



Molecular thermodynamics approach for polymer–polymer miscibility

Suk Yung Oh, Young Chan Bae *

Division of Chemical Engineering and Molecular Thermodynamics Lab.,¹ Hanyang University, Seoul 133-791, Republic of Korea

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ABSTRACT

We extended the previous lattice model for polymer solution systems to binary polymer blend systems. Based on Müller's Monte-Carlo simulation data for symmetric system ($r_1 = 32$ and $r_2 = 32$), the energy of mixing is correlated as a function of temperature and composition using an empirical expression. In addition, we introduce new universal functions which reflect the characteristics of polymer–polymer miscibility behaviors. In associated blend systems, specific interactions between polymer segments are considered by using a secondary lattice. Using only one or two adjustable parameters, the proposed model satisfactory correlates the experimental data of real polymer blend systems with greater accuracy than those of other models.

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1. Introduction

Miscibility of polymeric mixtures was once viewed as an interesting but very rare occurrence. However, the number of miscible polymer blends reported in the literature has increased by an order of magnitude in the past decade with the number of technical papers in this area increasingly accordingly. Polymer miscibility has become a major area of research in many industrial and academic laboratories [1].

Lattice models provide a convenient starting point for the theoretical description of the thermodynamic properties of polymer solutions and blends. A variety of lattice theories has been developed during the last century; most of them are revised forms of the classical work proposed by Flory and Huggins [2–5]. The Flory–Huggins theory is based on a lattice model for polymer solutions wherein all lattice sites are occupied by segments of molecules. A mean-field approximation was used to obtain the Helmholtz energy of mixing. Many theoretical improvements, including Guggenheim's quasi-chemical model [6], have been made by various workers, include chain connectivity and non-random mixing. The Flory–

Huggins model and the quasi-chemical model give too narrow or parabolic liquid–liquid coexistence curves near the critical region when compared with experiment data in which the interaction parameter is assumed to be only inversely proportional to temperature.

The lattice cluster theory (LCT) developed by Freed and co-workers [7–14] in 1990s was a new landmark because it is formally an exact mathematical solution of the Flory–Huggins lattice with a complete and systematic analysis. In this theory, instead of the usual approximate counting of microstates, Freed's technique begins with a rigorous formulation of the partition function of the lattice and expands the Helmholtz free energy as a series of integrals. The terms can then be grouped to provide an expansion in the reciprocal of the lattice coordination number z . The effects of nearest-neighbor interactions are evaluated via a perturbation expansion in the interaction energies whose individual coefficients are represented in a similar fashion and further expanded in the power of z^{-1} . However, because of the complexity of the expansion, pages of equations are involved even if truncated at the first order or at the second order. Therefore, this theory still remains deficient for the correlation of liquid–liquid equilibria (LLE).

Hu et al. [15,16] reported a double lattice model (DLM) based on Freed's LCT. The empirical parameters in their model arose from the truncation of higher order terms in the expansion of the Helmholtz energy of mixing, and were

* Corresponding author. Tel.: +82 2 2220 0529; fax: +82 2 2296 0568.

E-mail address: ycbae@hanyang.ac.kr (Y.C. Bae).

¹ <http://www.inchem.hanyang.ac.kr/lab/mtl>.

determined by using a few Monte-Carlo simulation data. Lambert et al. [17] and Oh and Bae [18] have taken similar approaches. Recently, Chang and Bae [19] extended their modified double lattice model (mDLM) to polymer blends and Yang et al. [20–23] developed a new lattice model for polymer solutions by combining molecular simulation with statistical mechanics. For the consideration of polymer blends, Utracki [24] and Xin et al. [25] developed a statistical thermodynamics theory to compute the miscibility behavior and Anthamatten [26], Schacht and Koberstein [27] and Lee et al. [28] investigated the effect of chain end groups on the thermodynamics of polymer blends.

At present most of the published lattice models provide good estimates of LLE for polymer/solvent systems. However, these are not suitable to apply to polymer blend systems because most of them do not consider the special qualities of the polymer blend systems.

