Polymer Vol. 39 No. 5, pp. 1149–1154, 1998
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00+0.00

PII: S0032-3861(97)00305-4

Liquid–liquid equilibria for binary polymer solutions from modified double-lattice model

Jeong Seok Oh and Young Chan Bae*
Department of Industrial Chemistry and Molecular Thermodynamics Laboratory, Hanyang University, Seoul 133-791, Korea
(Revised 24 March 1997)

A new double-lattice model, which is capable of describing and predicting the equilibrium properties of binary polymer solutions, was proposed by modifying Hu's double-lattice model by introducing a new interaction parameter and simplifying the expression of the Helmholtz energy of mixing. Using the proposed model, we investigated phase behaviours of various binary polymer solutions. The modified double-lattice model successfully describes the phase behaviours of binary polymer solutions having an upper critical solution temperature (UCST) and a lower critical solution temperature (LCST). © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: modified double-lattice model; phase equilibria)

INTRODUCTION

The phase behaviours of binary polymer systems differ from that for ordinary liquid mixtures because of the large molecular size difference of the components. Calculations involving phase behaviours of polymeric liquids are required in the design and operation of many polymer processes such as polymerization, devolatization, drying, extrusion and design of heat exchanger.

A variety of theories of polymer solutions and blends have been developed during the last 50 years. A lattice model, one of the molecular-based thermodynamic frame works, has been successfully used to describe phase behaviours of polymeric liquids.

The most widely used and best known of the incompressible-lattice model is the Flory–Huggins lattice[1,2], which illustrates in a simple way the competition between the entropy of mixing and the attraction forces producing liquid–liquid phase separation. Much work have been performed to improve the mathematical solution of the lattice model, including chain-connectivity and non-random mixing. However, the Flory–Huggins model and quasi-chemical model[3] show systematic deviations, giving too narrow or parabolic liquid–liquid coexistence curves near the critical region from the computer simulation data or experimental data.

To account for compressibility and density changes upon isothermal mixing, Sanchez and Lacombe[4,5] and Kleintjens and Koningsveld[6] have derived different forms of a lattice-fluid model based on the Flory–Huggins lattice, ignoring the equation of state properties of the pure components. A group-contribution lattice-fluid equation of state for the prediction of vapour–liquid equilibria in polymer solutions was developed by High and Danner[7–9] and modified by Lee and Danner[10]. On the other hand, free volume theories for polymer solutions were developed by numerous investigations, notably by Flory[11] and by Patterson and Delmas[12]. These theories were based on a generalized form of the van der Waals partition function, which is the product of two independent partition functions: one accounts for free volume and the other for attractive forces. Heil and Prausnitz[13], and later Brandani[14,15], Vera[16], McMaster[17] and Xie *et al.*[18] developed a theory taking into account local composition. Bae *et al.*[19–21] reported the extended Flory–Huggins theory for binary polymer systems.

If strong or oriented interactions from hydrogen bonding or other specific forces exist in the system, LCST or miscibility loops can arise as first indicated by Hirschfelder *et al.*[22] for mixtures of ordinary liquids, and Barker and Fock[23] proposed a quasi-chemical method to account for such specific interactions. Painter *et al.*[24] reported a Gibbs free energy method for polymers that hydrogen bond using the chemical theory to account for the formation of associated species and the lattice theory to describe the non-ideal interactions between the associated species. Sanchez and Balazs[25] generalized the lattice-fluid model to account for the specific interactions.

Furthermore, Freed *et al.*,[26–28] developed a complicated lattice-field theory for polymer solutions which is formally an exact mathematical solution of the Flory–Huggins lattice. Good agreement was found between predicted results and the computer simulation data by Dickman and Hall[29] for the chain insertion probability and for pressures in a system of athermal chains and voids. However, for practical reasons, the infinite series with respect to coordination number, temperature and composition in this theory are truncated at a certain order. Recently, Hu *et al.*[30,31] reported a double-lattice model based on Freed's theory. In their model, ordinary polymer solutions are described by the primary lattice, while a secondary lattice is introduced as a perturbation to account for oriented interactions.

In this study, we modified Hu's double-lattice model by introducing a new interaction parameter and simplifying the expression of the Helmholtz energy of mixing. Using our proposed model, we investigated phase behaviours of binary polymer solutions.

