

Liquid–liquid equilibria of binary polymer solutions with specific interactions

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In our previous study, we proposed a new expression for the configurational energy of mixing taking into account non-random mixing effect and chain-length dependence of the polymer. But our model can not predict lower critical solution temperature (LCST) behaviours of liquid–liquid equilibria for binary polymer solutions.

In this study, we extend our previous model to describe LCST behaviours of binary polymer solutions by employing a secondary lattice concept as a perturbation term to account for oriented interactions (or specific interactions). © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Many lattice models have been used to correlate the thermodynamic properties of polymer solutions. The most widely used and best known incompressible-lattice models is the Flory–Huggins theory^{1–4} which illustrates in a simple way the competition between the entropy of mixing and the attractive forces that produce liquid–liquid phase separation at low temperatures with an upper critical solution temperature (UCST)⁵. However, the Flory–Huggins model cannot describe the lower critical solution temperature (LCST)⁵ behaviour of polymer solutions. Phase equilibria in this behaviour are influenced by strong, orientation-dependent interaction forces, such as hydrogen bonds. The Flory–Huggins model does not take into account deviations from random mixing caused by these orientation-dependent interactions. Many theoretical improvements, including Guggenheim's Quasi-chemical model⁶, have been obtained by various workers to gain the mathematical solution of the lattice model, including chain connectivity and non-random mixing. In recent years, several authors have proposed molecular-thermodynamic models for polymer solutions that attempt to account for non-random mixing^{6–10}. These models are based on the local-composition concept where expressions for local composition are obtained either from essentially empirical relations or else are derived from Guggenheim's traditional quasi-chemical approximation.

While an UCST is readily understood in terms of intermolecular forces, interpretation of a LCST is more difficult. Generally a LCST is observed when either of the following conditions prevails:

(1) Large differences in thermal expansion of solvent and solute: this situation is often encountered in polymer/volatile–solvent systems when the system temperature approaches the critical temperature of the solvent. As the temperature rises, the solvent expands more rapidly than the solute; solubility decreases until two separate

phases are formed. This behaviour is well described by free-volume theories. Free volume theories for polymer solutions were developed by numerous investigations, notably by Flory³ and by Patterson and Delmas¹¹. 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. To account for compressibility and density changes upon isothermal mixing, Sanchez and Lacombe^{12–13} and Kleintjens and Koningsveld¹⁴ have derived different forms of a lattice–fluid model based on the Flory–Huggins lattice theory.

(2) Order-disorder transitions, as encountered in systems of molecules capable of forming hydrogen bonds. More than 50 years ago, Hirschfelder *et al.*¹⁵ suggested a qualitative physical picture to explain the occurrence of a LCST in hydrogen bonding systems: mutual solubility at temperatures below the LCST is attributed to highly orientation-dependent interactions (hydrogen bonds) between unlike species, which are weaker than those between like species, and so the system splits into two phases. Specific forces between adjacent sites can easily be introduced into the model to account for polymers that hydrogen bond. Painter *et al.*^{16,17} developed a Gibbs free energy model for polymers that hydrogen bond using chemical theory to account for the formation of associated species and lattice theory to describe the non-ideal interactions between the associated species. Sanchez and Balazs¹⁸ used a lattice–fluid equation of state to include specific interactions such as hydrogen bonding. In this model, a quantitative description of the spinodal phase diagram, as well as a semiquantitative description of the composition and temperature dependence of the χ interaction parameter, is possible. Recently, Hu *et al.*^{19,20} reported a new model called 'double-lattice model' based on Freed's lattice–cluster theory^{21–28}. In their model, ordinary polymer solutions are described by the primary lattice, while a secondary lattice is introduced as a perturbation to account for

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oriented interactions. Recently, Oh *et al.*²⁹ modified a double-lattice model by introducing new universal parameters and simplified the expression of the Helmholtz energy of mixing.

