

# What Has Brought on the Effects of Number-Average Molecular Weight on the Spinodals in Polymer Mixtures?

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On the basis of the thermodynamics of Gibbs, the spinodal for the quasibinary system was derived in the framework of the Sanchez–Lacombe lattice fluid theory. All of the spinodals were calculated based on a model polydisperse polymer mixture, where each polymer contains three different molecular weight sub-components. According to our calculations, the spinodal depends on both weight-average ( $\bar{M}_w$ ) and number-average ( $\bar{M}_n$ ) molecular weights, whereas that of the  $z$ -average molecular weight is invisible. Moreover, the extreme of the spinodal decreases when the polydispersity index ( $\eta = \bar{M}_w/\bar{M}_n$ ) of the polymer increases. The effect of polydispersity on the spinodal decreases when the molecular weight gets larger and can be negligible at a certain large molecular weight. It is well-known that the influence of polydispersity on the phase equilibrium (coexisting curve, cloud point curves) is much more pronounced than on the spinodal. The effect of  $\bar{M}_n$  on the spinodal is discussed as it results from the influence of composition temperatures, molecular weight, and the latter's distribution on free volume. An approximate expression, which is in the assumptions of  $v^* = v_1^* = v_2^*$  and  $1/r \rightarrow 0$  for both of the polymers, was also derived for simplification. It can be used in high molecular weight, although it failed to make visible the effect of number-average molecular weight on the spinodal.

## Introduction

In our previous paper,<sup>1</sup> the effects of polydispersity on the spinodal in polymer solutions were studied by using the Sanchez–Lacombe lattice fluid theory (SLLFT).<sup>2–5</sup> It is well-known that the behavior of the polymer in mixtures is much different from that in solutions. However, the study in this area is limited by the complexity of the mixture, because the system may contain thousands of components. In the 1960s, Koningsveld et al.<sup>6</sup> first developed the spinodal and critical point equations for quasibinary systems based on the Flory–Huggins (FH) lattice theory and the thermodynamics of Gibbs, by treating the system as a multicomponent one. They pointed out that the spinodal can only be determined by the weight-average length of polymer. As far as we know, Koningsveld et al. treated their system as quasiternary systems (solvent/polymer 1/polymer 2), such that the solvent composition can be considered as a dependent variable, and all of the compositions of the sub-components of the two polymers can be used as independent variables. Setting the solvent concentration as zero, they derived the spinodal and critical state for a mixture of polydisperse polymers. Their work is pioneering for polydisperse polymer systems. However, FH theory is quite a simple theoretical model, and its deficiencies are indicated by many authors.<sup>7–9</sup> Although Koningsveld and Kleintjens studied the spinodal, the critical point, and the cloud points of polydisperse systems using new

theoretical models afterward,<sup>10–15</sup> the conclusion is still unchanged and cited by many other researchers such as McMaster.<sup>16</sup> More recently, Rätzsch and co-workers<sup>17,18</sup> advanced the theory of continuous thermodynamics to deal with the polydisperse system. Browarzik et al.<sup>19</sup> studied the stability of polydisperse fluid mixtures under the guidance of continuous thermodynamics based on an equation of state with two parameters. Hu et al.<sup>20</sup> and Rochocz et al.<sup>21</sup> developed this method by means of hybridizing the continuous thermodynamics and multicomponent methods. These new methods are still in their developing stages, though in practice semicontinuous mixtures often play an important role in the theoretical estimation of the phase behavior of polydisperse systems.

In our previous work,<sup>1</sup> it was found that both  $\bar{M}_w$  and  $\bar{M}_n$  have effects on the spinodal, a conclusion which contradicts that presented by Koningsveld et al.<sup>6,10–15</sup> However, the effect of  $\bar{M}_n$  on the spinodal is very small compared with that of  $\bar{M}_w$ . A simple approximate expression of the spinodal in SLLFT was also obtained similar to the one presented by Sanchez and Lacombe.<sup>3</sup> On the basis of our calculation, we pointed out that the variance of free volume with composition, temperature, molecular weight, and its distribution was the reason for the effect of  $\bar{M}_n$  on the spinodal.<sup>1</sup> In this paper, the generalized phase-separation condition, which is based on that advanced by Gibbs,<sup>22</sup> is presented for the polydisperse polymer mixtures with the help of SLLFT. The spinodals for the model systems were calculated. From these results, it can be seen that a similar effect of polydispersity on the spinodal as that in polymer solutions was obtained. However, the effect of  $\bar{M}_n$  on the spinodal in polymer mixtures is greater than that in solutions.

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The influence of the change in free volume on the spinodal is also discussed in this paper.