---

* To whom correspondence should be addressed

MODEL DEVELOPMENT

At temperature T, the canonical partition function of the primary lattice for a binary mixture, Q, is given by

$$Q = \sum_{N_{12}} g(N_1, r_1, N_2, r_2, N_{12}) \left[\exp\left(\frac{\varepsilon_{11}}{\mathrm{k}T}\right)\right]^{N_{11}} \left[\exp\left(\frac{\varepsilon_{22}}{\mathrm{k}T}\right)\right]^{N_{22}} \times \left[\exp\left(\frac{\varepsilon_{12}}{\mathrm{k}T}\right)\right]^{N_{12}} \tag{1}$$

where N_1 and N_2 are numbers of molecules of solvent and polymer, respectively. N_{11}, N_{22} and N_{12} are the numbers of 1–1, 2–2, and 1–2 nearest-neighbour (non-bonded) segment–segment pairs, respectively. r_2 is the number of segments in the polymer molecule relative to $r_1 = 1$ for the solvent. $g(N_1, r_1, N_2, r_2, N_{12})$ is the combinatorial factor which depends on the number of 1–2 segment–segment pairs. The positive energy parameters, ε_{11}, ε_{22} and ε_{12} are for the corresponding nearest-neighbour segment–segment interactions. k is the Boltzmann's constant.

Primary lattice

The general form of the Helmholtz energy of mixing based on the Freed's theory can be expressed as

$$\Delta A/N_r\mathrm{k}T = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + \sum_m \sum_n a_{mn}\phi_1^m\phi_2^n \tag{2}$$

where N_r is the number of lattice sites for the mixture and ϕ_i is the volume fraction of component i. Coefficients a_{mn} are functions of z, r_1, r_2 and energy parameters. To obtain an analytical expression for the Helmholtz energy of mixing for the primary lattice, Hu *et al.*[30,31] employed only the first-order term multiplied by empirical coefficients.

In this study, we defined new Helmholtz energy of mixing as the form of the Flory–Huggins theory. This expression is given by

$$\Delta A/N_r\mathrm{k}T = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + \chi_{\mathrm{OB}}\phi_1\phi_2 \tag{3}$$

where χ_{OB} is a new interaction parameter defined by

$$\chi_{\mathrm{OB}} = C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\phi_2 + C_\gamma\tilde{\varepsilon}^2\phi_2^2 \tag{4}$$

where C_β and C_γ are universal constants. These constants are not adjustable parameters and are determined by comparing with Madden *et al.*'s Monte-Carlo simulation data[32]. $\tilde{\varepsilon}$ is a reduced interaction parameter given by

$$\tilde{\varepsilon} = \varepsilon/\mathrm{k}T = (\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})/\mathrm{k}T \tag{5}$$

Figure 1 shows the comparison of coexistence curves calculated from this work and the Flory–Huggins model with computer simulation results. The best-fit values of C_β and C_γ are 0.1415144 and 1.798599, respectively.

Secondary lattice

In Freed's theory, the solution of the Helmholtz energy of mixing for the Ising model is given by

$$\Delta A/N_r\mathrm{k}T = x_1\ln x_1 + x_2\ln x_2 + z\tilde{\varepsilon}x_1x_2/2 - z\tilde{\varepsilon}^2x_1^2x_2^2/4 + \ldots \tag{6}$$

