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Liquid-Liquid Equilibria of Binary Polymer Blends: Molecular Thermodynamic Approach

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Summary: We extended and simplified the modified double-lattice model to binary polymer blend systems. The model has two model parameters, C_β and C_γ. Those are not adjustable parameters but universal functions. In comparison with Ryu *et al.*'s simulation data for symmetric polymer blend with various chain lengths ($r_1=r_2=8$, 20, 50, 100), C_γ is determined. Our results show that C_β is negligible for symmetric polymer blend systems. The proposed model describes very well phase behaviors of weakly interacting polymer blend systems.

Keywords: binary polymer blend, chain length, liquid-liquid equilibria, molecular thermodynamics, simulation

Introduction

During the last decades, there are various theoretical and experimental approaches to investigate the structures and thermodynamic properties of polymers and their blends. However, most theoretical considerations on the miscibility of polymer-polymer blend systems have developed through the mean-field theory of Flory and Huggins[1~5] due to the simplicity for practical calculations. To overcome some problems of the mean-field theory and pursue a formal "exact" solution to the lattice model, Freed and coworkers[6~8] derived a lattice field theory (or lattice cluster theory) for polymer/solvent systems using advanced statistical-mechanical methods. This theory formally provides an exact mathematical solution for the Flory-Huggins model. However, for practical reasons, the infinite series with respect to coordination number, temperature, and composition are truncated at a certain order. Therefore, this theory still remains deficiency for the real system.

Hu *et al.*[9~10] reported a new and simple model based on Freed's lattice-cluster theory. However, the model has some arbitrary and empirical parameters.

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Recently, Oh *et al.*[11] modified Hu *et al.*'s model by introducing new universal parameters and simplified the expression of the Helmholtz energy of mixing to reduce the arbitrariness. The parameters were obtained by comparing simulation data for the polymer solutions with the model (r_1=1 and r_2=100). Therefore, the parameters are not suitable to apply to the polymer blend systems.

The purpose of this study is to extend Oh *et al.*'s model to the polymer blend systems by introducing a new universal parameter, C_γ, as a function of the chain length of a polymer. The coexistence curves are generated and then compared with the experimental data for polymer blend systems. Our model requires only one adjustable binary parameters to describe an upper critical solution temperature (UCST) of weakly interacting polymer blend systems.

Model Development

Helmholtz energy of mixing

Oh *et al.*[11] proposed a new Helmholtz energy of mixing as the form of the Flory and Huggins theory[1~5]. The expression is given by

$$\Delta A / N_r kT = (\phi_1/r_1)\ln\phi_1 + (\phi_2/r_2)\ln\phi_2 + \chi_{OB}\phi_1\phi_2 \tag{1}$$

where N_r is the total number of lattice sites and k is the Boltzmann's constant. ϕ_i and r_i are the volume fraction and the number of segments for component *i*, respectively. χ_{OB}, a new interaction parameter, is defined and rearranged by

$$\begin{aligned}\chi_{OB} &= C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + \left(2+\frac{1}{r_2}\right)\tilde{\varepsilon} - \left(\frac{1}{r_2}-\frac{1}{r_1}+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\phi_2 + C_\gamma\tilde{\varepsilon}^2\phi_2^{\,2} \\ &= C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + \left(2+\frac{\phi_1}{r_2}+\frac{\phi_2}{r_1}\right)\tilde{\varepsilon} - C_\gamma\tilde{\varepsilon}^2\phi_1\phi_2\end{aligned} \tag{2}$$

where the first term on the right-handed side represents degree of asymmetry between two molecules. However, we assume that in the polymer blend systems, the differences between r_1 and r_2 are not very large ($r_1 \cong r_2$) compared with those of polymer solution systems ($r_1 << r_2$), that is, phase diagrams of polymer blends nearly show the symmetric shapes and critical compositions are near 0.5. Therefore, this term can be neglected. χ_{OB} has only one model parameter, C_γ. $\tilde{\varepsilon}$ is a reduced interaction parameter given by

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

where $\varepsilon_{11}, \varepsilon_{22}$ and ε_{12} are the corresponding nearest-neighbor segment-segment interactions. χ_{OB} then is a function of temperature, composition and chain length of polymer and has the second order approximation form of $\tilde{\varepsilon}$. Figure 1 shows the simulation results by Ryu *et al.*[19] for various chain lengths of polymers ($r_1 = r_2 =$ 8, 20, 50, 100). As shown in Figure 1, the calculation results (dotted line) with the constant $C_\gamma = A_0$ (Case I) are narrower than those of the simulation data. We assume that C_γ is a function of temperature (Case II);

$$\begin{aligned} C_\gamma &= A_0 + A_1(T_r - 1) \\ T_r &= T/T_c \end{aligned} \tag{4}$$

where T_c is a critical temperature. When $T = T_c$, Case II returns to Case I. Results show that calculated values using Case II give much better agreements than those of Case I. The solid lines are the best fit given by the proposed model. From these calculations, we obtain the values of A_0 and A_1 for the various chain lengths of polymers.