### Theoretical Background

The Gibbs energy and equation-of-state in SLLFT can be expressed as the following:<sup>23, 24</sup>

$$G = rN\epsilon^* \left\{ -\tilde{\rho} + \tilde{P}\tilde{v} + \tilde{T} \left[ (\tilde{v} - 1) \ln(1 - \tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \sum_{i,j} \frac{\phi_{ij}^0}{r_{ij}^0} \ln \frac{\phi_{ij}^0}{\omega_{ij}^0} \right] \right\} \quad (1)$$

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] = 0 \quad (2)$$

The physical meaning of all of the variables in the above and the following equations is presented in the List of Symbols. Equation 1 is slightly different from the original one in that the expression

$$\sum_{i,j} \frac{\phi_{ij}^0}{r_{ij}^0} \ln \frac{\phi_{ij}^0}{\omega_{ij}^0}$$

is substituted for

$$\sum_{i,j} \frac{\phi_{ij}}{r_{ij}} \ln \frac{\phi_{ij}}{\omega_{ij}}$$

It can be easily known that there is no difference between them if we assume the same symmetry numbers both in mixtures and in pure states, i.e.,  $\sigma_{1i} = \sigma_{1i}^0$  and  $\sigma_{2j} = \sigma_{2j}^0$ , and the maximum flexibility parameters for all of the subcomponents, i.e.,  $\delta_{ij} = \delta_{ij}^{\max}$  and  $\delta_{ij}^0 = \delta_{ij}^{0\max}$ . These variables included are below:

$$\delta_{ij} = \delta_{ij}^{\max} = z(z-1)^{r_{ij}-2}; \quad \delta_{ij}^0 = \delta_{ij}^{0\max} = z(z-1)^{r_{ij}^0-2}$$

$$\omega_{ij} = \{\delta_{ij} r_{ij}\} / \{\sigma_{ij} e^{r_{ij}-1}\}; \quad \omega_{ij}^0 = \{\delta_{ij}^0 r_{ij}^0\} / \{\sigma_{ij}^0 e^{r_{ij}^0-1}\} \quad (3)$$

The reduced variables in eqs 1 and 2 can be written as

$$\tilde{X} = X/X^* \quad (4)$$

with  $X = T, P, v$  on the left-hand side and  $X = T, P, V$  on the right-hand side and

$$T^* = \epsilon^*/k; P^* = \epsilon^*/v^* \quad (5)$$

$$V^* = rNv^* = \sum_{i,j} r_{ij} N_{ij} v^* \quad (6)$$

The reduced density reads as

$$\tilde{\rho} = \frac{1}{\tilde{v}} = \frac{V^*}{V} \quad (7)$$

The close-packed volume fraction of subcomponent  $j$  of component  $i$  can be defined as

$$\phi_{ij} = \frac{r_{ij} N_{ij}}{rN} \quad (8)$$

whereas

$$\phi_{ij}^0 = \frac{r_{ij}^0 N_{ij}}{rN} \quad (9)$$

$$N = \sum_{i,j} N_{ij} \quad (10)$$

$$rN = \sum_{i,j} r_{ij} N_{ij} = \sum_{i,j} r_{ij}^0 N_{ij} \quad (11)$$

$$1/r = \sum_{i,j} \frac{\phi_{ij}}{r_{ij}} = \sum_{i,j} \frac{\phi_{ij}^0}{r_{ij}^0} \quad (12)$$

For quasibinary systems, the scaling parameters  $\epsilon^*$  and  $v^*$  for mixtures could be obtained by using “combining rules”,<sup>23,24</sup> which can be expressed as

$$\epsilon^* = \sum_{i=1}^h \sum_{j=1}^h \phi_{1i} \phi_{1j} \epsilon_{11,ij}^* + \sum_{i=1}^h \sum_{j=1}^l \phi_{1i} \phi_{2j} \epsilon_{12,ij}^* + \sum_{i=1}^l \sum_{j=1}^h \phi_{2i} \phi_{1j} \epsilon_{21,ij}^* + \sum_{i=1}^l \sum_{j=1}^l \phi_{2i} \phi_{2j} \epsilon_{22,ij}^* \quad (13)$$

$$v^* = \sum_{i=1}^h \phi_{1i}^0 v_{1i}^* + \sum_{j=1}^l \phi_{2j}^0 v_{2j}^* \quad (14)$$

If it is assumed that there is no influence of chain-length on  $\epsilon_{ij,i'j'}^*$  ( $i, j = 1, 2; i', j' = 1, 2, \dots, h$  or  $1, 2, \dots, l$ ) and the volume per lattice site,  $v_{ij}^*$ , then  $\epsilon_{11,ij}^* = \epsilon_{11}^*$ ,  $\epsilon_{22,ij}^* = \epsilon_{22}^*$ ,  $\epsilon_{12,ij}^* = \epsilon_{21,ij}^* = \epsilon_{12}^*$ , and  $v_{ij}^* = v_i^*$ . Equations 13 and 14 can be simplified into those for the monodisperse system in SLLFT,<sup>3</sup> which reads

