Molecular Thermodynamics of Binary Polymer Solutions Using Modified Double Lattice Model: Chain Length Dependence of Primary Lattice

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Received 5 May 1998; accepted 23 November 1998

ABSTRACT: In a previous study we modified a double lattice model by introducing a new interaction parameter, which improved the mathematical approximation defect, and gave a new expression for the Helmholtz energy of mixing. In the model the universal constants C_{β} and C_{γ} in the primary lattice were determined by comparing them with literature Monte Carlo simulation data, which is the only case for $r_1=1$ and $r_2=100$ (case I). In this study we introduce new universal constants, C_{β} and C_{γ} , as a function of the chain length of a polymer in a solvent (case II) by comparing them with other literature simulation data for various polymer chain lengths. The proposed model is compared with polymer–solvent systems. In an upper critical solution temperature phase behavior the theoretical results of case II were improved over those of case I. However, in a lower critical solution temperature phase behavior those of case I were not very sensitive to C_{β} and C_{γ} . © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2627–2633, 1999

Key words: molecular thermodynamics; modified double lattice model; chain length dependence; liquid–liquid equilibria; polymer solution

INTRODUCTION

The typical phase behaviors of binary polymersolvent mixtures exhibit upper critical solution temperature (UCST), lower critical solution temperature (LCST), hour-glass shaped, and closed miscibility loop types. In those phase behaviors the LCST or closed miscibility loop phase behavior may be mainly due to highly oriented interactions such as hydrogen bonding. If strong or oriented interactions from hydrogen bonding or other specific forces exist in the system, LCST or miscibility loops can arise, which was first indi-

cated by Hirschfelder et al., who gave a realistic qualitative explanation for such specific interactions. This phenomenon follows from competition among three contributions to the Helmholtz energy of mixing ($\Delta A_{\rm mix}$): dispersion forces, combinatorial entropy of mixing, and highly oriented specific interactions such as hydrogen bonding, donor–acceptor electron transfer, or strong dipole–dipole interactions.

Barker and Fock² proposed a quasichemical method to account for such specific interactions for a binary system of equal-sized molecules. However, this quasichemical method, which is a version of the mean-field approximation, cannot describe the system quantitatively. Sanchez and Balazs³ generalized the lattice-fluid model to account for the specific interactions.

Furthermore, to pursue a formal "exact" solution to the lattice model using advanced statistical and

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Contract grant sponsor: Ministry of Education, Republic of

mechanical methods, Freed and coworkers^{4–6} developed a lattice-field theory (or lattice-cluster theory) for polymer–solvent systems. This theory formally provides an exact mathematical solution for the Flory–Huggins model.^{7–10} However, for practical reasons, the infinite series with respect to the coordination number, temperature, and composition in this theory are truncated at a certain order. Therefore, this theory is still deficient for the correlation of liquid–liquid equilibria.

Hu et al. 11,12 reported a new model called the double lattice model based on Freed's lattice-cluster theory. In their model ordinary polymer solutions are described by the primary lattice and a secondary lattice is introduced as a perturbation to account for oriented interactions.

Lambert et al. 13 reported a new expression for $\Delta A_{\rm mix}$ for incompressible monomer/n-mer mixtures obtained by correlating with the Monte Carlo simulation results. In their study they used the algebraic form, which is a Redlich–Kister expansion 14 truncated after the third term, to correlate energy of mixing data with Monte Carlo simulation results. They introduced chain length dependent parameters using the simulation results.

Bae¹⁵ reported a modified version of the extended Flory–Huggins equation was applicable to represent the chain length dependence of liquid–liquid equilibria for some binary polymer solutions by adding the chain length dependence term in the interaction parameter. These improvements provided better agreement with experimental data by widening the liquid–liquid coexistence curve.

Chang and Bae¹⁶ introduced new universal constants to consider chain length dependence of polymer in a solvent. Their proposed model showed a slight discrepancy when compared with experimental data and gave a better understanding of phase equilibria dependency on the chain length of the polymer.

The purpose of this study was to improve the discrepancy in the modified double lattice model by introducing the chain length dependence of a polymer into the primary lattice for which only universal parameters were used. The coexistence curves generated by the modified double lattice model (case I) and the modified double lattice model taking into account the chain length dependence term (case II) were compared with experimental data.