The purpose of this study is to extend the previous lattice model to polymer blend systems by introducing new universal functions. Liquid–liquid coexistence curves are described by the proposed model and compared with the experimental data of ordinary and associated polymer blends. Our model requires a few adjustable model parameters to describe an upper critical solution temperature (UCST) or a lower critical solution temperature (LCST).

2. Model development

2.1. 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 r_1 lattice sites, and N_2 molecules of type 2, which occupy r_2 lattice sites. The energy of mixing is related to the number of nearest-neighbor 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.

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

where ε_{ij} is the i – j nearest-neighbor 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 mixing as 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 absolute temperature and k is 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.

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

2.2. Correlation of simulation data

The algebraic form to correlate energy of mixing data from Monte-Carlo simulations is a Redlich–Kister expansion truncated after the third term in a similar way to Lambert et al. [17]

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

In this equation, parameter B is rarely sensitive to r_2/r_1 value and converges to zero when r_1 equals r_2 . We assume that in the polymer blend system, the differences between r_1 and r_2 are not very large ($r_1 \cong r_2$) compared with those of polymer solution systems ($r_1 \ll r_2$). Therefore, parameter B can be neglected. Parameters A and C depend on temperature only, and are correlated by

$$\begin{aligned} A &= A_0 + A_1 \left[\exp\left(\frac{1}{\tilde{T}}\right) - 1 \right] \\ C &= C_0 + C_1 \left[\exp\left(\frac{1}{\tilde{T}}\right) - 1 \right] \end{aligned} \quad (9)$$

the function of temperature, $\exp\left(\frac{1}{\tilde{T}}\right) - 1$, arises in Guggenheim's Quasi-Chemical model. Lambert et al. [17] reported that parameter C_0 provides only a very small contributions to the energy of mixing. Fixing $C_0 = 0$ does not affect the quality of the fit of the simulation data nor the resulting coexistence curves.

For a binary liquid mixture, there is fluctuation, which is difference in composition between coexisting phases [29]. Near a critical region, all liquid mixtures exhibit similar behavior because the properties of a liquid mixture are dominated by the long range correlation. A quantitative description of a mixture near its critical point should take into account the effect of fluctuations. Attending to the coexistence curve, we introduce an essentially empirical expression for the fluctuation term as a function of temperature [30].

Therefore, we redefine A_0 as a temperature dependent function given by

$$\begin{aligned} A_0 &= A'_0(0.8T_r + 0.2) \\ T_r &= T/T_c \end{aligned} \quad (10)$$

where T_r and T_c are the reduced temperature and critical temperature, respectively.

Parameters A'_0 , A_1 , and C_1 are determined by comparison with Müller's Monte-Carlo simulation data [31] for the symmetric polymer blend system ($r_1 = 32$ and $r_2 = 32$). The best correlating values of A'_0 , A_1 , and C_1 are 5.725, -57.497 , and 37.455 , respectively. These are universal constants, not adjustable parameters. As shown in Fig. 1, the calculation results are accurate, and broader than those of Lambert et al. [17]. We define the above model as Case I in this study.

In the LLE calculation, only the interchange energy value (ε/k) is a fitting parameter. Chain length (r_i) is calculated by

$$r_i = \frac{V_{mi(vdW)}^u \cdot M_{wi}}{10.23(\text{cm}^3/\text{mol}) \cdot M_{wi}^u} \quad (11)$$

where the constant $10.23(\text{cm}^3/\text{mol})$, $V_{mi(vdW)}$, and M_{wi} are the molar van der Waals volume of a CH_2 group, which occupies one lattice site, from Bondi [32], the molar van der Waals volume of component i , and the molecular weight of component i , respectively. Superscript u represents the repeating unit of polymers. If the r_i values are fixed by Eq. (11), the critical composition is automatically determined from Eq. (19). It is well known that the F-H model gives $\chi = 0.5$ in Eq. (12):

$$\phi_c = \frac{1}{1 + (r_2/r_1)^x} \quad (12)$$

Yelash et al. [33] reported that for some small-chain solutions, $\phi_c \propto (r_2/r_1)^{-0.19}$ was obtained in the $r_2/r_1 = 1$ – 3.5 range, whereas for some polymer solutions ($r_2/r_1 \geq$ few thousand), the exponent was -0.38 to -0.43 . As mentioned previously, for polymer blend systems, r_2/r_1 values are very small relative to polymer solution systems. Therefore, to satisfy the results for $r_2/r_1 = 1$ – 3.5 range, we introduce a new universal function into C_0 as a chain length dependent term given by

$$C_0 = C'_0(1 - \tilde{R}) \\ \tilde{R} = r_2/r_1 \quad (13)$$

the correlating value of C'_0 is -2.679 . This is also universal constant, not adjustable parameter. We define this revised