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

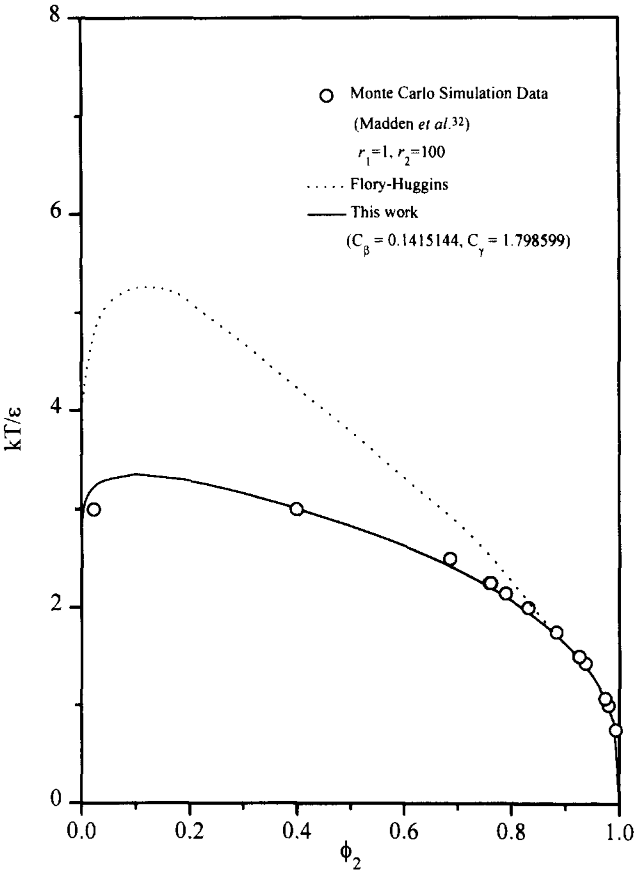

Figure 1 Comparison of coexistence curves calculated from this work and the Flory–Huggins model with computer simulation results. The dotted line is calculated from the Flory–Huggins model and the solid line is calculated from this work with $C_\beta = 0.1415144$ and $C_\gamma = 1.798599$. Open circles are from Madden's Monte-Carlo simulation data

To obtain an analytical expression for the secondary lattice, Hu *et al.*[30,31] revised equation (6) to improve the coexistence curves by introducing two empirical coefficients and adding the additional energy of the reference state. Hu *et al.*'s expression of Helmholtz energy of mixing is given by

$$\frac{\Delta A_{\mathrm{sec},ij}}{N_{ij}\mathrm{k}T} = \frac{2}{z}\left[\eta\ln\eta + (1-\eta)\ln(1-\eta) - z\delta\tilde{\varepsilon}_{ij}\eta^2/2 - c_2z(\delta\tilde{\varepsilon}_{ij})^2\eta^2(1-\eta)^2/4 - c_{10}z(\delta\tilde{\varepsilon}_{ij})^{10}\eta^{10}(1-\eta)^{10}\right] \tag{7}$$

where $\Delta A_{\mathrm{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for i–j segment–segment pair and N_{ij} is the number of i–j pairs, $\delta\tilde{\varepsilon}$ is the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions. For simplicity, Hu *et al.* arbitrarily set η to 0.3. C_2 and c_{10} are empirical coefficients in their model.

In this study, we defined a new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect and to reduce the number of parameters. The expression is given by

$$\frac{\Delta A_{\mathrm{sec},ij}}{N_{ij}\mathrm{k}T} = \frac{2}{z}\left[\eta\ln\eta + (1-\eta)\ln(1-\eta) + \frac{zC_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}{1 + C_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}\right] \tag{8}$$

where C_α is a universal constant.

C_α is also not an adjustable parameter and is determined by comparing with Panagiotopolous *et al.*'s Gibbs-ensemble

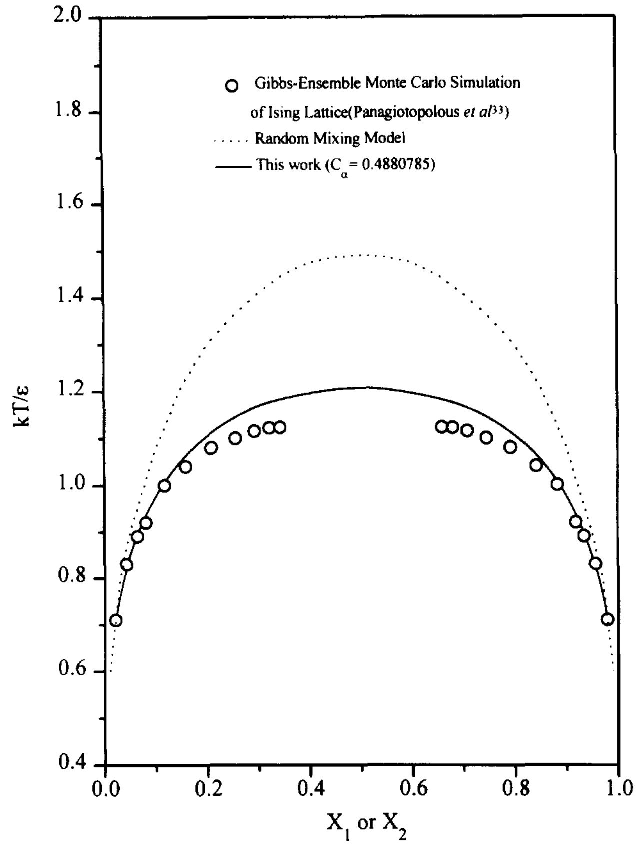

Figure 2 Comparison of the Ising lattice coexistence curves calculated from this work and a random mixing model with computer simulation results. The dotted line is calculated from the random mixing model and the solid line is calculated from this work with $C_\alpha = 0.4880785$. Open circles are from Panagiotopolous's Gibbs–ensemble Monte-Carlo simulation data

Monte-Carlo simulation data of the Ising lattice[33]. *Figure 2* shows the comparison of the Ising lattice coexistence curve calculated from this work and random mixing model with computer simulation results. The best-fit value of C_α is 0.4880785.

