고분자 용액의 용매의 활동도: 그룹 기여 방법

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Solvent Activity of Polymer Solution: Group-contribution Method

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Theory

Primary lattice

Oh *et al.* proposed a new Helmholtz energy of mixing as the form of the Flory and Huggins theory. 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 compared with those of polymer solution systems ($r_1 << r_2$), that is, phase diagrams of polymer blend systems nearly show the symmetric shapes and critical compositions are around 0.5. We find that the entropic correction by C_β is not very significant; therefore, C_β is fixed to 0.1415 obtained from mDLM, in which C_γ is 1.7985 as a universal constant. $\tilde{\varepsilon}$ is a reduced interchanging energy as defined by

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

where ε_{ij} is the *i-j* nearest-neighbor interaction energy. Therefore, χ_{OB} is a function of temperature, composition and polymer chain length and has the second order approximation form of $\tilde{\varepsilon}$. For systems without oriented interactions between the segments of two polymers, only a primary lattice is needed to describe LLE of polymer blends.

Universal function (Interaction energy correction term)

In this work, we assume that C_β and C_γ correct independently χ_{OB}, respectively. The simulation results from Ryu *et al.* for various polymer chain lengths of symmetric polymer blend systems ($r_1 = r_2$ = 8, 20, 50, 100) are used to obtain the C_β and C_γ. The calculated results with the constant $C_\gamma = C_\gamma^c$ (Case I) are narrower than those of the simulation data. The C_γ is calculated as a function of temperature (Case II);

$$\begin{aligned} C_\gamma &= C_\gamma^c \cdot (4.0/T_r - 3.0) \\ T_r &= T/T_c \end{aligned} \tag{4}$$

where T_c is a critical temperature and C_γ^c is calculated at T_c. When $T = T_c$, Case II returns to Case I. Results show that values calculated from Case II give much better agreements with simulation results than those of Case I. As well known, C_γ is implicating the correction of defects from the truncation of higher order interaction energy terms. Therefore, we regard C_γ as a function of interaction energy.

The interaction energy dependence of C_γ fitted with the previous calculation results are obtained. The parameter is appeared to be linear with respect to reduced critical temperature ($\tilde{\varepsilon}_c^{-1}$). The following equations are suggested the interaction energy dependence of the values of C_γ as a universal function:

$$C_\gamma^c = 35.1377 + 7.1749 \cdot \tilde{\varepsilon}_c^{-1} \tag{5}$$

$$C_\gamma = C_\gamma^c \cdot (4.0/T_r - 3.0) \tag{6}$$

In our proposed model, parameter C_γ, which is not an adjustable parameter, depends on temperature and interaction energy.

Secondary lattice

To take into account the oriented interactions between the segments of molecules, Oh *et al.* defined a new Helmholtz energy of mixing to improve the mathematical approximation defect of the Ising model proposed by Freed. The expression for the secondary lattice is given by

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

where N_{ij} is the number of *i-j* segment-segment pairs, $\delta\tilde{\varepsilon}_{ij}$ is the reduced energy parameter contributed by the oriented interactions between *i-j* segment-segment pairs and η, which is set to 0.3, is the surface fraction permitting oriented interactions. C_α is the universal constant determined by comparing with Gibbs-Ensemble Monte-Carlo simulation data of Ising lattice. The best fitting value of C_α is 0.4880. Following the definition of $\tilde{\varepsilon}$ in Equation (3), if the oriented interaction occurs in *i-j* segment-segment pairs, we replace $\tilde{\varepsilon}$ by $\varepsilon/kT + 2\,\Delta A_{\sec,ij}/N_{ij}kT$ in Equation (2). If the oriented interaction occurs in *i-i* segment-segment pairs, $\tilde{\varepsilon}$ is replaced by $\varepsilon/kT - \Delta A_{\sec,ii}/N_{ii}kT$.

Correlating Equations

Chemical potential of polymer 1 is given by

$$
\begin{aligned}
\frac{\Delta\mu_1}{kT} &= \ln(1-\phi_2) - \left(\frac{r_1}{r_2}-1\right)\phi_2 \\
&+ \left[r_1 C_\beta \left(\frac{1}{r_1}-\frac{1}{r_2}\right)^2 + \left\{\left(\frac{r_1}{r_2}-1\right) - r_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + r_1\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2^{\,2} \\
&- 2\left[\left\{\left(\frac{r_1}{r_2}-1\right) - r_1 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} - r_1 C_\gamma \tilde{\varepsilon}^2\right]\phi_2^{\,3} - 3 r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^{\,4}
\end{aligned}
\tag{8}
$$

and a similar relation holds for chemical potential of polymer 2

$$
\begin{aligned}
\frac{\Delta\mu_2}{kT} &= \ln\phi_2 + \left(1-\frac{r_2}{r_1}\right) + r_2 C_\beta \left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + (2r_2+1)\tilde{\varepsilon} \\
&- \left[\left(1-\frac{r_2}{r_1}\right) + 2\left\{\left(1-\frac{r_2}{r_1}\right) - r_2 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + 2 r_2 C_\beta \left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + 2(2r_2+1)\tilde{\varepsilon}\right]\phi_2 \\
&+ \left[4\left\{\left(1-\frac{r_2}{r_1}\right) - r_2 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon} + (2r_2+1)\tilde{\varepsilon} + r_2 C_\beta \left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 - 3 r_2 C_\gamma \tilde{\varepsilon}^2\right]\phi_2^{\,2} \\
&+ \left[6 r_2 C_\gamma \tilde{\varepsilon}^2 - 2\left\{\left(1-\frac{r_2}{r_1}\right) - r_2 C_\gamma \tilde{\varepsilon}\right\}\tilde{\varepsilon}\right]\phi_2^{\,3} - 3 r_2 C_\gamma \tilde{\varepsilon}^2 \phi_2^{\,4}
\end{aligned}
\tag{9}
$$

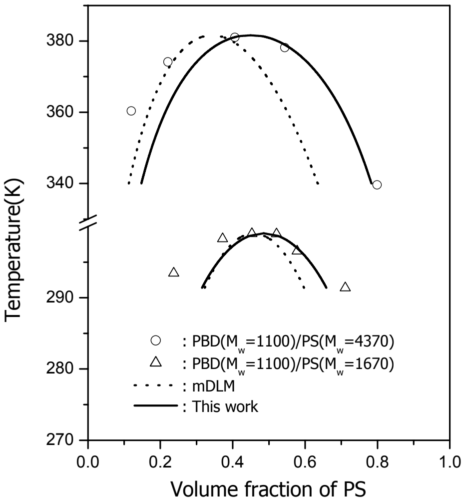
The coexistence curve is found from the following conditions:

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

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

where $\Delta\mu_i$ is the change in chemical potential upon isothermally transferring component i from the pure state to the mixture. Superscripts $'$ and $''$ denote two phases at equilibrium. For phase equilibrium calculation, we require the experimental coordinates of the critical point. The critical temperature and critical volume fraction can be obtained by solving the following two equations simultaneously.

Results and Conclusion



In LLE calculation of polymer blend systems, the interaction energy correction term to reduce the truncation error gives the better results in the comparison of the numerical critical points and the coexistence curves with experimental data. In our model, the critical point determined numerically by the difference between the chain lengths of two polymers is the most important parameter in generating calculated coexistence curves. In spite of its simplicity and using only a few model parameters, the proposed model describes fairly well phase behavior of polymer blend systems and gives a general correlation of the mathematical model with the computer simulation in the phase behavior of polymer blend systems.

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