$$\epsilon^* = \phi_1^2 \epsilon_{11}^* + 2\phi_1 \phi_2 \epsilon_{12}^* + \phi_2^2 \epsilon_{22}^* \quad (15)$$

$$v^* = \phi_1^0 v_1^* + \phi_2^0 v_2^* \quad (16)$$

Let

$$g = \frac{G}{rNkT} = \frac{\bar{G}}{kT} \quad (17)$$

where  $\bar{G}$  is the Gibbs energy per lattice site occupied in SLLFT. Thus, the following expression can be easily obtained, i.e.:

$$g = \frac{-\tilde{\rho} + \tilde{P}\tilde{v}}{\tilde{T}} + (\tilde{v} - 1) \ln(1 - \tilde{\rho}) + \frac{1}{r} \ln \tilde{\rho} + \sum_{i,j} \frac{\phi_{ij}^0}{r_{ij}^0} \ln \frac{\phi_{ij}^0}{\omega_{ij}^0} \quad (18)$$

where

$$\sum_{i=1}^h \phi_{1i}^0 + \sum_{j=1}^l \phi_{2j}^0 = 1 \text{ or } \sum_{i=1}^h \phi_{1i}^0 + \sum_{j=1}^{l-1} \phi_{2j}^0 + \phi_{2l}^0 = 1 \quad (19)$$

According to the thermodynamics of Gibbs,<sup>22</sup> the spinodal criteria is given as

$$J_{\text{sp}} = |\partial^2 \xi / \partial m_i \partial m_j| = 0 \quad (i, j = 1, 2, \dots, n-1) \quad (20)$$

where  $J_{\text{sp}}$  is a  $(n-1) \times (n-1)$  determinant under the condition

$$J_{sp} = \begin{vmatrix} \frac{\partial^2 \bar{G}}{\partial \phi_1^2} & \frac{\partial^2 \bar{G}}{\partial \phi_1 \partial \phi_2} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_1 \partial \phi_n} & \frac{\partial^2 \bar{G}}{\partial \phi_1 \partial \phi_{21}} & \frac{\partial^2 \bar{G}}{\partial \phi_1 \partial \phi_{22}} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_1 \partial \phi_{2,j-1}} \\ \frac{\partial^2 \bar{G}}{\partial \phi_2 \partial \phi_1} & \frac{\partial^2 \bar{G}}{\partial \phi_2^2} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_2 \partial \phi_n} & \frac{\partial^2 \bar{G}}{\partial \phi_2 \partial \phi_{21}} & \frac{\partial^2 \bar{G}}{\partial \phi_2 \partial \phi_{22}} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_2 \partial \phi_{2,j-1}} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \bar{G}}{\partial \phi_n \partial \phi_1} & \frac{\partial^2 \bar{G}}{\partial \phi_n \partial \phi_2} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_n^2} & \frac{\partial^2 \bar{G}}{\partial \phi_n \partial \phi_{21}} & \frac{\partial^2 \bar{G}}{\partial \phi_n \partial \phi_{22}} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_n \partial \phi_{2,j-1}} \\ \frac{\partial^2 \bar{G}}{\partial \phi_{21} \partial \phi_1} & \frac{\partial^2 \bar{G}}{\partial \phi_{21} \partial \phi_2} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_{21} \partial \phi_n} & \frac{\partial^2 \bar{G}}{\partial \phi_{21}^2} & \frac{\partial^2 \bar{G}}{\partial \phi_{21} \partial \phi_{22}} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_{21} \partial \phi_{2,j-1}} \\ \frac{\partial^2 \bar{G}}{\partial \phi_{22} \partial \phi_1} & \frac{\partial^2 \bar{G}}{\partial \phi_{22} \partial \phi_2} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_{22} \partial \phi_n} & \frac{\partial^2 \bar{G}}{\partial \phi_{22} \partial \phi_{21}} & \frac{\partial^2 \bar{G}}{\partial \phi_{22}^2} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_{22} \partial \phi_{2,j-1}} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 \bar{G}}{\partial \phi_{2,j-1} \partial \phi_1} & \frac{\partial^2 \bar{G}}{\partial \phi_{2,j-1} \partial \phi_2} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_{2,j-1} \partial \phi_n} & \frac{\partial^2 \bar{G}}{\partial \phi_{2,j-1} \partial \phi_{21}} & \frac{\partial^2 \bar{G}}{\partial \phi_{2,j-1} \partial \phi_{22}} & \cdots & \frac{\partial^2 \bar{G}}{\partial \phi_{2,j-1}^2} \end{vmatrix} = 0 \quad (21)$$

of intensive energy  $\zeta$  and composition fractions  $m_i$  or  $m_j$ . For the quasibinary polymer mixtures, we have eq 21 (see above).

