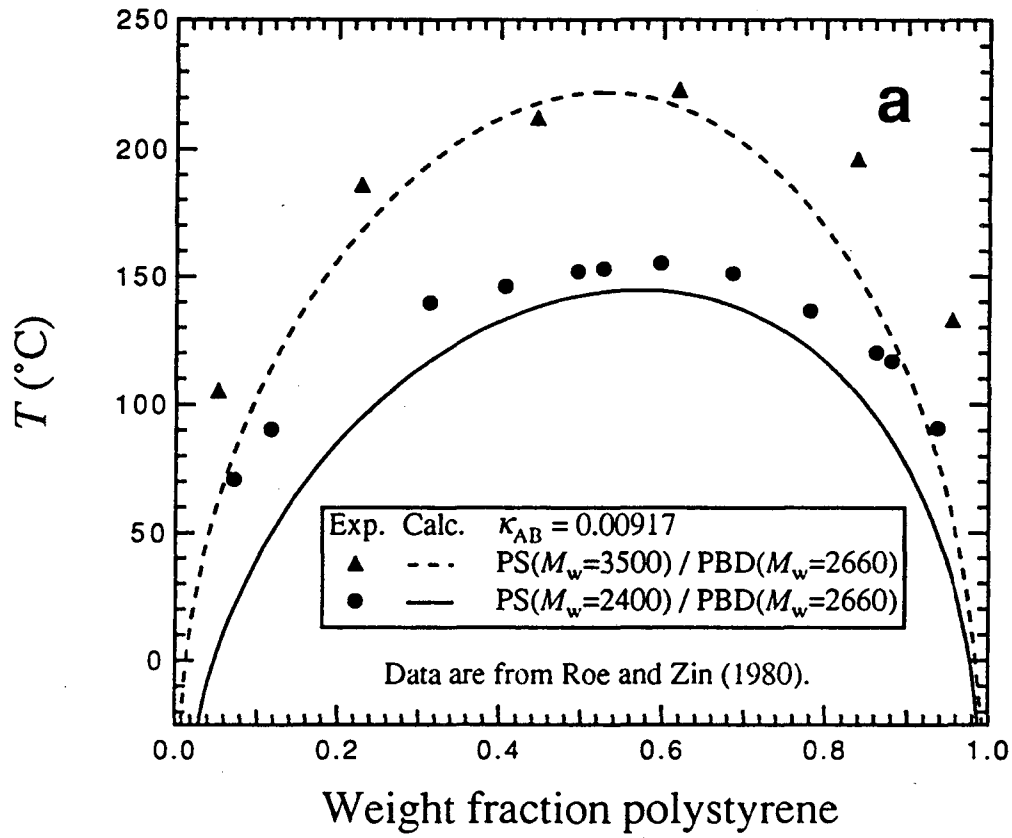

b
T (°C)
250
200
150
100
50
0
-50
2
4
6
8
10
Calc. κ_{AB} = –0.000207
PS(M_w=120000)–*block*–PMS(M_w=135000)
PS(M_w=130000)–*block*–PMS(M_w=50000)
x

Figure 3


a
T (°C)
250
200
150
100
50
0
0.0
0.2
0.4
0.6
0.8
1.0
Weight fraction polystyrene
Exp. Calc. κ_{AB} = 0.00917
PS(M_w=3500) / PBD(M_w=2660)
PS(M_w=2400) / PBD(M_w=2660)
Data are from Roe and Zin (1980).