EXPERIMENTAL

Primary Lattice

Oh and Bae²⁵ proposed a new Helmholtz energy of mixing as a form of the Flory–Huggins theory.^{7–10} This expression is given by

$$\Delta A/N_r kT = (\phi_1/r_1) \ln \phi_1 + (\phi_2/r_2) \ln \phi_2 + \chi \phi_1 \phi_2$$
(1)

where N_r is the total number of lattice sites, k is the Boltzmann constant, r_i is the number of segments per molecule i, and ξ is a new interaction parameter defined by

$$\chi = C_{\beta} \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\varepsilon}$$
$$- \left(\frac{1}{r_2} - \frac{1}{r_1} + C_{\gamma} \tilde{\varepsilon}\right) \tilde{\varepsilon} \phi_2 + C_{\gamma} \tilde{\varepsilon}^2 \phi_2^2 \quad (2)$$

 $\tilde{\epsilon}$ is a reduced interaction parameter given by

$$\tilde{\varepsilon} = \varepsilon/kT = (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})/kT \tag{3}$$

where ε_{11} , ε_{22} , and ε_{12} are for the corresponding nearest neighbor segment–segment interactions.

In our previous model the parameters C_{β} and C_{γ} were universal constants. These constants are not adjustable parameters and are determined by comparing them with Madden et al.'s Monte Carlo simulation data $(r_1) = 1$ and $(r_2) = 100$. The best fitting values of $(r_3) = 100$ and $(r_3) = 100$. The best fitting values of $(r_3) = 100$ and $(r_3) = 100$ are chain length. Figure 1 shows the configurational bias vaporization method simulation results by Yan et al. The solid lines are the best fit given by the proposed primary lattice.

Figure 2 represents the chain length dependence of C_{β} and C_{γ} fitted from the results shown in Figure 1 (case II). The parameters appeared to be asymptotic values with respect to r_2 . The following equations suggest the r-mer dependence of C_{β} and C_{γ} :

$$C_{\beta} = 0.1080 + \frac{1.0647}{1.9907 + (r_2 - 1)}$$
 (4)

$$C_{\gamma} = 1.1529 + \frac{1.1035}{0.0738 + (r_2 - 1)}$$
 (5)

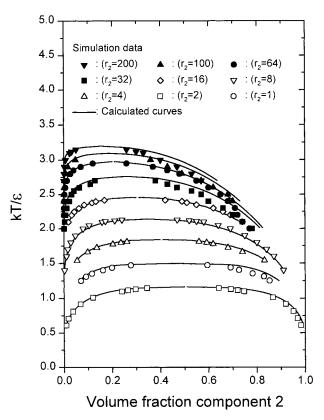


Figure 1 Phase diagram of lattice-polymer systems with chain length $r_2=1$ –200: (—) calculated with a primary lattice.

Equations (4) and (5) can be applied for large r_2 . For $r_2 > 100$, C_{β} and C_{γ} are very weakly dependent on r_2 according to Figure 2.

Secondary Lattice

In Freed et al.'s theory $^{4-6}$ the solution of the Helmholtz energy of mixing for the Ising model is given by

$$\Delta A/N_r k T = x_1 \ln x_1 + x_2 \ln x_2$$

+ $z \tilde{\epsilon} x_1 x_2 / 2 - z \tilde{\epsilon}^2 x_1^2 x_2^2 / 4 + \cdots$ (6)

where z is the coordination number and x_i is the mole fraction of the component i.