In this study, we extend our previous model^{30,31} to describe a LCST behaviour of polymer solutions. We employ the secondary lattice concept from Hu *et al.*'s work^{19,20} as a perturbation to account for oriented interactions.

MODEL DEVELOPMENT

Internal and Helmholtz energies of mixing

The description of the lattice model starts with a simple cubic lattice (coordination number, $z = 6$) containing N_r sites. The lattice is filled completely by N_1 molecules of type 1, which occupy only one lattice site ($r_1 = 1$), and N_2 molecules of type 2, which occupy r_2 nearest-neighbour lattice sites (r -mer). The energy of mixing is related to the number of nearest-neighbour pairs by

$$\frac{\Delta_{\text{mix}}U}{N_r\varepsilon} = \frac{1}{2} \frac{N_{12}}{N_r} \quad (1)$$

where N_{12} is the total number of 1–2 pairs and ε is the interchange energy as defined by

$$\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \quad (2)$$

where ε_{ij} is the i – j nearest-neighbour interaction energy. The Helmholtz energy of mixing ($\Delta_{\text{mix}}A$) is obtained by integrating the Gibbs–Helmholtz equation using the Guggenheim's athermal entropy of mixing⁶ as a boundary condition:

$$\frac{\Delta_{\text{mix}}A}{N_r kT} = \left(\frac{\Delta_{\text{mix}}A}{N_r kT} \right)_{1/\tilde{T}=0} + \int_0^{1/\tilde{T}} \frac{\Delta_{\text{mix}}U}{N_r\varepsilon} d\left(\frac{1}{\tilde{T}}\right) \quad (3)$$

$$\begin{aligned} \left(\frac{\Delta_{\text{mix}}A}{N_r kT} \right)_{1/\tilde{T}=0} &= \frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \\ &+ \frac{z}{2} \left[\phi_1 \frac{q_1}{r_1} \ln \frac{\theta_1}{\phi_1} + \phi_2 \frac{q_2}{r_2} \ln \frac{\theta_2}{\phi_2} \right] \end{aligned} \quad (4)$$

A dimensionless temperature is defined by $\tilde{T} = kT/\varepsilon$, where T is an absolute temperature and k is a Boltzmann's constant. r_i , ϕ_i , and θ_i are the number of segments per molecule, volume fraction, and surface fraction of component i , respectively. ϕ_i and θ_i are defined by:

$$\phi_i = \frac{N_i r_i}{N_1 r_1 + N_2 r_2} \quad (5)$$

$$\theta_i = \frac{N_i q_i}{N_1 q_1 + N_2 q_2} \quad (6)$$

where q_i is the surface area parameter defined as:

$$zq_i = r_i(z-2) + 2 \quad (7)$$

Correlation of simulation data

The fractional form to improve the mathematical approximation defect and to correlate energy of mixing data from Monte-Carlo simulation⁷ is given by

$$\frac{2\Delta_{\text{mix}}U}{N_r\varepsilon} = \phi_1\phi_2 \left[\frac{B'}{1 - A'(\phi_2 - \phi_1)} \right] \quad (8)$$

where

$$A' = a_0 + a_1 [\exp(1/\tilde{T}) - 1] \quad (9)$$

$$B' = b_0 + b_1 [\exp(1/\tilde{T}) - 1] \quad (10)$$

where ϕ_1 and ϕ_2 are monomer and r -mer volume fractions, respectively. Parameters, A' and B' , depend on the dimensionless temperature only. Parameters a_0 , a_1 , b_0 , and b_1 depend on r -mer chain length. The following equations represent the r -mer dependence of a_0 , a_1 , b_0 and b_1 :

$$a_0 = 0.00012 + \frac{0.22999(r_2 - 1)}{1 + 1.37129(r_2 - 1)} \quad (11)$$

$$a_1 = -0.01717 + \frac{0.02160(r_2 - 1)}{1 + 0.09642(r_2 - 1)} \quad (12)$$

$$b_0 = 5.79880 - \frac{1.45604(r_2 - 1)}{1 + 1.83417(r_2 - 1)} \quad (13)$$

$$b_1 = -1.42112 - \frac{0.16059(r_2 - 1)}{1 - 1.34296(r_2 - 1)} \quad (14)$$

These equations gain the parameters to larger values of r_2 not simulated by smooth extrapolation. The determination procedure for equations (11)–(14) is described elsewhere³¹.