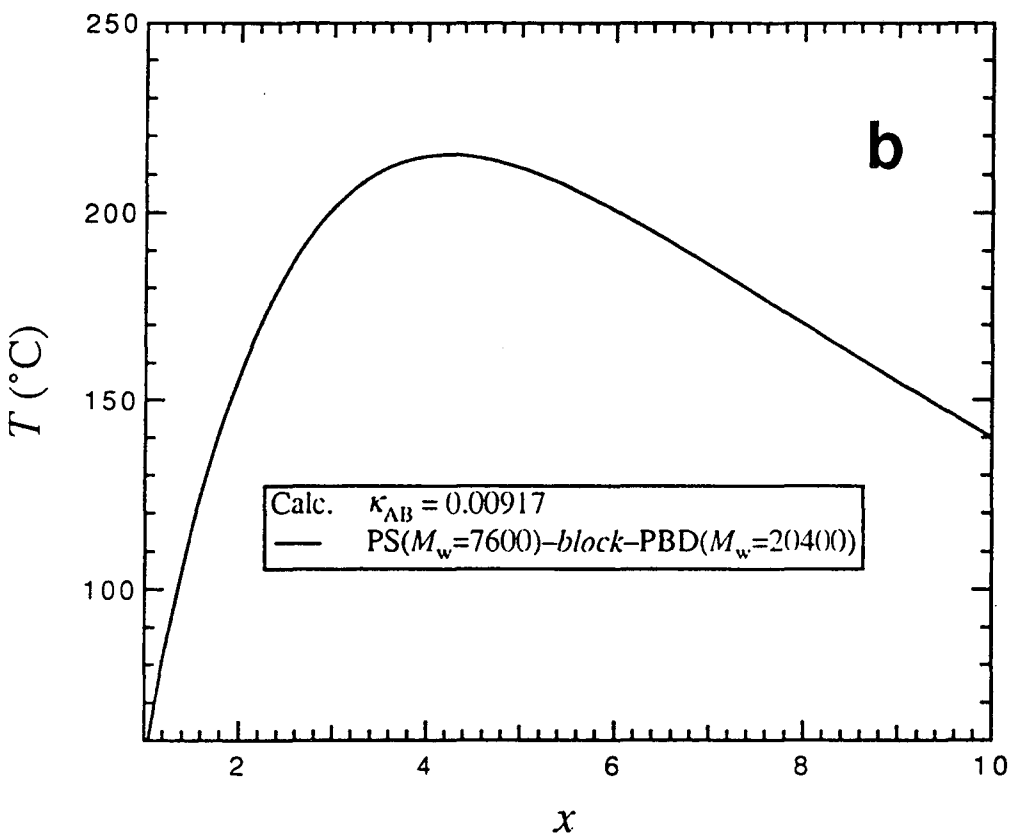
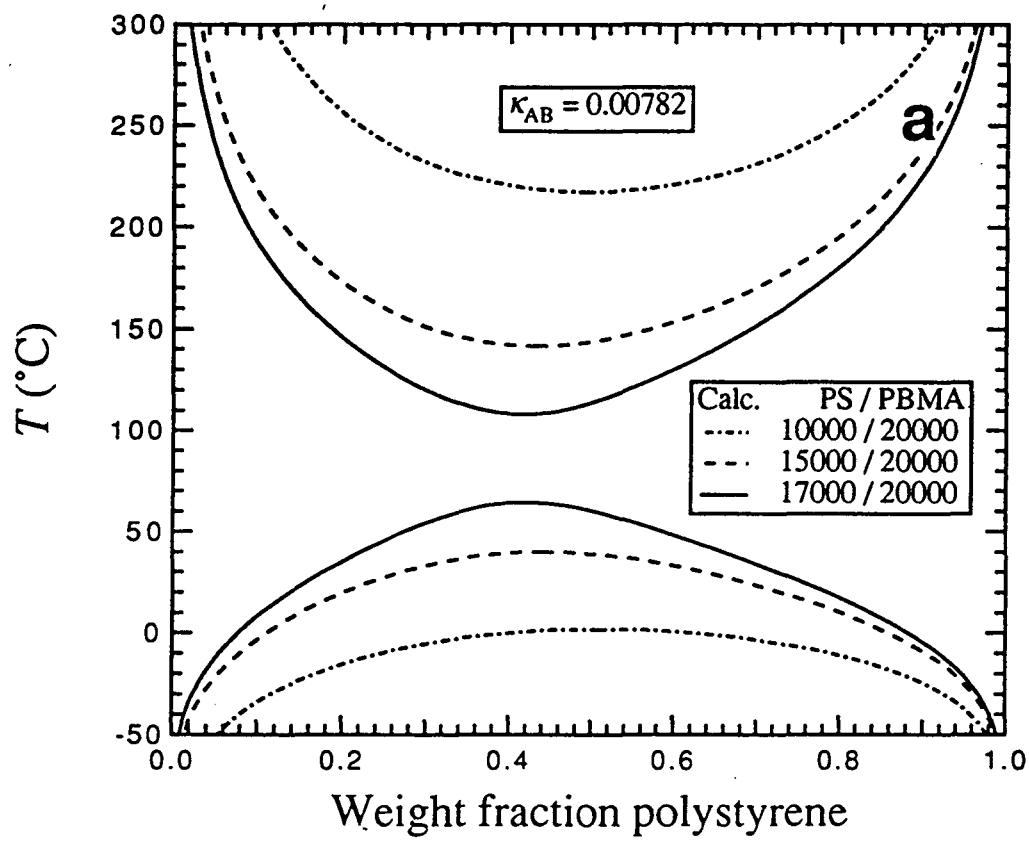

b
T (°C)
250
200
150
100
2
4
6
8
10
x
Calc. κ_{AB} = 0.00917
PS(M_w=7600)–*block*–PBD(M_w=20400)