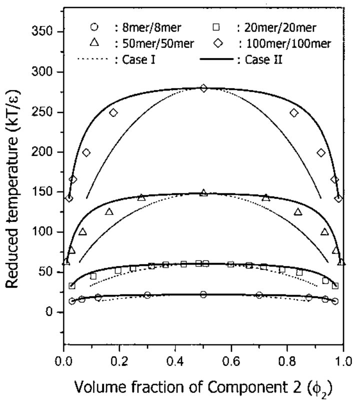

Figure 1. Phase diagram of symmetric polymer blend systems with various chain lengths of polymers

Figure 2 represents the chain length dependence of C_γ. The parameters are appeared to be asymptotic values with respect to r_2. The following mathematical equations are suggested the r-mer dependence of the values of A_0 and A_1 in C_γ, respectively:

$$A_0 = 50.7921 - \frac{30.3247(r_2 - 1)}{1 + 0.0046(r_2 - 1)} \tag{5}$$

$$A_1 = -1124.0506 + \frac{386.4166(r_2 - 1)}{1 + 0.0038(r_2 - 1)} \tag{6}$$

Eqs. (5) and (6) can be applied for large r_2. For r_2>10000, C_γ is very weakly dependent on r_2 according to Figure 2. In our proposed model, parameter C_γ , which is not an adjustable parameter, has fixed value at given temperature and r-mer chain length of each system.

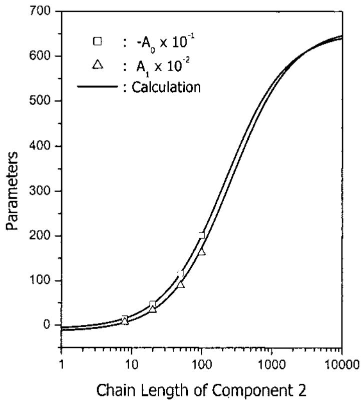

Figure 2. Dependence of parameter C_γ on *r*-mer chain length. The solid lines are generalized by equation (5) and (6). The open triangles and squres are the results obtained from the previous calculation step

Chemical potentials of component 1 and 2 for calculating the binary coexistence curve are given by

$$\frac{\Delta\mu_1}{kT} = \ln(1-\phi_2) - \left(\frac{r_1}{r_2}-1\right)\phi_2 + \left[\left\{\left(\frac{r_1}{r_2}-1\right) + r_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + r_1\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2^{\,2}$$
$$-2\left[\left\{\left(\frac{r_1}{r_2}-1\right) + r_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + r_1 C_\gamma \tilde{\varepsilon}^2\right]\phi_2^{\,3} + 3 r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^{\,4} \tag{7}$$

$$\frac{\Delta\mu_2}{kT} = \ln\phi_2 + \left(1-\frac{r_2}{r_1}\right) + (2r_2+1)\tilde{\varepsilon}$$
$$-\left[\left(1-\frac{r_2}{r_1}\right) + 2\left\{\left(1-\frac{r_2}{r_1}\right) + r_2 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + 2(2r_2+1)\tilde{\varepsilon}\right]\phi_2$$
$$+\left[\left\{\left(1-\frac{r_2}{r_1}\right) + r_2 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + (2r_2+1)\tilde{\varepsilon} + 3 r_2 C_\gamma \tilde{\varepsilon}^2\right]\phi_2^{\,2} \tag{8}$$
$$-\left[6 r_2 C_\gamma \tilde{\varepsilon}^2 + 2\left\{\left(1-\frac{r_2}{r_1}\right) + r_2 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon}\right]\phi_2^{\,3} + 3 r_2 C_\gamma \tilde{\varepsilon}^2 \phi_2^{\,4}$$

The coexistence curve is found from the following conditions:

$$\Delta\mu_1{}' = \Delta\mu_1{}'' \tag{9}$$

$$\Delta\mu_2{}' = \Delta\mu_2{}'' \tag{10}$$

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 conditions are given by,

$$\frac{\partial^2(\Delta A/N_r kT)}{\partial\phi_2^{\,2}}$$
$$= \frac{-1}{1-\phi_2} + \left(1-\frac{r_1}{r_2}\right) + 2\left[\left\{\left(\frac{r_1}{r_2}-1\right) + r_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + r_1\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2 \tag{11}$$
$$-6\left[\left\{\left(\frac{r_1}{r_2}-1\right) + r_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + r_1 C_\gamma \tilde{\varepsilon}^2\right]\phi_2^{\,2} + 12 r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^{\,3} = 0$$

and

$$\begin{aligned}&\frac{\partial^3(\Delta A/N_r kT)}{\partial\phi_2{}^3}\\&=\frac{-1}{(1-\phi_2)^2}+2\left[\left(\left(\frac{r_1}{r_2}-1\right)+r_1C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+r_1\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\\&-12\left[\left\{\left(\frac{r_1}{r_2}-1\right)+r_1C_\gamma\tilde{\varepsilon}\right\}\tilde{\varepsilon}+r_1C_\gamma\tilde{\varepsilon}^2\right]\phi_2+36r_1C_\gamma\tilde{\varepsilon}^2\phi_2{}^2=0\end{aligned}\tag{12}$$