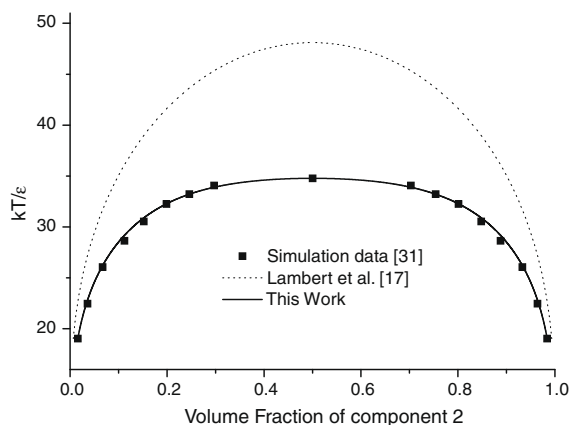


Fig. 1. Phase diagram of $r_1 = 32/r_2 = 32$ mixture. The dark squares are simulation data [31]. The solid and dotted lines are calculated by this work and Lambert et al. [17], respectively.

model as Case II in this study. When r_2 is equal to r_1 (perfect symmetric system), $C_0 = 0$, so Case II returns to Case I. Fig. 2 shows calculation results of critical composition for various lattice models compared with the result of Yelash et al. [33]. As shown in Fig. 2, Case II is less sensitive to the chain length difference of two components and in better agreement with the analysis of Yelash et al. [33]. Therefore, for describing real polymer blend systems, Case II is chosen in this work.

2.3. Oriented interactions

To consider the oriented interactions between the segments of molecules, Oh and Bae [18] defined a new Helmholtz energy of mixing to improve the mathematical approximation defect of the Ising model proposed by Freed. The expression is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij,kT}} = \frac{2}{z} \left[\eta \ln \eta + (1 - \eta) \ln(1 - \eta) + \frac{z C_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta}{1 + C_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta} \right] \quad (14)$$

where $\Delta A_{\text{sec},ij}$ 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, $\delta \tilde{\varepsilon}(\delta \varepsilon/kT)$ is the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions. For simplicity, we arbitrarily set η to 0.3 as suggested by Hu et al. [15] C_α is a universal constant that is determined by comparison with Panagiotopoulos et al.'s Gibbs-ensemble Monte-Carlo simulation data of the Ising lattice [34]. The best-fit value of C_α is 0.4881. To incorporate a secondary lattice, we replace ε_{ij} by $\varepsilon_{ij} = \frac{\Delta A_{\text{sec},ij}}{N_{ij}}$. If oriented interaction occurs in the i – j segment–segment pairs, we replace $1/\tilde{T}$ by $\frac{\varepsilon}{kT} + 2 \frac{\Delta A_{\text{sec},ij}}{N_{ij,kT}}$. If oriented interaction occurs in the i – i segment–segment pairs, we replace $1/\tilde{T}$ by $\frac{\varepsilon}{kT} - \frac{\Delta A_{\text{sec},ij}}{N_{ii,kT}}$.

2.4. Phase equilibrium calculations

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

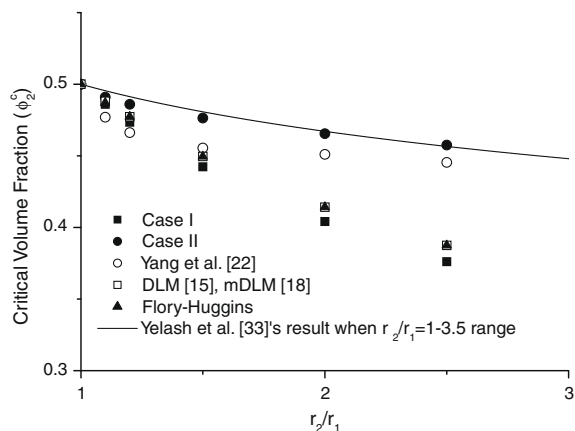


Fig. 2. Calculation results of critical composition for various lattice models versus the ratio of the polymer chain lengths.