In the above determinant  $J_{sp}$ ,  $(\partial^2 \bar{G})/(\partial \phi_{1i}^0 \partial \phi_{1j}^0)$ ,  $(\partial^2 \bar{G})/(\partial \phi_{1i}^0 \partial \phi_{2j}^0)$ , and  $(\partial^2 \bar{G})/(\partial \phi_{2i}^0 \partial \phi_{2j}^0)$  are the general terms. The above determinant can be reduced to the spinodal condition of Sanchez-Lacombe,<sup>3</sup> when both polymers are monodisperse. In this paper,  $\phi^0$ 's are used to calculate the spinodal as the composition variables.

Those general terms in eq 21 can be written as (see Appendix I for details for all of the deduction and definition of symbols)

$$\frac{\partial^2 \bar{G}}{\partial \phi_{ij}^0 \partial \phi_{i'j'}^0} = kT \frac{\partial^2 g}{\partial \phi_{ij}^0 \partial \phi_{i'j'}^0} \quad (22)$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} = \begin{cases} -\tilde{\rho}\Theta + \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta \psi_{1i} \psi_{1j} & (i \neq j) \\ -\tilde{\rho}\Theta + \frac{1}{r_{2l}^0 \phi_{2l}^0} + \frac{1}{r_{1i}^0 \phi_{1i}^0} - \tilde{\rho}\tilde{T}P^* \beta \psi_{1i}^2 & (i = j) \end{cases} \quad (23)$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} = \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta \psi_{1i} \psi_{2j} \quad (24)$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = \begin{cases} \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta \psi_{2i} \psi_{2j} & (i \neq j) \\ \frac{1}{r_{2i}^0 \phi_{2i}^0} + \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta \psi_{2i}^2 & (i = j) \end{cases} \quad (25)$$

The closed-packed volume fraction can be assumed to be the same as that in normal state,<sup>9</sup> that is, we can use  $\phi$  to represent the actual volume fraction in the polymer mixture. From eqs 21–25, the spinodal for polydisperse mixtures can be calculated by means of computer programming.

As indicated in our previous paper,<sup>1</sup> a quite simple expression can be obtained if some assumptions are used. Here we still use the following assumptions:

Assumption I:  $v^* = v_1^* = v_2^*$

Assumption II:  $1/r_{ij} \rightarrow 0$  for polymers. Under these two assumptions, we have

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} = -2\tilde{\rho}\chi + \left( \frac{1}{r_{1i} \phi_{1i}} + \frac{1}{r_{2l} \phi_{2l}} \right) - \tilde{\rho}\tilde{T}P^* \beta (\tilde{\rho}\lambda_{12})^2 \quad (26)$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} = -2\tilde{\rho}\chi + \frac{1}{r_{2l} \phi_{2l}} - \tilde{\rho}\tilde{T}P^* \beta (\tilde{\rho}\lambda_{12})^2 \quad (27)$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} = \frac{1}{r_{2l} \phi_{2l}} \quad (28)$$

$$\frac{\partial^2 g}{\partial \phi_{2j}^0 \partial \phi_{2j}^0} = \frac{1}{r_{2j} \phi_{2j}} + \frac{1}{r_{2l} \phi_{2l}} \quad (29)$$

$$\frac{\partial^2 g}{\partial \phi_{2j}^0 \partial \phi_{2i}^0} = \frac{1}{r_{2l} \phi_{2l}} \quad (30)$$

Here superscript 0 can be removed due to the assumption  $v^* = v_1^* = v_2^*$ . Let

$$J_{11} = -2\tilde{\rho}\chi + \frac{1}{r_{2l} \phi_{2l}} - \tilde{\rho}\tilde{T}P^* \beta \psi^2 \quad (31)$$

$$J_{22} = \frac{1}{r_{2l} \phi_{2l}} \quad (32)$$

$$L_{1i} = \frac{1}{r_{1i} \phi_{1i}} \quad (33)$$

$$L_{2j} = \frac{1}{r_{2j} \phi_{2j}} \quad (34)$$

where

$$\psi = \tilde{\rho}\lambda_{12} \quad (35)$$

we have

$$\frac{\partial^2 g}{\partial \phi_{1i}^2} = J_{11} + L_{1i} \quad (36)$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} = J_{11} \quad (i \neq j) \quad (37)$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} = J_{22} \quad (38)$$

$$\frac{\partial^2 g}{\partial \phi_{2j}^2} = J_{22} + L_{2j} \quad (39)$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} = J_{22} \quad (i \neq j) \quad (40)$$

Thus

$$(kI)^{k+l} J_{sp} = \begin{vmatrix} J_{11}+L_{11} & J_{11} & \cdots & J_{11} & J_{22} & J_{22} & \cdots & J_{22} \\ J_{11} & J_{11}+L_{12} & \cdots & J_{11} & J_{22} & J_{22} & \cdots & J_{22} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ J_{11} & J_{11} & \cdots & J_{11}+L_{1k} & J_{22} & J_{22} & \cdots & J_{22} \\ J_{22} & J_{22} & \cdots & J_{22} & J_{22}+L_{21} & J_{22} & \cdots & J_{22} \\ J_{22} & J_{22} & \cdots & J_{22} & J_{22} & J_{22}+L_{22} & \cdots & J_{22} \\ \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \ddots & \vdots \\ J_{22} & J_{22} & \cdots & J_{22} & J_{22} & J_{22} & \cdots & J_{22}+L_{2l-1} \end{vmatrix} = 0 \quad (41)$$