Incorporation of secondary lattice into primary lattice

To account for the oriented interaction, Hu *et al.* employed a secondary lattice. The secondary lattice contribution is a perturbation to the primary lattice. To incorporate a secondary lattice, we replace ε_{ij} by $\varepsilon_{ij} - \Delta A_{\mathrm{sec},ij}/N_{ij}$ in equation (1). Following the definition of ε in equation (5), if oriented interactions occur in i–j segment–segment pairs, we replace $\tilde{\varepsilon}$ by $\varepsilon/\mathrm{k}T + 2\Delta A_{\mathrm{sec},ij}/N_{ij}\mathrm{k}T$ in equation (4). If oriented interactions occur in i–i segment–segment pairs, $\tilde{\varepsilon}$ is replaced by $\varepsilon/\mathrm{k}T + \Delta A_{\mathrm{sec},ii}/N_{ii}\mathrm{k}T$.

Correlating equations

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

$$\Delta\mu_1/\mathrm{k}T = \partial(\Delta A/\mathrm{k}T)/\partial N_1,$$

$$\begin{aligned}\frac{\Delta\mu_1}{\mathrm{k}T} = {} & \ln(1-\phi_2) - r_1\left(\frac{1}{r_2}-\frac{1}{r_1}\right)\phi_2 \\ & + r_1\left[C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + \left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\right. \\ & \left.+\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2^2 - 2r_1\left[\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\right. \\ & \left.+C_\gamma\tilde{\varepsilon}^2\right]\phi_2^3 + 3r_1C_\gamma\tilde{\varepsilon}^2\phi_2^4 \end{aligned} \tag{9}$$

$$\Delta\mu_2/\mathrm{k}T = \partial(\Delta A/\mathrm{k}T)/\partial N_2,$$

$$\begin{aligned}\frac{\Delta\mu_2}{\mathrm{k}T} = {} & \ln\phi_2 + r_2\left[\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2\right. \\ & \left.+\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right] - r_2\left[\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+2\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)\right.\right. \\ & \left.\left.+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+2C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2+2\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2 \\ & + r_2\left[4\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right. \\ & \left.+C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2+3C_\gamma\tilde{\varepsilon}^2\right]\phi_2^2 \\ & - r_2\left[6C_\gamma\tilde{\varepsilon}^2+2\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\right]\phi_2^3 \\ & + 3r_2C_\gamma\tilde{\varepsilon}^2\phi_2^4 \end{aligned} \tag{10}$$

The coexistence curve is found from the following conditions:

$$\Delta\mu'_1 = \Delta\mu''_1 \tag{11}$$

$$\Delta\mu'_2 = \Delta\mu''_2 \tag{12}$$

where a prime (′) and double prime (″) denote two phases at equilibrium.

For phase equilibrium calculation, we require the experimental coordinates of the critical point. We find these coordinates using

$$\frac{\partial^2(\Delta A/N_r\mathrm{k}T)}{\partial\phi_2^2} = 0$$

which leads to

$$\begin{aligned}\frac{\partial^2(\Delta A/N_r\mathrm{k}T)}{\partial\phi_2^2} = {} & \frac{-1}{1-\phi_2} - r_1\left(\frac{1}{r_2}-\frac{1}{r_1}\right) \\ & + 2r_1\left(C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2+\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)\right.\right. \\ & \left.\left.+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right)\phi_2 \\ & - 6r_1\left(\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+C_\gamma\tilde{\varepsilon}^2\right)\phi_2^2 \\ & + 12r_1C_\gamma\tilde{\varepsilon}^2\phi_2^3 \end{aligned} \tag{13}$$

and

$$\frac{\partial^3(\Delta A/N_r\mathrm{k}T)}{\partial\phi_2^3} = 0$$

which leads to

$$\begin{aligned}\frac{\partial^3(\Delta A/N_r\mathrm{k}T)}{\partial\phi_2^3} = {} & \frac{-1}{(1-\phi_2)^2} + 2r_1\left(C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2\right. \\ & \left.+\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right) \end{aligned}$$

$$
\begin{aligned}
&- 12r_1\left(\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+C_\gamma\tilde{\varepsilon}^2\right)\phi_2\\
&+36r_1C_\gamma\tilde{\varepsilon}^2\phi_2^2 \qquad (14)
\end{aligned}
$$