$$\frac{\Delta\mu_1}{kT} = \left[\frac{\partial(\Delta A/N_r kT)}{\partial N_1} \right]_{T,V,N_2} \quad (15)$$

$$\frac{\Delta\mu_2}{kT} = \left[\frac{\partial(\Delta A/N_r kT)}{\partial N_2} \right]_{T,V,N_1} \quad (16)$$

A coexistence curve can be determined from the following conditions

$$\Delta\mu'_1 = \Delta\mu''_1 \quad (17)$$

$$\Delta\mu'_2 = \Delta\mu''_2 \quad (18)$$

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. For phase equilibrium calculation, we require the experimental coordinates of the critical point. And the critical condition is given by

$$\frac{\partial(\Delta\mu_1/kT)}{\partial\phi_2} = \frac{\partial^2(\Delta\mu_1/kT)}{\partial\phi_2^2} = 0 \quad (19)$$

3. Results and discussion

Our model has a few basic assumptions. Firstly, flexibilities and structural effects of polymer chains are neglected. All polymer chains are freely flexible. Secondly, volume change of mixing and free volume are not considered, that is, incompressible. Lastly, polydispersities of polymers are neglected, and all polymers are regarded as monodisperse.

For ordinary polymer blend systems we need only one adjustable parameter, ε/k to obtain a satisfactory fit to describe UCST curves. For systems that interact strongly, they must be in the proper orientation to each other (i.e., a specific interaction). Therefore, to describe this phenomenon, we introduce a secondary lattice concept and need one more adjustable parameter, $\delta\varepsilon/k$.

Fig. 3 shows the phase diagrams of polystyrene (PS)/poly(α -methyl styrene) (P α MeS) systems [35] and these systems exhibit UCST behaviors. In these systems, the secondary lattice contribution has been neglected since there is no evidence of any specific interaction between the two polymers. r_1 for the PS, r_2 for the P α MeS, a critical volume fraction of P α MeS (ϕ_2^c) and ε/k for two systems are listed in Table 1. The very small values of ε/k are due to the similar interaction energies between the segments of PS and P α MeS ($\varepsilon_{11} \approx \varepsilon_{22} \approx \varepsilon_{12}$). In other words, this is because the segments of PS and P α MeS have similar structures. In addition, as the molecular weight increases, the value of ε/k also reasonably increases. The prediction of phase behavior using the proposed model is more accurate and has broader results than those of other models. This is mainly because the proposed model considers the effect of fluctuation near a critical region whereas the other models do not take this into account.

Fig. 4 shows phase diagram of polybutadiene (PBD)/PS system [36] and this system also exhibits UCST behavior. In this system, specific interaction is not considered, either. r_1 for the PBD, r_2 for the PS, a critical volume fraction of PS (ϕ_2^c) and values are listed in Table 2. In comparison with the PS/P α MeS system, the molecular weights of this

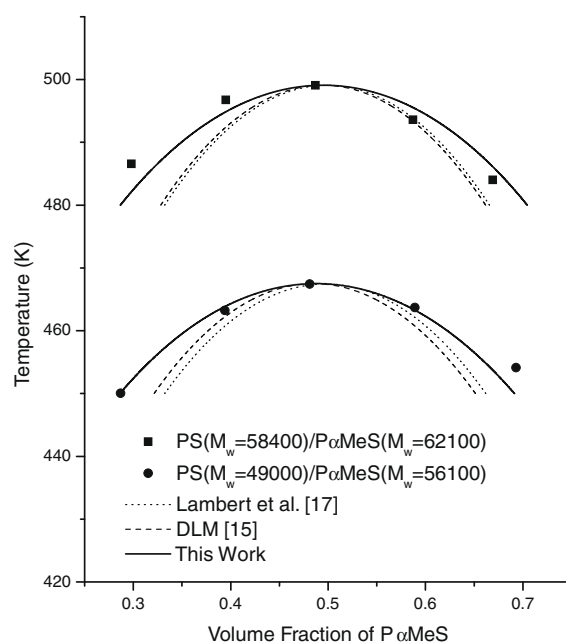


Fig. 3. Coexistence curves for PS/P α MeS systems. Discrete points are experimental data, and lines are calculated by various lattice models.