From the above determinant, we have

$$1 + J_{11} \sum_{i=1}^k L_{1i}^{-1} + J_{22} \sum_{j=1}^{l-1} L_{2j}^{-1} + J_{22}(J_{11} - J_{22}) \sum_{i=1}^k L_{1i}^{-1} \sum_{j=1}^{l-1} L_{2j}^{-1} = 0 \quad (42)$$

Substituting  $J_{11}$ ,  $J_{22}$ ,  $L_{1i}$ , and  $L_{2j}$  into eq 42, we can obtain the spinodal as following:

$$\frac{1}{r_{w,1}\phi_1} + \frac{1}{r_{w,2}\phi_2} = \tilde{\rho}(2\chi + \tilde{T}\psi^2 P^* \beta) \quad (\text{see Appendix II}) \quad (43)$$

where  $r_{w,1}$  and  $r_{w,2}$  are the weight-average chain length of polymer 1 and polymer 2 and  $\phi_1$  and  $\phi_2$  are the volume fraction of polymer 1 and polymer 2, respectively.

If the system is reduced into monodisperse system, then  $r_{w,1} = r_1$ ,  $r_{w,2} = r_2$ , and the spinodal is

$$\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2} = \tilde{\rho}(2\chi + \tilde{T}\psi^2 P^* \beta) \quad (44)$$

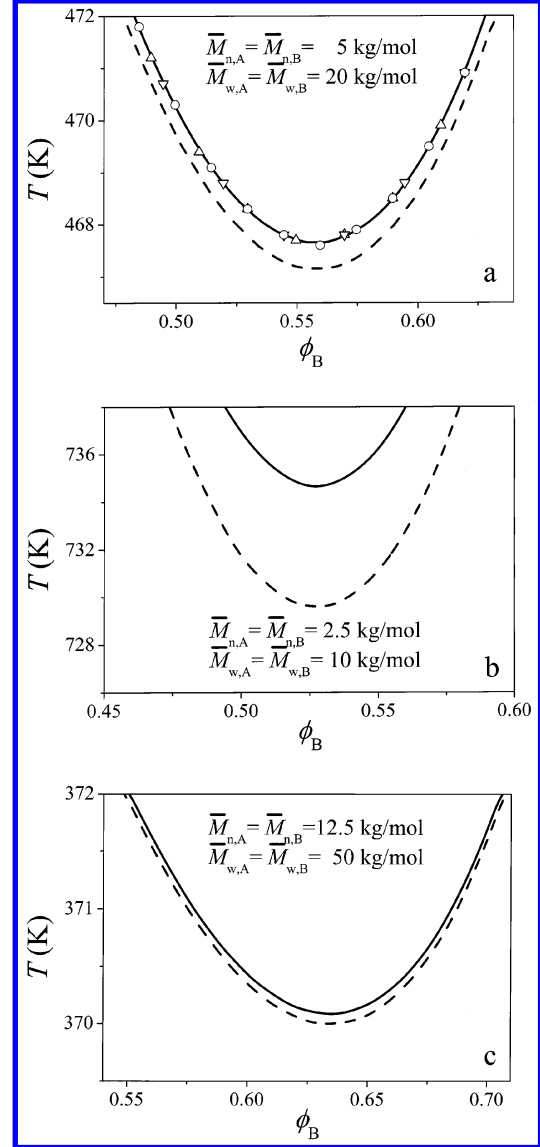
The spinodal is identical with that obtained by Sanchez and Lacombe.<sup>3</sup>

As indicated in our previous paper,<sup>1</sup> the approximate expression of the spinodal is not related with the number-average weight of both of the polymers. However, we know that the number-average molecular weight does have some effect on the spinodal in polydisperse polymer solutions. So here we still need to know the difference between the exact determinant and the approximate expression in polydisperse polymer mixtures. The

**TABLE 1: Scaling Parameters of Model System (Based on PES/Phenoxy Mixtures)**

	$P^*(\text{MPa})$	$\rho^*(\text{kg/m}^3)$	$T^*(\text{K})$
polymer A	646.6	1468.9	833.99
polymer B	578.5 <sup>a</sup>	1239.5	746.2

<sup>a</sup>  $P^*$  of polymer B should be 603.7 MPa in ref 25. The data listed in Table 1 was obtained under the assumption of  $v_1^* = v_2^* = v^*$ .