Figure 4


a
$\kappa_{AB} = 0.00782$
Calc. PS / PBMA
10000 / 20000
15000 / 20000
17000 / 20000
T (°C)
Weight fraction polystyrene
300
250
200
150
100
50
0
-50
0.0
0.2
0.4
0.6
0.8
1.0

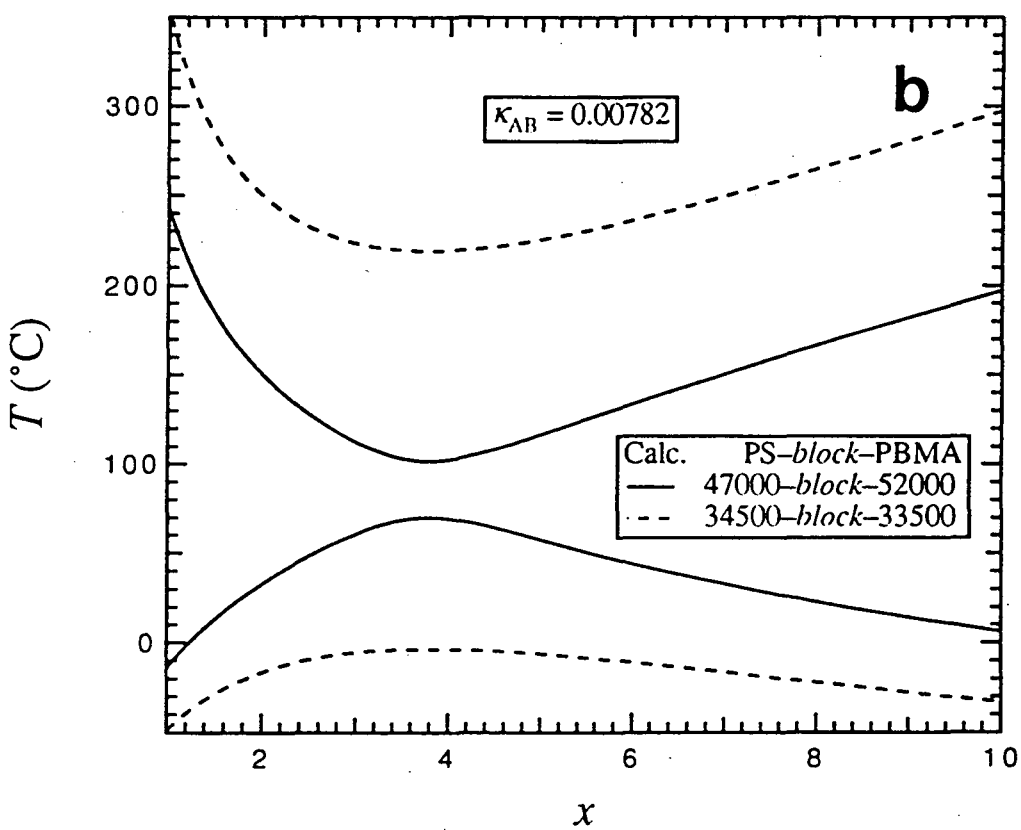

b
$\kappa_{AB} = 0.00782$
Calc. PS–*block*–PBMA
47000–*block*–52000
34500–*block*–33500
T (°C)
x
300
200
100
0
2
4
6
8
10