A simple lattice model expression for predicting liquid–liquid equilibria is given by

$$\begin{aligned} \frac{\Delta_{\text{mix}}A}{N_r kT} &= \left(\frac{\Delta_{\text{mix}}A}{N_r kT} \right)_{1/\tilde{T}=0} + \frac{1}{2} \phi_1 \phi_2 \left[C \frac{1}{\tilde{T}} \right. \\ &\left. - \frac{B}{a_1(2\phi_2 - 1)} \ln \left\{ 1 - \frac{a_1(2\phi_2 - 1)}{1 - a_0(2\phi_2 - 1)} \{ \exp(1/\tilde{T}) - 1 \} \right\} \right] \end{aligned} \quad (15)$$

$$\begin{aligned} B &= \frac{(a_1 b_0 - a_0 b_1)(2\phi_2 - 1) + b_1}{1 + (a_1 - a_0)(2\phi_2 - 1)}, \\ C &= \frac{b_0 - b_1}{1 + (a_1 - a_0)(2\phi_2 - 1)} \end{aligned} \quad (16)$$

Specific interaction term

In Freed's theory^{21–28}, the Helmholtz energy of mixing for the Ising model is given by

$$\Delta A/N_r kT = x_1 \ln x_1 + x_2 \ln x_2 + z\bar{\varepsilon}x_1x_2/2 - z\bar{\varepsilon}^2x_1^2x_2^2/4 + \dots \quad (17)$$

where z is the coordination number and x_i is the mole fraction of component i . To obtain an analytical expression of the secondary lattice, Oh *et al.*²⁹ defined new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect and to reduce the number of adjustable model parameters by revising equation (17). Their expression is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij}kT} = \frac{2}{z} \left[\eta \ln \eta + (1-\eta) \ln(1-\eta) + \frac{zC_\infty \delta \tilde{\varepsilon}_{ij} (1-\eta)\eta}{1 + C_\infty \delta \tilde{\varepsilon}_{ij} (1-\eta)\eta} \right] \quad (18)$$

where $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of mixing for the secondary lattice for an 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. In general, η is different for different components; for simplicity, we arbitrarily set η to 0.3 as both Oh *et al.*²⁹ and Hu *et al.*^{19,20}

suggested previously. C_α is a universal constant determined by comparing with Panagiotopoulos *et al.*'s³² Gibbs-Ensemble Monte-Carlo simulation data for the Ising lattice. Oh *et al.*²⁹ reported that the best fitting value of C_α obtained from Monte-Carlo simulation results for the Ising lattice was 0.4880785.

Incorporation of specific interaction term

The specific interaction contribution is a perturbation to our proposed model. To incorporate a specific interaction term, we replace ε_{ij} by $\varepsilon_{ij} - \Delta A_{\text{sec},ij}/N_{ij}$. If oriented interaction occurs in 1-2 segment-segment pairs, we replace $1/\varepsilon_{12}$ by $\varepsilon/kT + 2\Delta A_{\text{sec},12}/N_{12}kT$ in equation (15). If oriented interaction occurs in 1-1 segment-segment pairs and 2-2 segment-segment pairs, $1/\tilde{T}$ is replaced by $\varepsilon/kT - \Delta A_{\text{sec},11}/N_{11}kT$ and $\varepsilon/kT - \Delta A_{\text{sec},22}/N_{22}kT$, respectively.