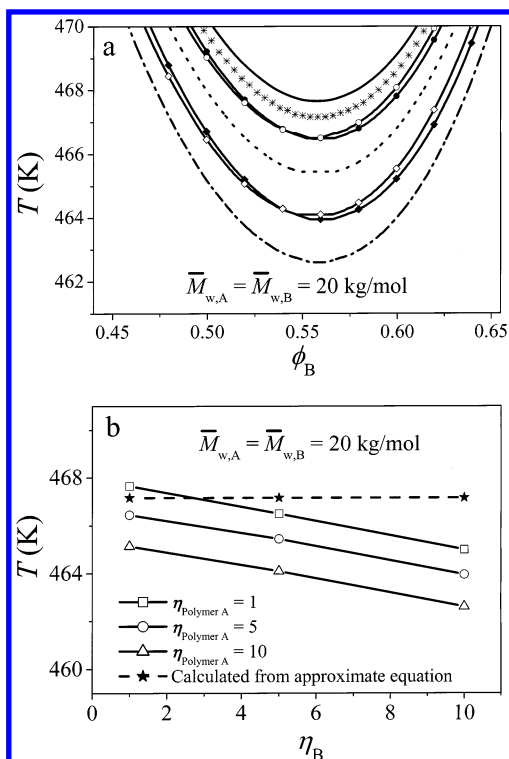


**Figure 1.** Effects of changing  $\bar{M}_z$  on the spinodals for a model polymer A/polymer B system at the fixed  $\bar{M}_n$  and  $\bar{M}_w$  ( $\eta_{w/n} = \bar{M}_w/\bar{M}_n = 4$ ) calculated by eqs 21–25 (symbols and solid lines) and by eq 43 (dash lines). a.  $\bar{M}_{n,A} = \bar{M}_{n,B} = \bar{M}_n = 5$  kg/mol and  $\bar{M}_{w,A} = \bar{M}_{w,B} = \bar{M}_w = 20$  kg/mol. (—)  $\bar{M}_z = 40$  kg/mol; ( $\Delta$ )  $\bar{M}_z = 100$  kg/mol; ( $\nabla$ )  $\bar{M}_z = 125$  kg/mol; ( $\circ$ )  $\bar{M}_z = 150$  kg/mol. b.  $\bar{M}_{n,A} = \bar{M}_{n,B} = \bar{M}_n = 2.5$  kg/mol and  $\bar{M}_{w,A} = \bar{M}_{w,B} = \bar{M}_w = 10$  kg/mol. c.  $\bar{M}_{n,A} = \bar{M}_{n,B} = \bar{M}_n = 12.5$  kg/mol and  $\bar{M}_{w,A} = \bar{M}_{w,B} = \bar{M}_w = 50$  kg/mol.

source of the effect of number-average molecular weight on the spinodal should also be considered.

## Results and Discussion

With the method developed in the previous section, it is possible to calculate the spinodals for a representative polymer pair by using the exact determinant and the approximate expression. To discuss the effects of molecular weight and its distribution on the spinodal, we introduce a model system based