To obtain an analytical expression for the secondary lattice, we defined a new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect by revising eq. (6). The expression¹⁷ is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij}kT} = \frac{2}{z} \left[\eta \ln \eta + (1 - \eta)\ln(1 - \eta) + \frac{zC_{\alpha}\delta\tilde{\varepsilon}_{ij}(1 - \eta)\eta}{1 + C_{\alpha}\delta\tilde{\varepsilon}_{ij}(1 - \eta)\eta} \right]$$
(7)

where $\Delta A_{\sec,ij}$ is the Helmholtz energy of mixing of the secondary lattice for the $i\!-\!j$ segment–segment pair, N_{ij} is the number of $i\!-\!j$ pairs, $\delta \tilde{\epsilon}$ is the reduced energy parameter contributed by the oriented interactions, and η is the surface fraction permitting oriented interactions. For simplicity, η was arbitrarily set to 0.3 as Soane et al. 11,12 suggested. C_{α} is a universal constant. C_{α} is also not an adjustable parameter and is determined by comparing it with Panagiotopolous et al.'s Gibbs ensemble Monte Carlo simulation 20 data of the Ising lattice. The best fitting value of C_{α} is 0.4880.

To account for the oriented interaction, the secondary lattice contribution is a perturbation to the primary lattice. To incorporate a secondary lattice, we replace ε_{ij} by $\varepsilon_{ij} - \Delta A_{\sec,ij}/N_{ij}$ in eq. (2). Following the definition of $\tilde{\epsilon}$ in eq. (3), if oriented interaction occurs in the i-j segment–segment pairs, we replace $\tilde{\epsilon}$ by $\varepsilon/kT + 2\Delta A_{\sec,ij}/N_{ij}kT$ in eq. (2). If an oriented interaction occurs in the i-i segment–segment pairs, $\tilde{\epsilon}$ is replaced by $\varepsilon/kT - \Delta A_{\sec,ij}/N_{ii}kT$.

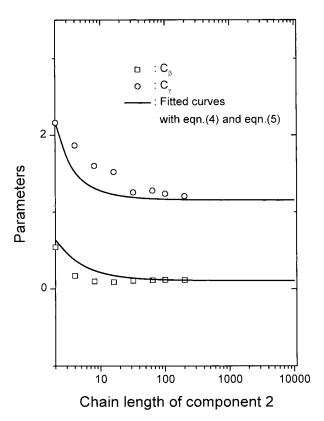


Figure 2 Dependence of parameters C_{β} and C_{γ} on the r-mer chain length: calculated by a primary lattice from the simulation results representing (\Box) C_{β} and (\bigcirc) C_{γ} and (\bigcirc) calculated by eqs. (4) and (5).

Correlating Equations

For calculating the binary coexistence curve we need the chemical potential of components 1 and 2. They are given by

$$\begin{split} \frac{\Delta \mu_1}{kT} &= \left(\frac{\partial A/N_{,k}T}{\partial n_1}\right)_{T,P,n} \\ &= \ln(1-\phi_2) - r_1 \left(\frac{1}{r_2} - \frac{1}{r_1}\right) \phi_2 \\ &+ r_1 \bigg[C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_{,\tilde{\mathcal{E}}}\right) \tilde{\mathcal{E}} \\ &+ \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \phi_2^2 - 2r_1 \bigg[\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_{,\tilde{\mathcal{E}}}\right) \tilde{\mathcal{E}} \\ &+ C_{,\tilde{\mathcal{E}}} \tilde{\mathcal{E}} + C_{,\tilde{\mathcal{E}}}^2 \phi_2^3 + 3r_1 C_{,\tilde{\mathcal{E}}}^2 \phi_2^4 \quad (8) \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right) + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\mathcal{E}} \bigg] \\ &+ C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right) \tilde{\mathcal{E}} \bigg]$$

Figure 3 Coexistence curve for the perfluoromethane (PFM)/methane (ME) system: (\bigcirc) experimental data, (\cdots) calculated curve of case I, and (\longrightarrow) calculated by eqs. (10) and (11) (case II).

Mole fraction PFM

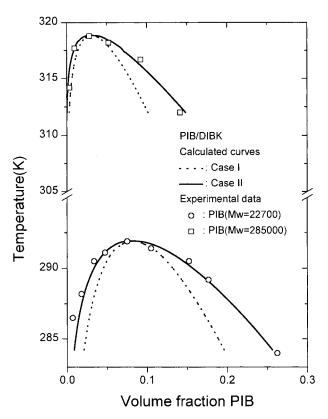


Figure 4 Coexistence curve for the PIB/diisobutyl ketone (DIBK) system: (\bigcirc) experimental data for PIB with a molecular weight of 22,700, (\square) experimental data for PIB with a molecular weight of 285,000, (\cdots) calculated curve of case I, and (\square) calculated curve of case II.