Correlating equations

The critical condition is given by,

$$\left[\frac{\partial^2 \left(\frac{\Delta_{\text{mix}} A}{N_r kT} \right)}{\partial \phi_1^2} \right]_{T,V} = \left[\frac{\partial^3 \left(\frac{\Delta_{\text{mix}} A}{N_r kT} \right)}{\partial \phi_1^3} \right]_{T,V} = 0 \quad (19)$$

The critical temperature and critical volume fraction are obtained by solving the following two equations simultaneously:

$$\begin{aligned} & \frac{-1}{1-\phi_2} + \left(1 - \frac{r_1}{r_2}\right) + \frac{Z}{2} \left[q_1 \left(\frac{\phi_2 - \theta_2}{\phi_2 \phi_1} \right) + \left(\frac{\theta_1 \theta_2}{\phi_2 \phi_1} - 1 \right) \right. \\ & \times \left. \left(q_1 + q_2 \frac{r_1 \phi_2}{r_2 \phi_1} \right) + q_2 \frac{r_1 (\phi_1 - \theta_1)}{r_2 \phi_1^2} \right] \\ & + 2r_1 \phi_2 Y + 2r_1 \phi_2 (2\phi_2 - 1) \left(\frac{\partial Y}{\partial \phi_2} \right) - r_1 (\phi_2^2 - \phi_2^3) \\ & \times \left(\frac{\partial^2 Y}{\partial \phi_2^2} \right) = 0 \end{aligned} \quad (20)$$

$$\begin{aligned} & \frac{1}{(1-\phi_2)^2} + \frac{Z}{2} \left[q_1 \frac{\{(\phi_2 \phi_1 - \theta_2 \theta_1) - (\phi_2 - \theta_2)(1 - 2\phi_2)\}}{(\phi_2 \phi_1)^2} \right. \\ & + \frac{\theta_1 \theta_2 (\theta_1 - \theta_2 - 1 + 2\phi_2)}{(\phi_2 \phi_1)^2} \left(q_1 + q_2 \frac{r_1 \phi_2}{r_2 \phi_1} \right) + \left(\frac{\theta_1 \theta_2}{\phi_2 \phi_1} - 1 \right) \\ & \times \left. \left(\frac{r_1 q_2}{r_2 \phi_1^2} \right) + q_2 \frac{r_1}{r_2} \left(\frac{\phi_2 \phi_1 + \theta_2 \theta_1 - 2\phi_2 \theta_1}{\phi_1^3 \phi_2} \right) \right] \\ & + 2r_1 Y + 2r_1 (5\phi_2 - 1) \left(\frac{\partial Y}{\partial \phi_2} \right) + r_1 \phi_2 (7\phi_2 - 4) \left(\frac{\partial^2 Y}{\partial \phi_2^2} \right) \\ & - r_1 (\phi_2^2 - \phi_2^3) \left(\frac{\partial^3 Y}{\partial \phi_2^3} \right) = 0 \end{aligned} \quad (21)$$

where

$$Y = \frac{1}{2} \left[C \frac{1}{\tilde{T}} - \frac{B}{a_1 (2\phi_2 - 1)} \ln \left\{ 1 - \frac{a_1 (2\phi_2 - 1)}{1 - a_0 (2\phi_2 - 1)} \{ \exp(1/\tilde{T}) - 1 \} \right\} \right] \quad (22)$$