RESULTS AND DISCUSSION

For the systems (two different polymer chains, polymer/solvent system, etc.) that interact strongly, they must be in the correct orientation to each other, i.e. a specific interaction. In these systems, the primary lattice alone always yields a narrower coexistence curve. Therefore, to obtain a satisfactory fit, we introduced the secondary lattice.

Figure 3 shows coexistence curves for poly(isobutene) (PIB, Mw = 22 700)/diisobutyl ketone (DIBK) and the system shows a UCST behaviour. The dotted line is predicted by using a single lattice and the solid line is predicted using a double lattice. Open circles are experimental data by Shultz and Flory[34]. As shown in *Figure 3*, a single lattice gives a narrow coexistence curve, while using a double lattice, we obtain an excellent fit. The model adjustable parameter values are r_2 = 139.48, ε/k = −334.87K and $\delta\varepsilon_{11}/k$ = −1087.1K when using a double lattice and r_2 = 139.48 and ε/k = 84.863K for a single lattice.

Figure 4 shows coexistence curves for polystyrene (PS)/ethyl acetate systems and those systems exhibit LCST behaviours. The solid lines are predicted by this work. Open circles are experimental data by Bae *et al.*[19]. The proposed model agrees very well with the experimental data. The model adjustable parameter values are r_2 = 170.39, ε/k = −786.28K and $\delta\varepsilon_{12}/k$ = 7053.2K for a PS molecular weight of 100 000 (Mw/Mn = 1.06); r_2 = 405.10, ε/k = 1318.3K and $\delta\varepsilon_{12}/k$ = −1564.3K for a PS molecular weight of 233 000 (Mw/Mn = 1.06); r_2 = 1110.5, ε/k = 1109.2K and $\delta\varepsilon_{12}/k$ = − 1352.6K for a PS molecular weight of 600 000 (Mw/Mn = 1.10).

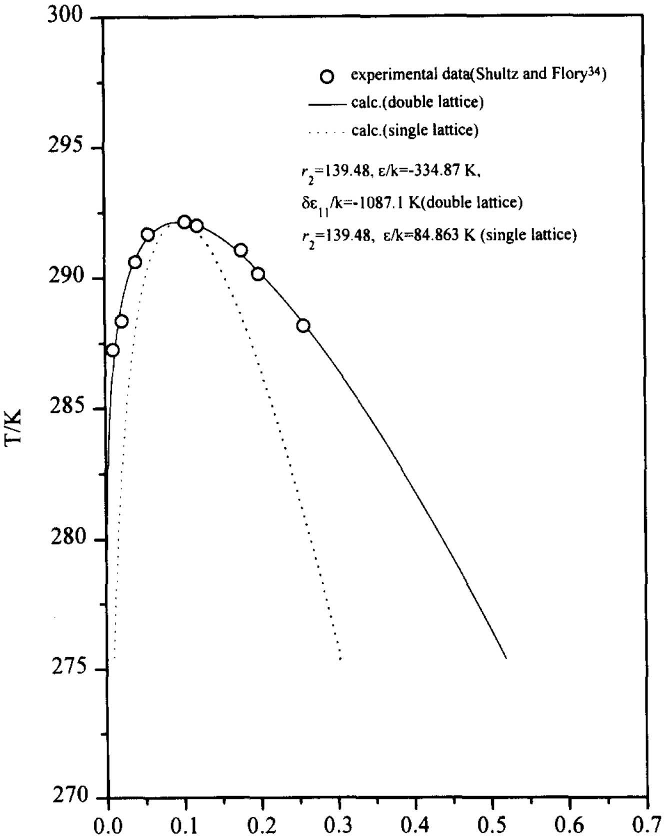

Figure 3 Coexistence curves for PIB (Mw = 22 700)/DIBK system showing cloudpoint temperatures as functions of the weight fraction of PIB. The dotted line is calculated using a single lattice and the solid line is calculated using a double lattice. Open circles are from Shultz and Flory's experimental data