$$-r_{2}\left[\left(\frac{1}{r_{2}}-\frac{1}{r_{1}}\right)+2\left(\left(\frac{1}{r_{2}}-\frac{1}{r_{1}}\right)+C_{\gamma\tilde{\varepsilon}}\right)\tilde{\varepsilon}\right]$$

$$+2C_{\beta}\left(\frac{1}{r_{2}}-\frac{1}{r_{1}}\right)^{2}+2\left(2+\frac{1}{r_{2}}\right)\tilde{\varepsilon}\right]\phi_{2}$$

$$+r_{2}\left[4\left(\left(\frac{1}{r_{2}}-\frac{1}{r_{1}}\right)+C_{\gamma\tilde{\varepsilon}}\right)\tilde{\varepsilon}+\left(2+\frac{1}{r_{2}}\right)\tilde{\varepsilon}\right]$$

$$+C_{\beta}\left(\frac{1}{r_{2}}-\frac{1}{r_{1}}\right)^{2}+3C_{\gamma\tilde{\varepsilon}}^{2}\phi_{2}^{2}$$

$$-r_{2}\left[6C_{\gamma\tilde{\varepsilon}}^{2}+2\left(\left(\frac{1}{r_{2}}-\frac{1}{r_{1}}\right)+C_{\gamma\tilde{\varepsilon}}\right)\tilde{\varepsilon}\right]\phi_{2}^{3}$$

$$+3r_{2}C_{\gamma\tilde{\varepsilon}}^{2}\phi_{2}^{4} \qquad (9)$$

The coexistence curve is found from the following conditions:

$$\Delta\mu_1' = \Delta\mu_1'' \tag{10}$$

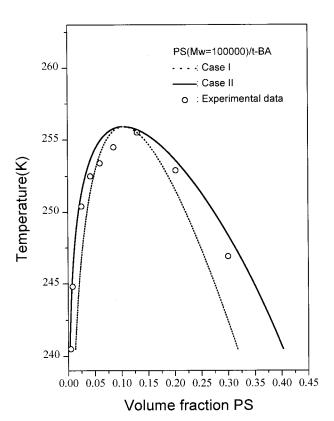


Figure 5 Coexistence curve for the PS/t-butyl acetate (t-BA) system: (\bigcirc) experimental data for PS with a molecular weight of 100,000, ($\cdot\cdot\cdot$) calculated curve of case I, and (\longrightarrow) calculated curve of case II.

$$\Delta \mu_2' = \Delta \mu_2'' \tag{11}$$

where $\Delta\mu_i$ is the change in chemical potential upon isothermally transferring component i from the pure state to the mixture. The primes (', ") denote two phases at equilibrium. For a phase equilibrium calculation we require the experimental coordinates of the critical point. The critical condition is given by

$$\frac{\partial^2(\Delta A/N_{,k}T)}{\partial \phi_2^2} = \frac{\partial^3(\Delta A/N_{,k}T)}{\partial \phi_2^3} = 0 \qquad (12)$$

$$\begin{split} &\frac{\partial^2 (\Delta A/N_r kT)}{\partial \phi_2^2} = \frac{-1}{1-\phi_2} \\ &- r_1 \bigg(\frac{1}{r_2} - \frac{1}{r_1}\bigg) + 2r_1 \bigg(C_\beta \bigg(\frac{1}{r_2} - \frac{1}{r_1}\bigg)^2 \\ &+ \bigg(\bigg(\frac{1}{r_2} - \frac{1}{r_1}\bigg) + C_\gamma \tilde{\varepsilon}\bigg) \tilde{\varepsilon} + \bigg(2 + \frac{1}{r_2}\bigg) \tilde{\varepsilon}\bigg) \phi_2 \end{split}$$

$$\begin{split} &-6r_1\!\!\left(\!\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_{\gamma\!\tilde{\varepsilon}}\right)\!\tilde{\varepsilon}+C_{\gamma\!\tilde{\varepsilon}^2}\!\right)\!\phi_2^2\\ &+12r_1\!C_{\gamma\!\tilde{\varepsilon}^2}\!\phi_2^3=0 \quad (13) \end{split}$$