The coexistence curve is found from the following conditions:

$$\Delta \mu_1' = \Delta \mu_1'' \quad (23)$$

$$\Delta \mu_2' = \Delta \mu_2'' \quad (24)$$

where $\Delta \mu_i$ is the change in chemical potential upon isothermally transferring component i from the pure state to the mixture. Superscripts ' and '' denote two phases at equilibrium. Relative to pure component 1, the chemical potential $\Delta \mu_1$ of component 1 in the solution is defined by,

$$\begin{aligned} \Delta \mu_1 &= \left(\frac{\partial \Delta_{\text{mix}} A}{\partial N_1} \right)_{T,N_2} = \ln(1 - \phi_2) + \phi_2 \left(1 - \frac{r_1}{r_2} \right) \\ &+ \frac{z}{2} \left[q_1 \ln \frac{\theta_1}{\phi_1} + q_1 (\theta_2 - \phi_2) + q_2 \frac{r_1 \phi_2}{r_2 \phi_1} (\phi_1 - \theta_1) \right] \\ &+ r_1 \phi_2^2 Y + r_1 \phi_2^2 \phi_1 \left(\frac{\partial Y}{\partial \phi_1} \right) \end{aligned} \quad (25)$$

and a similar relation holds for $\Delta \mu_2$

$$\begin{aligned} \Delta \mu_2 &= \left(\frac{\partial \Delta_{\text{mix}} A}{\partial N_2} \right)_{T,N_1} = \ln \phi_2 + (1 - \phi_2) \left(1 - \frac{r_2}{r_1} \right) \\ &+ \frac{z}{2} \left[q_2 \ln \frac{\theta_2}{\phi_2} + q_2 (\theta_1 - \phi_2) + q_1 \frac{r_2 \phi_1}{r_1 \phi_2} (\phi_2 - \theta_2) \right] \\ &+ r_2 \phi_1^2 Y + r_2 \phi_1^2 \phi_2 \left(\frac{\partial Y}{\partial \phi_2} \right) \end{aligned} \quad (26)$$

RESULTS AND DISCUSSION

For the systems of two different polymer chains or polymer/solvent systems that interact strongly, they must be in the proper orientation to each other. Our previous model could not describe such behaviour (e.g. LCST). We employ a secondary lattice concept to take into account the specific interaction contribution to our previous model.

It is essential that r_2 , ε/k and $\delta\varepsilon/k$ are adjustable model parameters in order to compare calculated results with experimental data.

Figure 1 shows phase diagrams of various molecular weights of polystyrene (PS) in tert-butyl acetate³³⁻³⁵. As shown in Figure 1, calculated curves agree very well with experimental data. The model adjustable parameter values are $r_2 = 288.31$, $\varepsilon/k = -588.50$ K and $\delta\varepsilon_{12}/k = 4420.45$ K for PS ($M_w = 100\,000$, $M_w/M_n = 1.06$); $r_2 = 895.90$, $\varepsilon/k = -520.48$ K and $\delta\varepsilon_{12}/k = 3766.60$ K for PS ($M_w = 233\,000$, $M_w/M_n = 1.06$); $r_2 = 3096.02$, $\varepsilon/k = -458.07$ K and $\delta\varepsilon_{12}/k = 3219.00$ K for PS ($M_w = 600\,000$, $M_w/M_n = 1.10$).

Figure 2 shows coexistence curves for PS/ethyl acetate (EA) systems³³⁻³⁵. The model adjustable parameter values are $r_2 = 293.90$, $\varepsilon/k = -658.83$ K and $\delta\varepsilon_{12}/k = 5131.29$ K for PS ($M_w = 100\,000$, $M_w/M_n = 1.06$); $r_2 = 1155.79$, $\varepsilon/k = -573.76$ K and $\delta\varepsilon_{12}/k = 4204.50$ K for PS ($M_w = 233\,000$, $M_w/M_n = 1.06$); $r_2 = 3701.21$, $\varepsilon/k = -499.79$ K and $\delta\varepsilon_{12}/k = 3519.97$ K for PS ($M_w = 600\,000$, $M_w/M_n = 1.10$). For PS molecular weight of 100 000, there is a slight deviation between theory and experimental data in high the concentration range of PS. As shown in Figure 1 Figure 2, calculated values of ε/k increase with molecular weight of PS, while $\delta\varepsilon/k$ decrease with molecular weight of PS.