Results and Discussion

We introduce three basic assumptions as follow:

1. Flexibilities and structure effects of polymer chains are neglected. All polymer chains are freely flexible.
2. Volume change of mixing and free volume is not considered, that is, incompressible.
3. Polydispersities of polymers are neglected. All polymers are regarded as monodisperse.

In the proposed model, only one parameter, ε/k, is needed to calculate theoretical coexistence curves. r_i is calculated by

$$r_i=\frac{V^u_{mi(vdW)}\cdot M_{wi}}{10.23(cm^3/mol)\cdot M^u_{wi}}\tag{13}$$

where the constant $10.23(cm^3/mol)$, $V_{mi(vdW)}$ and M_{wi} are the molar van der Waals (vdW) volume of a CH_2 group, which occupies one lattice site, from Bondi[13], the molar vdW volume and molecular weight of component *i*, respectively. Superscript *u* represents a repeating unit of polymers. If r_i's are fixed by Equation (13), the critical composition of each system is numerically determined from critical conditions obtained by Equation (11) and (12).

Figure 3 shows phase diagrams of Polystyrene (PS) / Poly (α - methyl styrene) (Pα MeS) systems[14]. This is the ordinary system showing a UCST phase behavior without the oriented interaction.

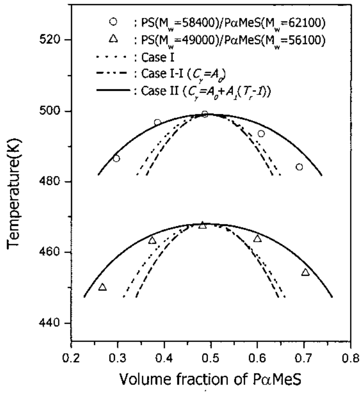

Figure 3. Cloud-point data for PS/Pα MeS systems

For these systems, the values of r_1 and r_2 calculated by Equation (13), respectively. From these values, the numerically determined critical volume fraction of Pα MeS (ϕ_2^c) and ε/k are listed in Table 1, respectively.

Table 1. The values of model parameters for PS/Pα MeS.

r_1	r_2	$\varepsilon/k(K)$	ϕ_c	$T_c(K)$
3641.18	3802.91	0.1019	0.4968	499.2
3055.10	3435.48	0.1071	0.4852	468.1

The very small values of ε/k are due to the similar interaction energies between segments of PS and Pα MeS ($\varepsilon_{11} \cong \varepsilon_{22} \cong \varepsilon_{12}$). In other word, it is due to the structural similarity of segments of PS and Pα MeS. In addition, ε/k is likely to be slightly dependent of molecular weights of polymers. The Case I-I is calculated with C_γ as a fuction of the chain length of polymer at $T_r = 1$. Case II shows a better agreement than thoese of the others.

Figure 4 shows phase diagrams of Polybutadiene (PBD) / PS system[15].

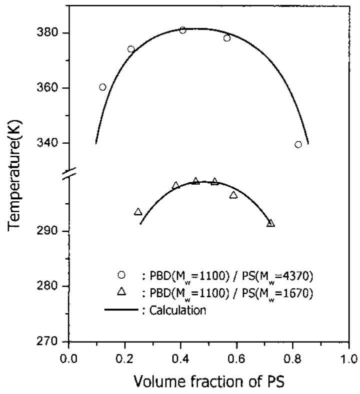

Figure 4. Cloud-point data for PBD/PS systems

r_1, r_2, a critical volume fraction of PS (ϕ_2^c) and ε/k for different molecular weight of PS's are listed in Table 2.

Table 2. The values of model parameters for PBD/PS systems

r_1	r_2	$\varepsilon/k(K)$	ϕ_c	$T_c(K)$
74.26	272.47	0.9827	0.4519	381.6
74.26	104.12	1.1518	0.4860	299.05

The systems having low molecular weight and slightly large asymmetry of polymers show the similar results as those of Figure 3.

In LLE calculation of polymer blends, the critical composition plays a very important role to determine shapes of phase diagrams.

Conclusion

We derived the simple molecular thermodynamic framework for polymer blends. In our model, the critical composition obtained numerically by the asymmetry between two polymers is the most important parameter to determine the shape of calculated coexistence curves. The proposed model describes fairly well phase behavior of polymer blend systems in spite of its simplicity and using only one model parameter.

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