Table 1
Model parameters for PS/P α MeS systems.

Systems	r_1	r_2	ϕ_2^c	ε/k (K)
PS(58,400)/ P α MeS(62,100)	3641.18	3802.91	0.4954	0.1518
PS(49,000)/ P α MeS(56,100)	3055.10	3435.48	0.4878	0.0673

system are smaller but the ε/k value is larger. This is because the structural similarity of the segments of PBD and PS is smaller than PS/P α MeS. As shown in this figure, the prediction of mDLM is narrower and underestimates the critical composition. However, the proposed model

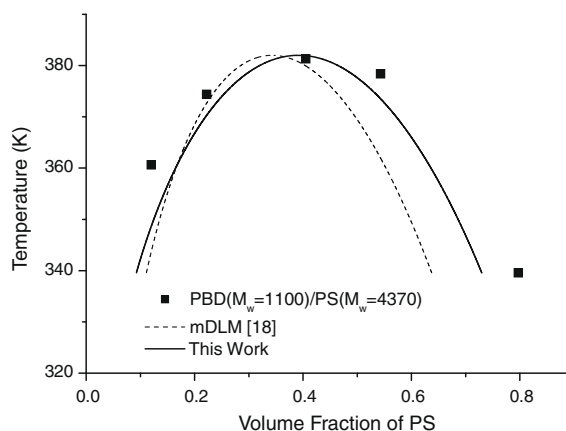


Fig. 4. Coexistence curve for PBD/PS system. Discrete points are experimental data, and lines are calculated by mDLM [18] and this work.

Table 2
Model parameters for PBD/PS systems.

Systems	r_1	r_2	ϕ_2^c	ε/k (K)
PBD(1100)/PS(4370)	74.26	272.47	0.3915	0.4732

gives better estimates of the critical composition and broader curves than mDLM, but still has discrepancies. This is because universal constants are determined only from the simulation data for $r_1 = 32/r_2 = 32$.

Fig. 5 shows phase diagrams of polyethylene glycol mono-methyl ether (PEGE)/polypropylene glycol (PPG) systems [37] and these systems also exhibit UCST behaviors. Two different polymer chains interact strongly; there exists the proper orientation exists with regards to each other. In these cases, we introduce the secondary lattice to account for specific interactions. Table 3 lists r_1 for the PEGE, r_2 for the PPG, a critical volume fraction of PPG (ϕ_2^c), ε/k , and $\delta\varepsilon_{12}/k$. The calculated results also agree well with the experimental data. In addition, the absolute values of ε/k and $\delta\varepsilon_{12}/k$ are likely to be slightly dependent on molecular weights of PEGE.

Fig. 6 shows phase diagrams of poly (5-acetyl-2,6-dimethyl-1,4-phenylene oxide) (APPO)/PS [38] and poly (vinyl methyl ether) (PVME)/PS [39] systems having LCST curves. APPO and PVME have oxygen atoms in their structure that lead to strong dipole–dipole interactions. Therefore, a secondary lattice is incorporated by $\delta\varepsilon_{11}/k$ not $\delta\varepsilon_{12}/k$. The model parameter values are listed in Table 4. APPO has a much smaller molecular weight than PVME, but specific energy value ($\delta\varepsilon_{11}/k$) is higher. Because PVME has only ether group but APPO has not only an ether group but also a ketone group, it is possible to induce specific