Figure 5

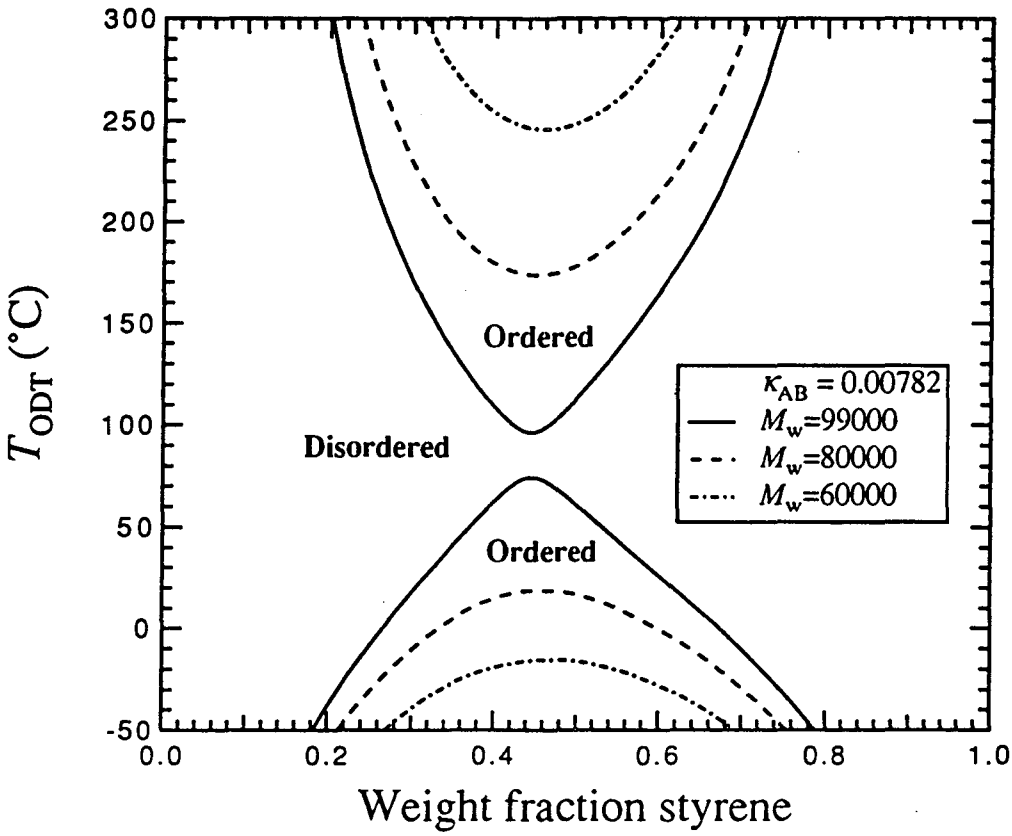

300
250
200
150
100
50
0
-50
0.0
0.2
0.4
0.6
0.8
1.0
T_{ODT} (°C)
Weight fraction styrene
Ordered
Disordered
Ordered
κ_{AB} = 0.00782
M_w=99000
M_w=80000
M_w=60000