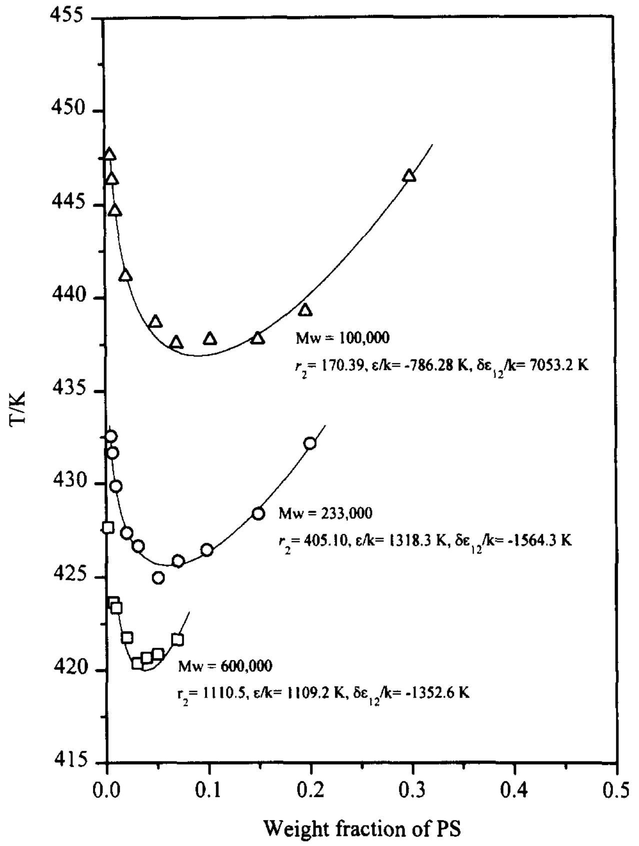

Figure 4 Coexistence curves for three PS/ethyl acetate systems showing cloudpoint temperatures as functions of the weight fraction of PS. The solid lines are calculated from this work. Squares, circles and triangles are from Bae's experimental data for molecular weights (Mw) 600 000, 233 000 and 100 000, respectively[19]

Figure 5 shows coexistence curves for poly(methyl methacrylate) (PMMA)/ethyl acetate and these systems exhibit LCST behaviours. The solid lines are predicted by this work. Open circles are experimental data by Muller[35]. The model adjustable parameter values are r_2 = 122.85, ε/k = 1648.3K and $\delta\varepsilon_{12}/k$ = −1897.8K (PMMA Mw = 37 100, Mw/Mn = 1.13); r_2 = 1300.0, ε/k = −1051.5K and $\delta\varepsilon_{12}/k$ = 12085.0K (PMMA Mw = 92 800, Mw/Mn = 2.0). For a PMMA molecular weight of 92 800, the r_2 value is slightly higher than expected. This may be due to the polydispersity of PMMA.

Figure 6 shows coexistence curves for PMMA/tetrahydrofuran (THF) systems and the systems exhibit LCST behaviours. The solid lines are predicted by this work. Open circles are experimental data by Muller[35]. The proposed model also predicts remarkably well the phase behaviours of the PMMA/THF systems. The model adjustable parameter values are r_2 = 179.78, ε/k = 2040.8K and $\delta\varepsilon_{12}/k$ = −2266.9K (PMMA Mw = 37 100, Mw/Mn = 1.13); r_2 = 216.43, ε/k = 1811.2K and $\delta\varepsilon_{12}/k$ = −2077.3K (PMMA Mw = 100 100, Mw/Mn = 1.4).

The proposed model does not consider the various flexibilities of chain molecules. However, a polymer molecule is not an ideal flexible chain, i.e. PS does not