Figure 3 shows phase diagrams of poly(methyl methacrylate) (PMMA)/EA systems³⁶. The model adjustable parameter values are $r_2 = 254.30$, $\varepsilon/k = -823.97$ K and $\delta\varepsilon_{12}/k = 7013.05$ K for PMMA ($M_w = 37\,100$, $M_w/M_n = 1.13$); $r_2 = 2864.44$, $\varepsilon/k = -807.29$ K and $\delta\varepsilon_{12}/k = 6691.46$ K for PMMA ($M_w = 92\,800$, $M_w/M_n = 2.0$). For

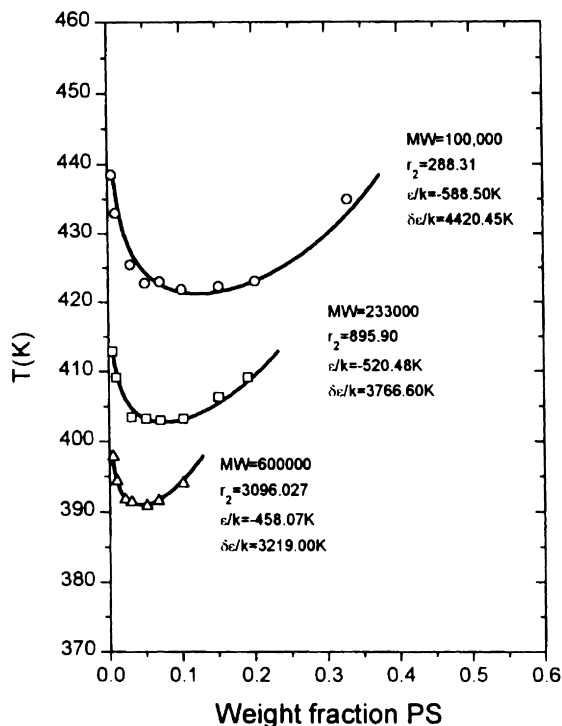


Figure 1 The coexistence curves for PS/tert-butyl acetate systems. The triangles, squares, and circles are experimental data³⁴ for PS molecular weights of 600 000, 233 000 and 100 000, respectively. The solid lines are calculated by equations (23) and (24)

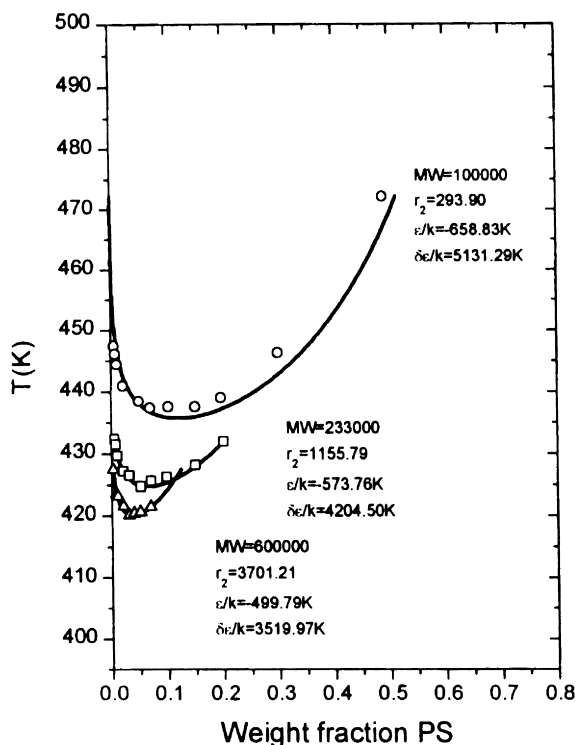


Figure 2 The coexistence curves for PS/EA systems. The triangles, squares, and circles are experimental data³⁴ for PS molecular weights of 600 000, 233 000 and 100 000, respectively. The solid lines are calculated by equations (23) and (24)

PMMA molecular weight of 92 800, the r_2 value is slightly higher than that of our expected value. It may be due to the polydispersity of PMMA. The same results are observed in