Figure 6

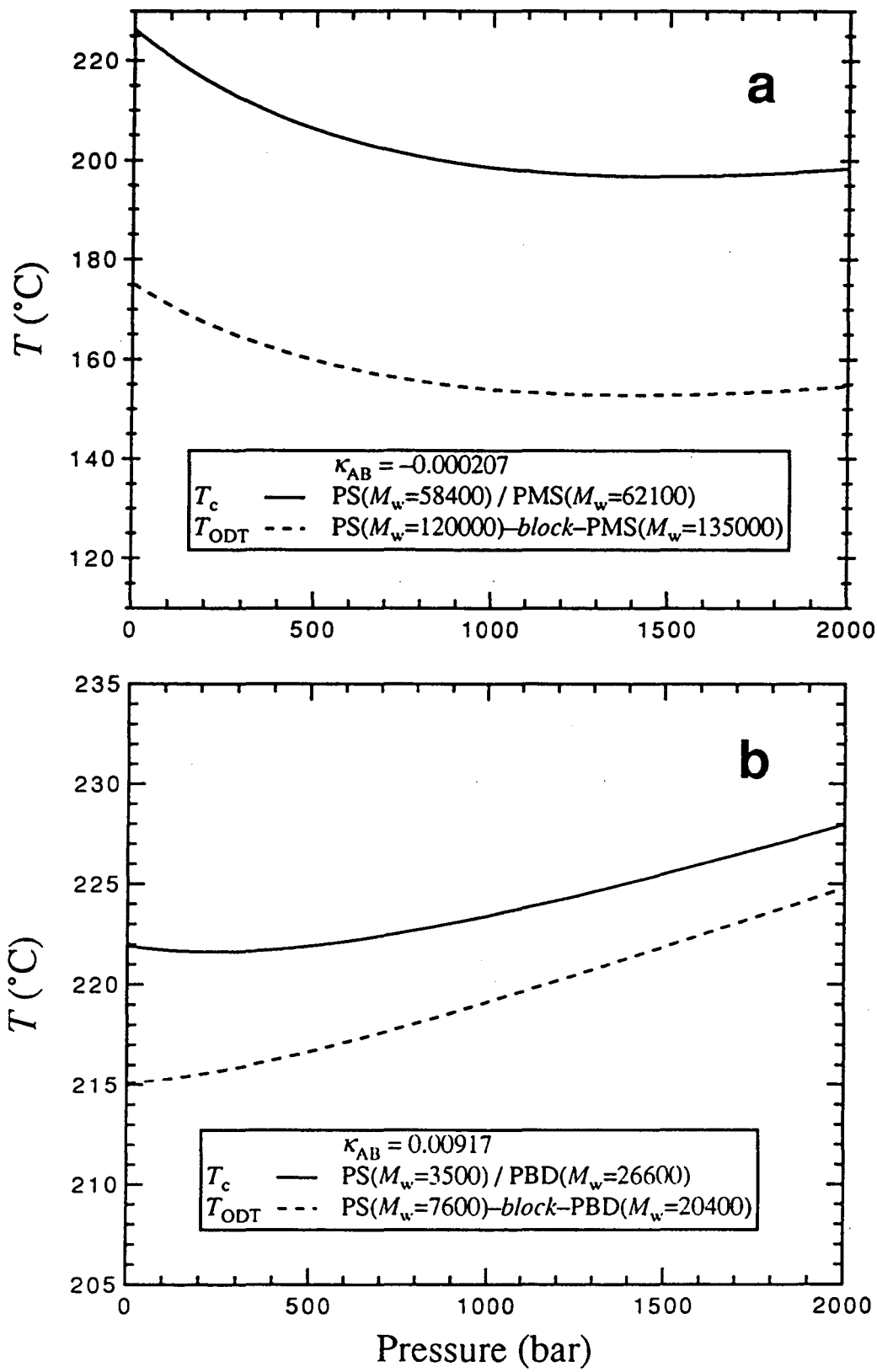
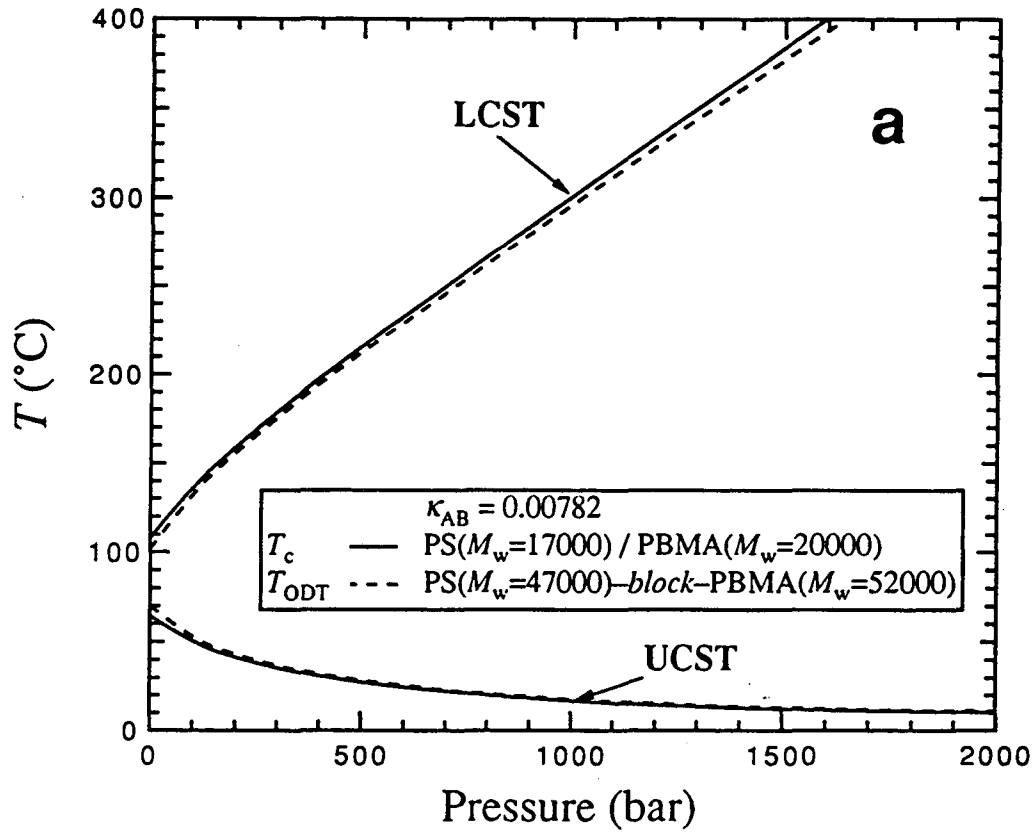
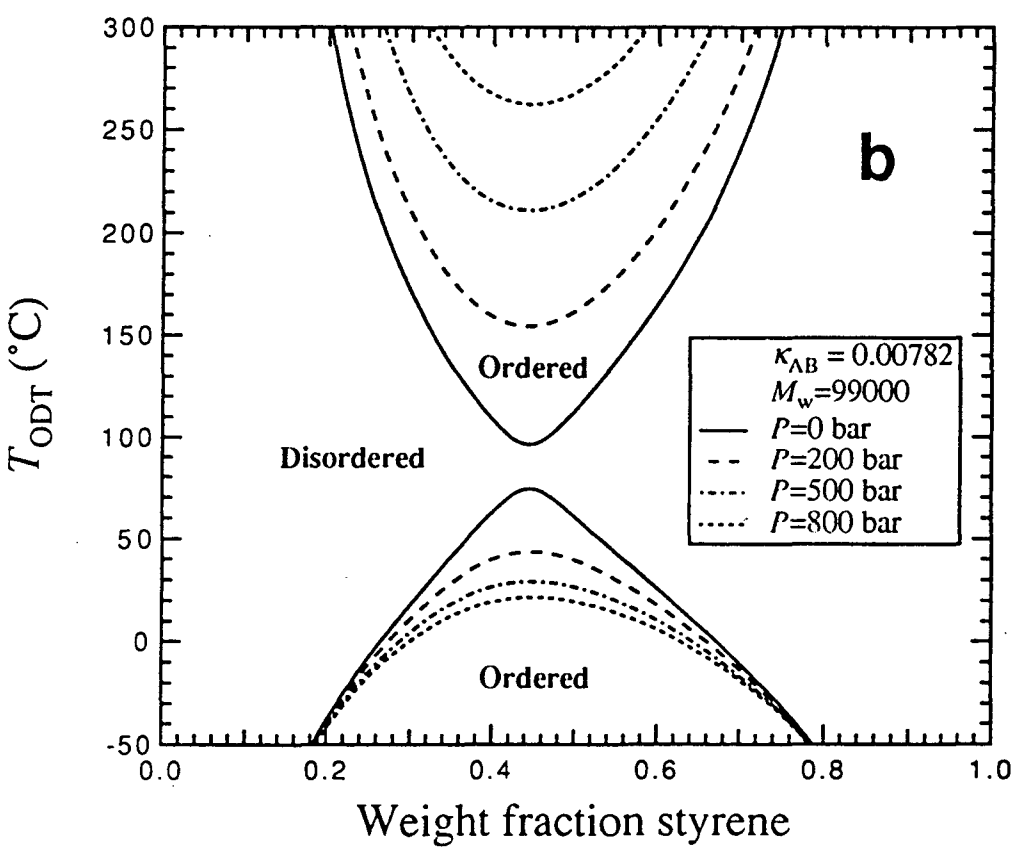

a
220
200
180
160
140
120
T (°C)
0
500
1000
1500
2000
κAB = –0.000207
Tc —— PS(Mw=58400) / PMS(Mw=62100)
TODT - - - PS(Mw=120000)–block–PMS(Mw=135000)
b
235
230
225
220
215
210
205
T (°C)
0
500
1000
1500
2000
κAB = 0.00917
Tc —— PS(Mw=3500) / PBD(Mw=26600)
TODT - - - PS(Mw=7600)–block–PBD(Mw=20400)
Pressure (bar)

Figure 7


a
LCST
UCST
κ_{AB} = 0.00782
T_c — PS(M_w=17000) / PBMA(M_w=20000)
T_{ODT} - - - PS(M_w=47000)–*block*–PBMA(M_w=52000)
T (°C)
Pressure (bar)
0
100
200
300
400
500
1000
1500
2000


b
Ordered
Disordered
Ordered
κ_{AB} = 0.00782
M_w=99000
P=0 bar
P=200 bar
P=500 bar
P=800 bar
T_{ODT} (°C)
Weight fraction styrene
-50
0
50
100
150
200
250
300
0.0
0.2
0.4
0.6
0.8
1.0

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