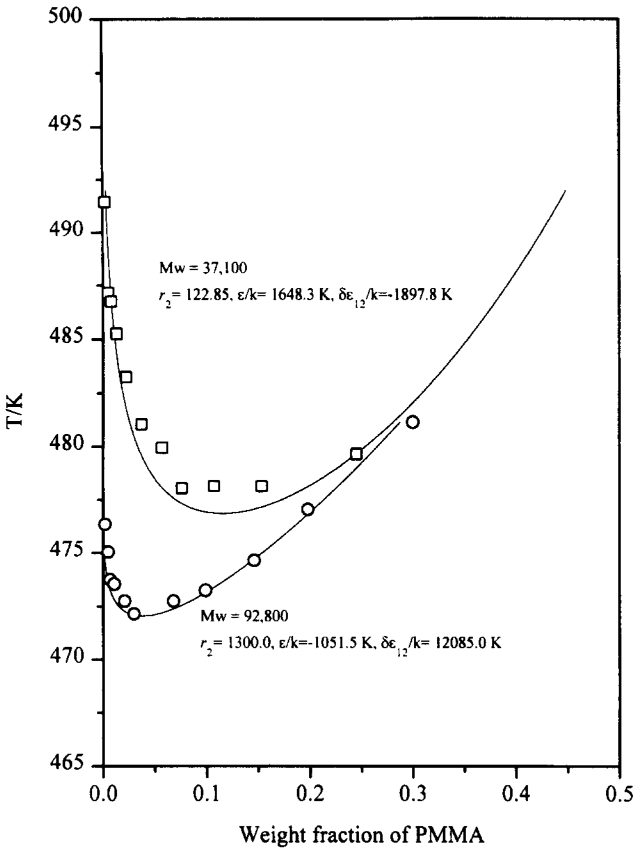

Figure 5 Coexistence curves for two PMMA/ethyl acetate systems showing cloudpoint temperatures as functions of the weight fraction of PMMA. The solid lines are calculated from this work. Squares and circles are from Muller's experimental data for molecular weights (Mw) 37 100 and 92 800, respectively[35]

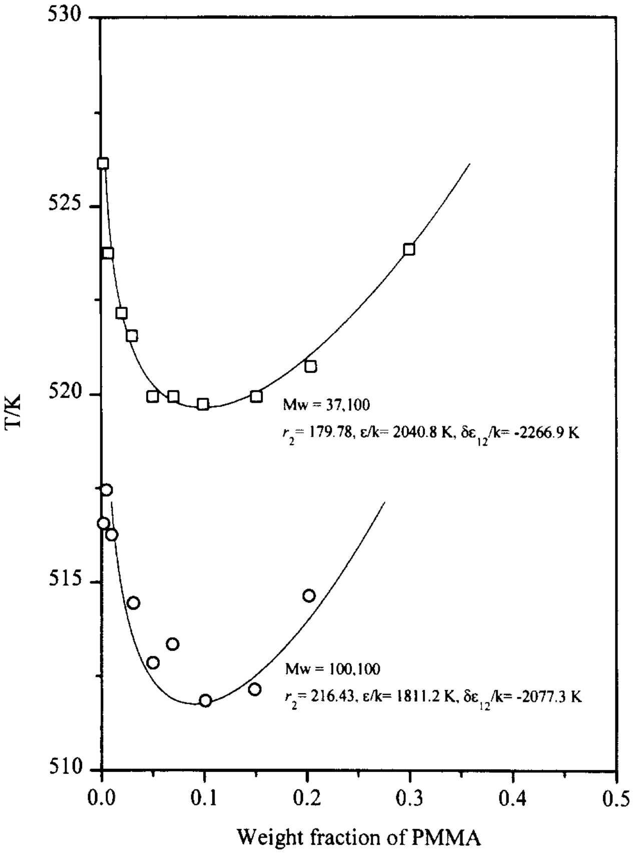

Figure 6 Coexistence curves for two PMMA/THF systems showing cloudpoint temperatures as functions of the weight fraction of PMMA. The solid lines are calculated from this work. Squares and circles are from Muller's experimental data for molecular weights (Mw) 37 100 and 100 100, respectively[35]

have the same flexibility as PMMA. Furthermore, solvent molecules are considered to be monomers where the concept of flexibility does not apply. One more thing to be considered is that a segment of a polymer and a solvent molecule can hardly be considered as a sphere. Nevertheless, the proposed model successfully predicts phase behaviours of the given polymer systems.

CONCLUSIONS

We proposed a modified double-lattice model by introducing a new interaction parameter and simplifying the expression of the Helmholtz energy of mixing. We have shown several phase diagrams of some binary polymer solutions. For those binary polymer solutions, our proposed model appears to be useful in describing and predicting the liquid–liquid equilibria using a few adjustable parameters. The proposed model still needs to take into account free volume effects of polymers.

ACKNOWLEDGEMENTS

This work was supported by the Korea Science and Engineering Foundation (KOSEF) under contract no. 96-0300-12-01-3. J.S. Oh is grateful to the Graduate School of Advanced Materials and Chemical Engineering at the Hanyang University for a fellowship.