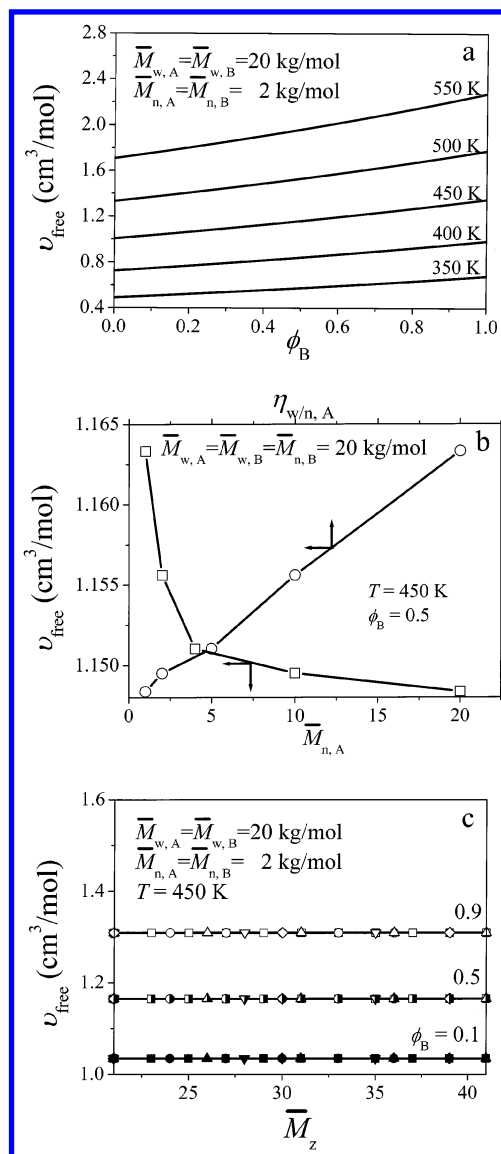


**Figure 2.** Effects of changing  $\bar{M}_n$  on the spinodals for a model polymer A/polymer B system at  $\bar{M}_{w,A} = \bar{M}_{w,B} = 20$  kg/mol, where  $\eta_{w/n,A} = \bar{M}_{w,A}/\bar{M}_{n,A}$ ,  $\eta_{w/n,B} = \bar{M}_{w,B}/\bar{M}_{n,B}$  and  $\gamma = \eta_{w/n,A}/\eta_{w/n,B}$ . The monodisperse model systems were also calculated by the method presented by Horst.<sup>26</sup> The star points (★) present the results from eq 43. a. The spinodals at different number-average molecular weights. (—)  $\gamma = 1/1$ ; (---)  $\gamma = 5/5$ ; (-·-·-)  $\gamma = 10/10$ ; (-○-)  $\gamma = 5/1$ ; (-●-)  $\gamma = 1/5$ ; (-◇-)  $\gamma = 10/5$ ; (-◆-)  $\gamma = 5/10$ . b. Dependence of the minimum temperature of the spinodal on the polydispersity index.

on the polyethersulfone (PES)/phenoxy polydisperse system. The three scaling parameters, which are listed in Table 1, are obtained elsewhere.<sup>25</sup> For convenience,  $v_1^* = v_2^* = v^*$  is assumed to be similar to that in SLLFT.<sup>3</sup> In our calculation, the interaction energy parameter ( $\epsilon_{12}^*/k$ ) between polymers A and B is independent of molecular weight and equal to 790.4 K. For simplification, both of the polydisperse polymers in this model system are assumed to contain three subcomponents, and their molecular weights and contents can be obtained via the definitions of  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_z$ .<sup>1</sup>

**Effect of  $\bar{M}_z$  on the Spinodal at the Fixed  $\bar{M}_w$  and  $\bar{M}_n$ .** Four different  $\bar{M}_z$ 's (40, 100, 125, and 150 kg/mol) were chosen for each polymer at the same  $\bar{M}_w$  (20 kg/mol) and  $\bar{M}_n$  (5 kg/mol) as we did in the previous paper.<sup>1</sup> As shown in Figure 1a, similar to that in solutions, all of the spinodals calculated from eq 21 are coincident with each other. This indicates that if  $\bar{M}_w$  and  $\bar{M}_n$  remain constant, the variance of  $z$ -average molecular weights of the polymers has no visible effect on the position of the spinodal of the polymer mixtures. Also, the results obtained from eq 43 are slightly different from the ones in eq 21. To elucidate this, we chose two other different molecular weights with the same polydispersity index to calculate the spinodals as shown in parts b and c of Figure 1. It is seen that the difference between the results from eq 21 and from eq 43 decrease when the weight-average molecular weight increases. That means the larger the weight-average molecular weight is, the closer the approximate results of the spinodal (eq 43) to the real one are.

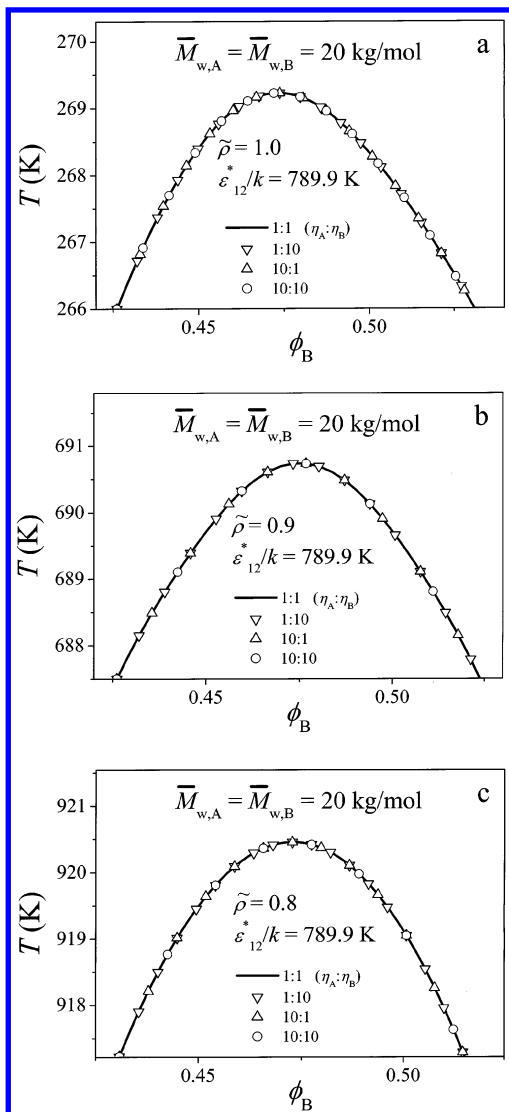
**Effect of  $\bar{M}_n$  on the Spinodal at the Fixed  $\bar{M}_w$ .** From our former discussion,<sup>1</sup> it is known that changing  $\bar{M}_n$  of the polymer