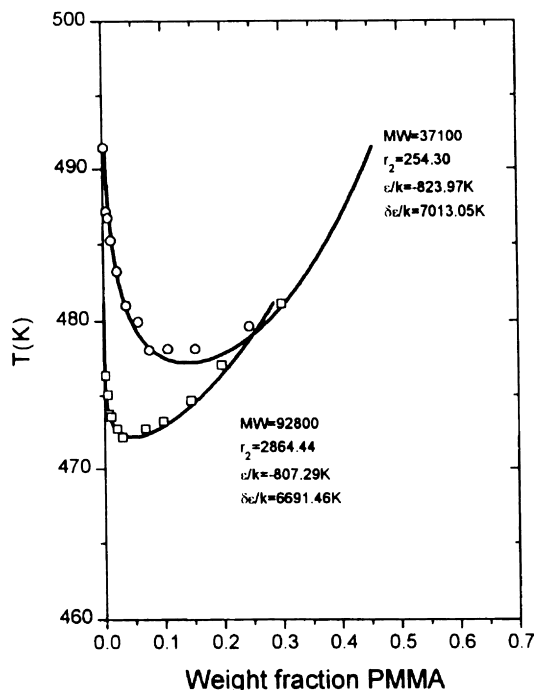


Figure 3 The coexistence curves for PMMA/EA systems. The squares and circles are experimental data³⁶ for PMMA molecular weights of 92 800 and 37 100, respectively. The solid lines are calculated by equations (23) and (24)

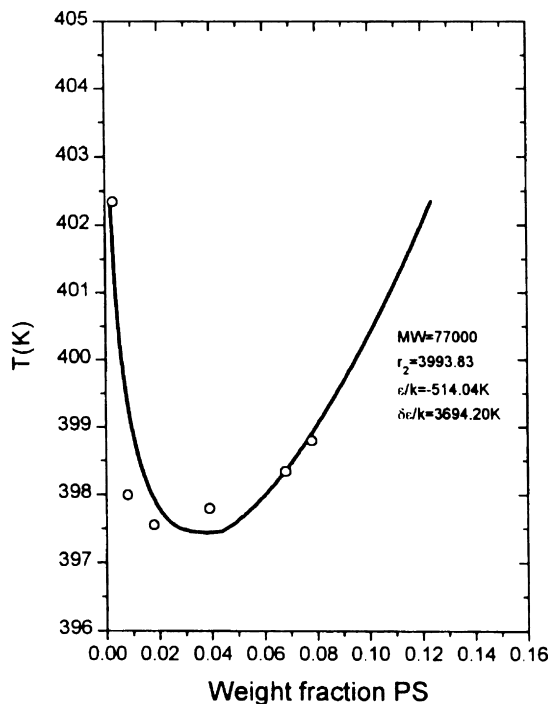


Figure 4 The coexistence curve for PS/MA system. The circles are experimental data³⁴ for PS molecular weight of 77 000. The solid line is calculated by equations (23) and (24)

these systems as shown in both PS/tert-butyl acetate and PS/EA systems. ε/k increases with molecular weight of PMMA and $\delta\varepsilon/k$ decreases with molecular weight of PMMA.

Figure 4 shows phase diagram of PS/methyl acetate (MA) system³³⁻³⁵. The model adjustable parameter values are $r_2 = 3993.83$, $\varepsilon/k = -514.04$ K and $\delta\varepsilon_{12}/k = 3694.20$ K for PS ($M_w = 77\ 000$, $M_w/M_n = 1.04$). Though