and

$$\begin{split} \frac{\partial^{3}(\Delta A/N_{r}kT)}{\partial\phi_{2}^{3}} &= \frac{-1}{(1-\phi_{2})^{2}} + 2r_{1}\bigg(C_{\beta}\bigg(\frac{1}{r_{2}} - \frac{1}{r_{1}}\bigg)^{2} \\ &+ \bigg(\bigg(\frac{1}{r_{2}} - \frac{1}{r_{1}}\bigg) + C_{\gamma}\tilde{\varepsilon}\bigg)\tilde{\varepsilon} + \bigg(2 + \frac{1}{r_{2}}\bigg)\tilde{\varepsilon}\bigg) \\ &- 12r_{1}\bigg(\bigg(\bigg(\frac{1}{r_{2}} - \frac{1}{r_{1}}\bigg) + C_{\gamma}\tilde{\varepsilon}\bigg)\tilde{\varepsilon} + C_{\gamma}\tilde{\varepsilon}^{2}\bigg)\phi_{2} \\ &+ 36r_{1}C_{\gamma}\tilde{\varepsilon}^{2}\phi_{2}^{2} = 0 \quad (14) \end{split}$$

RESULTS AND DISCUSSION

For ordinary binary mixtures we introduce the primary lattice with chain length dependence to

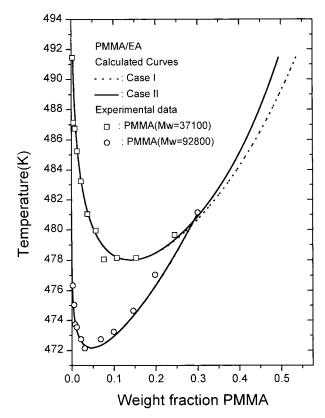


Figure 6 Coexistence curve for the PMMA/ethyl acetate (EA) system: (\bigcirc) experimental data for PMMA with a molecular weight of 92,800, (\square) experimental data for PMMA with a molecular weight of 37,100, (\cdots) calculated curve of case I using a double lattice, and (\square) calculated curve of case II using a double lattice.

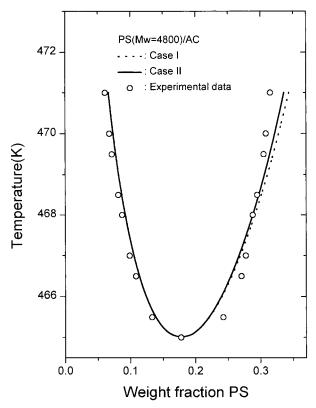


Figure 7 Coexistence curve for the PS/acetate (AC) system: (\bigcirc) experimental data for PS with a molecular weight of 4800, ($\cdot \cdot \cdot$) calculated curve case I using a double lattice, and (\bigcirc) calculated curve of case II using a double lattice.

obtain a satisfactory fit. For the systems (two different polymer chains, polymer—solvent system, etc.) that interact strongly, they must be in the proper orientation to each other (i.e., a specific interaction). These systems show LCST phase behavior, which the primary lattice alone cannot describe. Therefore, to describe this phenomenon, we introduce the secondary lattice.

Figure 3 shows a phase diagram of perfluoromethane/methane system. ²¹ The dotted line presents a coexistence curve generated by the primary lattice without the chain length dependence term (case I). The solid line presents a coexistence curve generated by the primary lattice with the chain length dependence term (case II). The parameters r_2 and ε/k of case I are 2.81 and 57.41 K, respectively. For case II those values are 2.02 and 64.791 K, respectively.

Figure 4 shows a phase diagram of the poly-(isobutylene) (PIB, $M_w=22{,}700$ and 285,000)/ diisobutyl ketone system. 22 The theoretical coex-

istence curve of case I shows more deviation than that of case II. The parameter r_2 and ε/k values of case I are 153.59 and 84.20 K for PIB with $M_w=22,700$ and 1175.59 and 83.61 K for PIB with $M_w=285,000$, respectively. Those of case II are 330.71 and 91.15 K for PIB with $M_w=22,700$ and 2390.59 and 95.86 K for PIB with $M_w=285,000$, respectively.