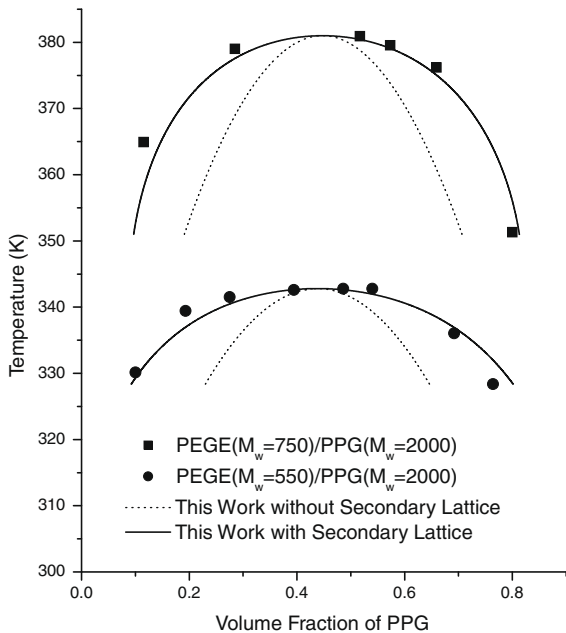


Fig. 5. Coexistence curves for PEGE/PPG systems. Discrete points are experimental data, and lines are calculated by this work.

Table 3
Model parameters for PEGE/PPG systems.

Systems	r_1	r_2	ϕ_2^c	ε/k (K)	$\delta\varepsilon_{12}/k$ (K)
PEGE(750)/PPG(2000)	43.20	121.79	0.4287	552.88	−766.71
PEGE(550)/PPG(2000)	31.68	121.79	0.3636	539.39	−754.50

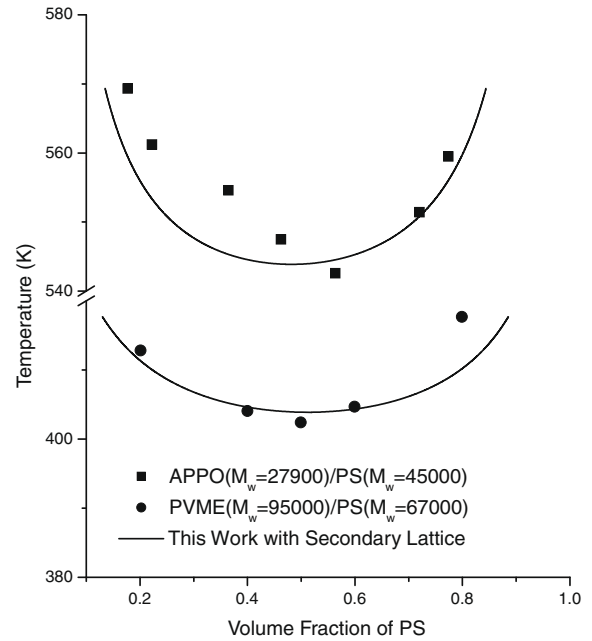


Fig. 6. Coexistence curves for APPO/PS and PVME/PS systems. Discrete points are experimental data, and lines are calculated by this work.

Table 4
Model parameters for APPO/PS and PVME/PS systems.

Systems	r_1	r_2	ϕ_2^c	ε/k (K)	$\delta\varepsilon_{11}/k$ (K)
APPO(27,900)/PS(45,000)	1459.05	2655.81	0.4712	210.86	2222.95
PVME(95,000)/PS(67,000)	5712.87	4177.38	0.5191	176.19	1626.64

interactions. The proposed model agrees well with the experimental data but a slight deviation between theoretical and experimental results is observed. This deviation might be due to the high polydispersity of PVME ($M_w/M_n = 1.27$) and APPO ($M_w/M_n = 1.88$) and the neglect of the free volume effect [40] that leads to LCST.

4. Conclusion

We propose a simple molecular thermodynamic model for polymer blend systems. Our semi-empirical approach based on molecular simulation results gives us new universal functions to develop more accurate models. We have observed some advantages in the LLE calculation of or-

dinary polymer blend systems. Firstly, the critical composition calculated by the proposed model is less sensitive to the chain length difference of the two polymers and gives better agreement with the experimental data than those of other models. Secondly, the calculated coexistence curves show broader two-phase regions than those of other models. Lastly, a secondary lattice also gives better agreement with the experimental data by widening the two-phase regions. The proposed model describes phase behavior of polymer blend systems fairly well in spite of its simplicity and use of only a few model parameters; however, it has a limitation in describing LCST curves.

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