REFERENCES

1. Flory, P.J., *Journal of Chemistry and Physics*, 1942, **10**, 51.
2. Huggins, M.L., *Journal of Physics and Chemistry*, 1942, **46**, 151.
3. Guggenheim, E. A., *Mixtures*. Clarendon, Oxford, Ch. 4, 10 and 11.
4. Sanchez, I.C. and Lacombe, R.H., *Journal of Physics and Chemistry*, 1976, **21**, 2352.
5. Sanchez, I.C. and Lacombe, R.H., *Macromolecules*, 1978, **11**, 1145.
6. (a) Kleintjens, L. A. and Koningsveld, R., *Colloid Polymer Science*, 1980, **258**, 711; (b) Kleintjens, L. A. and Koningsveld, R., *Seperation Science and Technology*, 1982, **17**, 215.
7. High, M. S., Ph.D. thesis, The Pennsylvania State University, University Park, PA, 1990.
8. High, M.S. and Danner, R.P., *Fluid Phase Equilibria*, 1989, **53**, 323.
9. High, M.S. and Danner, R.P., *AIChE Journal*, 1990, **36**, 1625.
10. Lee, B.C. and Danner, R.P., *AICHE Journal*, 1996, **42**, 837.
11. (a) Flory, P. J., *Journal of the American Chemical Society*, 1965, **87**, 1833; (b) Flory, P. J., *Discussions of the Faraday Society*, 1970, **49**, 7.
12. Patterson, D. and Delmas, G., *Transactions of the Faraday Society*, 1969, **65**, 708.
13. Heil, J.F. and Prausnitz, J.M., *AICHE Journal*, 1966, **12**, 678.
14. Brandani, V., *Macromolecules*, 1979, **12**, 883.
15. Brandani, V., Del Re, G. and Di Giacomo, F., *Macromolecules*, 1991, **24**, 2391.
16. Vera, J.H., *Fluid Phase Equilibria*, 1982, **8**, 315.
17. McMaster, L.P., *Macromolecules*, 1973, **6**, 760.
18. Xie, H., Nies, E., Stroeks, A. and Simha, R., *Polymer Engineering and Science*, 1992, **32**, 1654.
19. Bae, Y.C., Shim, J.J., Soane, D.S. and Prausnitz, J.M., *Journal of Applied Polymer Science*, 1993, **47**, 1193.
20. Bae, Y.C., Lambert, S.M., Soane, D.S. and Prausnitz, J.M., *Macromolecules*, 1991, **24**, 4403.
21. Bae, Y.C., *Journal of Industrial and Engineering Chemistry*, 1995, **1**, 18.
22. Hirschfelder, J., Stevenson, D. and Erying, H., *Journal of Chemistry and Physics*, 1937, **5**, 896.
23. Barker, J.A. and Focker, W., *Discussions of the Faraday Society*, 1953, **15**, 188.

24. Painter, P.C., Graf, J. and Coleman, M.M., *Journal of Chemistry and Physics*, 1990, **92**, 6166.
25. Sanchez, I.C. and Balazs, A.C., *Macromolecules*, 1989, **22**, 2325.
26. Freed, K.F., *Journal of Physics A: Mathematics Generalized*, 1985, **18**, 871.
27. Bawendi, M.G., Freed, K.F. and Mohanty, U., *Journal of Chemistry and Physics*, 1988, **87**, 5534.
28. Bawendi, M.G. and Freed, K.F., *Journal of Chemistry and Physics*, 1988, **88**, 2741.
29. Dickman, R. and Hall, C., *Journal of Chemistry and Physics*, 1988, **85**, 4108.
30. Hu, Y., Lambert, S.M., Soane, D.S. and Prausnitz, J.M., *Macromolecules*, 1991, **24**, 4356.
31. Hu, Y., Liu, H., Soane, D.S. and Prausnitz, J.M., *Fluid Phase Equilibria*, 1991, **67**, 65.
32. Madden, W.G., Pesci, A.I. and Freed, K.F., *Macromolecules*, 1990, **23**, 1181.
33. Panagiotopolous, A.Z., Quirke, N., Stapleton, M. and Tildesley, D.J., *Molecular Physics*, 1988, **63**, 527.
34. Shultz, A.R. and Flory, P.J., *Journal of the American Chemistry Society*, 1952, **74**, 4760.
35. Muller, C., Diploma Thesis, University of Karlsruhe, 1991.