Figure 5 shows a phase diagram of the polystyrene (PS, $M_w=100{,}000$, $M_w/M_n=1.06$)/tbutyl acetate system. The model parameter values of case I are $r_2=89.89$ and $\varepsilon/k=77.12$ K. Those of case II are $r_2=197.27$ and $\varepsilon/k=81.14$ K.

As shown in Figures 3–5, the ε/k value of case II is larger than that of case I over the wide range of molecular weights. This larger ε/k value causes the energetically unstable region (two-phase region) to be wide.

Figure 6 shows a coexistence curve for the poly(methyl methacrylate) (PMMA, $M_w = 92,800$, $M_w/M_n=2.0; M_w=37,100, M_w/M_n=1.13)$ /ethyl acetate system,²⁴ and this system exhibits LCST behavior. Although the polydispersity index $(M_{"})$ M_n) of PMMA ($M_w = 92,800$) is a little high, we consider it to be a monodisperse PMMA. The dotted line was calculated by a double lattice with universal constants (case I). The solid line was calculated by a double lattice with chain length dependence (case II). The model parameter values are: $r_2 = 835.16$, $\varepsilon/k = -1052.96$ K, and $\delta \varepsilon/k$ = 12178.61 K for PMMA with M_w = 92,800 and r_2 = 78.89, ε/k = -1127.59 K, and $\delta\varepsilon/k$ = 15425.01 K for PMMA with $M_w = 37,100$ (case I); and r_2 = 1709.96, ε/k = -819.98 K, and $\delta \varepsilon/k$ = 7249.66 K for PMMA with $M_w = 92,800$ and $r_2 = 173.89$, $\varepsilon/k = -855.14 \text{ K}$, and $\delta \varepsilon/k = 7895.30 \text{ K}$ for PMMA with $M_w = 37,100$ (case II). In the representation of LCST behavior, case I and case II show almost the same results for a relatively higher molecular weight of polymer: the theoretical coexistence curve is not very sensitive to C_{β} and C_{γ} . However, for a lower molecular weight polymer, case II gives a narrower theoretical coexistence curve than that of case I. This is because of the lower $\Delta A_{\text{sec},ij}$ value of case II than that of case I. A slight deviation in the higher concentration region of PMMA ($M_w = 92,800$) between the theoretical curve and experimental data may be due to the polydispersity of PMMA.

Figure 7 shows a coexistence curve for the PS $(M_w=4800)$ /acetone system. ²⁵ The dotted line was calculated by a double lattice with universal constants (case I). The solid line was calculated by

a double lattice with chain length dependence (case II). The model parameter values are: $r_2 = 47.62$, $\varepsilon/k = -774.84$ K, and $\delta\varepsilon_{12}/k = 6777.97$ K (case I); and $r_2 = 105.42$, $\varepsilon/k = -631.98$ K, and $\delta\varepsilon_{12}/k = 4995.66$ K (case II). In the polymer rich region a slight discrepancy is shown between cases I and II and the experimental data. Again, case II gives a narrower theoretical coexistence curve than that of case I.

In this study, we considered polymers at temperatures well below the solvent's critical temperature. Thus, we expect that the free volume effect that leads to LCST as described by Patterson²⁵ is almost negligible in the given model systems. Also, the various flexibilities of chain molecules are not considered in the proposed model. The model implicitly assumes that all polymers have the same flexibility. Further, solvent molecules are considered to be monomers where the concept of flexibility does not apply. It is likely that this deficiency is basically responsible for the discrepancy between the proposed model and the experimental results.

CONCLUSIONS

In UCST behaviors our proposed model, which takes into account the chain length dependence (case II), successfully represents liquid–liquid equilibria of binary mixtures with various molecular weights of component 2 and gives a better agreement with experimental data than that of the model with no chain length dependence (case I). On the other hand, in the case of using a double lattice, the theoretical results of cases I and II are not very sensitive to C_{β} and C_{γ} for a higher molecular weight polymer. However, the model parameter values are different in each case.

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