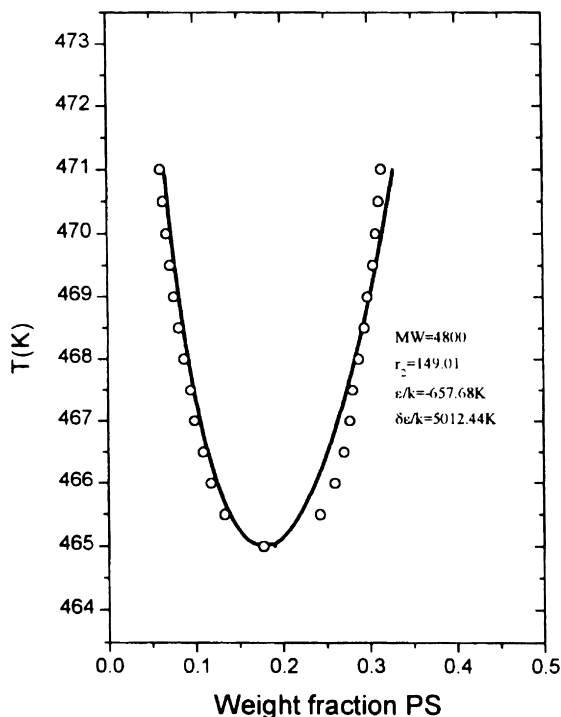


Figure 5 The coexistence curve for PS/acetone system. The circles are experimental data¹¹ for PS molecular weight of 4800. The solid line is calculated by equations (23) and (24)

there is little experimental data, our proposed model describes well the phase behaviour of the system.

Figure 5 shows phase diagram of PS/acetone system¹¹. The model adjustable parameter values are $r_2 = 149.01$, $\varepsilon/k = -657.68$ K and $\delta\varepsilon_{12}/k = 5012.44$ K for PS ($M_w = 4800$). In this system, for the higher concentration range of PS, there shows a slight deviation between theory and experimental data.

In our proposed model, the energy parameters, ε/k and $\delta\varepsilon/k$ are less sensitive than r_2 to the polymer molecular weights on the shape of the coexistence curve. r_2 is the more important parameter to determine the shape of a calculated coexistence curve than the energy parameter. As shown in Figures 1–3, r_2 , ε/k and $\delta\varepsilon/k$ vary with the molecular weight of the polymer. The values of ε/k and $\delta\varepsilon/k$ are dependent on the critical solution temperature of a given system. As the molecular weight of the polymer increases, the critical solution temperature of the polymer solution shifts to the lower temperature. Such a decrease in the critical solution temperature may affect the values of ε/k and $\delta\varepsilon/k$. On the other hand, r_2 is dependent on the critical concentration of the polymer solution. The critical concentration of the polymer solution is shifted to polymer poor phase with increasing molecular weight of the polymer. Therefore, r_2 increases with increasing molecular weight of the polymer.

In this study, we considered polymer mixtures at temperatures well below the solvent's critical temperature (T_c of tert-butyl acetate, EA, MA and acetone are 579 K, 523.3 K, 506.55 K and 508.1 K, respectively). Therefore, we expect that the free volume effect that leads to LCST, as described by Patterson³⁷, is almost negligible in our model systems. Also, various flexibilities of chain molecules are not considered in the proposed model. The model implicitly assumes that PS (Figures 1, 2, 4 and 5) has the same flexibility as that of PMMA (Figure 3). Further, solvent molecules (tert-butyl acetate in Figure 1, EA in Figure 2

and Figure 3, MA in Figure 4, and acetone in Figure 5) are considered to be monomers where the concept of flexibility does not apply. It is likely that the deficiency is basically responsible for the discrepancy between the proposed model and experimental results

CONCLUSION

We previously proposed a simplified and improved expression for the Helmholtz energy of mixing for the monomer/ r -mer mixture that takes into account the non-random mixing effect³⁰ and polymer chain-length dependence³¹. In this study, we employ a secondary lattice concept to take into account the specific interactions contribution to our previous model. We have shown several phase diagrams of some binary polymer solutions showing LCST behaviours. Our new model predicts remarkably well phase behaviours of polymer solutions with oriented interactions.

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