**Figure 3.** Dependence of the free volume on composition, temperature, polydispersity index,  $z$ -average molecular weight, and molecular weight distribution in the polydisperse polymer mixture. a. Relationship between the free volume and volume fraction of polymer B at different temperature, where  $\bar{M}_{w,A} = \bar{M}_{w,B} = 20$  kg/mol and  $\bar{M}_{n,A} = \bar{M}_{n,B} = 2$  kg/mol. b. Relationship between the free volume and polydispersity index at  $\phi_B = 0.5$  and  $T = 450$  K, where  $\bar{M}_{w,A} = \bar{M}_{w,B} = \bar{M}_{n,A} = \bar{M}_{n,B} = 20$  kg/mol. c. Relationship between the free volume and  $\bar{M}_z$  at  $T = 450$  K for the different volume fractions where  $\bar{M}_{w,A} = \bar{M}_{w,B} = 20$  kg/mol and  $\bar{M}_{n,A} = \bar{M}_{n,B} = 2$  kg/mol. Squares:  $w_{11} = w_{21} = 0.25$ ,  $w_{12} = w_{22} = 0.50$ ,  $w_{13} = w_{23} = 0.25$ . Circles:  $w_{11} = w_{21} = 0.20$ ,  $w_{12} = w_{22} = 0.60$ ,  $w_{13} = w_{23} = 0.20$ . Up-triangles:  $M_{11} = M_{21} = 1.0$  kg/mol,  $M_{12} = M_{22} = 1.5$  kg/mol. Down-triangles:  $M_{12} = M_{22} = 1.5$  kg/mol,  $M_{13} = M_{23} = 2.0$  kg/mol. Diamonds:  $M_{11} = M_{21} = 2.0$  kg/mol,  $M_{13} = M_{23} = 2.5$  kg/mol.

can also affect the position of the spinodal even though  $\bar{M}_w$  remains a constant in the polymer solution. This is a novel conclusion and different from that of Koningsveld et al.,<sup>6</sup> but in solutions, that effect is quite small compared with the phase separation temperature. Here, we continue discussing that effect in polymer mixtures. The  $\bar{M}_w$ 's of the two polymers were fixed at 20 kg/mol and  $\bar{M}_n$ 's varied according to the polydispersity indices of the polymers. The effect of changing  $\bar{M}_n$  of the polymer on the spinodal is perceptible according to the calculated results shown in Figure 2. When  $\bar{M}_n$  decreases, i.e., the polydispersity index increases, the phase separation area is enhanced and the minimum of the spinodals decreases. More-

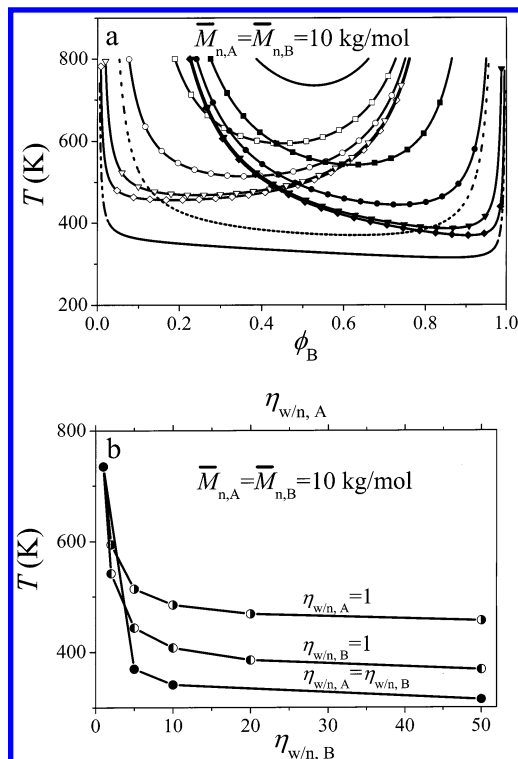




**Figure 4.** Spinodals of different number-average molecular weight at  $\bar{M}_{w,A} = \bar{M}_{w,B} = 20$  kg/mol when the reduced density is constant, where  $\eta_{w/n,A} = \bar{M}_{w,A}/\bar{M}_{n,A}$ ,  $\eta_{w/n,B} = \bar{M}_{w,B}/\bar{M}_{n,B}$  and  $\gamma = \eta_{w/n,A}/\eta_{w/n,B}$ . (—)  $\gamma = 1/1$ ; ( $\nabla$ )  $\gamma = 1/10$ ; ( $\Delta$ )  $\gamma = 10/1$ ; ( $\circ$ )  $\gamma = 10/10$ . a.  $\tilde{\rho} = 1.0$ ; b.  $\tilde{\rho} = 0.9$ ; c.  $\tilde{\rho} = 0.8$ .

over, the extremum gets lower when the polydispersity index of the polymer is increasing. At the same time, the trend of decrease accelerates also when both  $\eta$ 's are increasing simultaneously. The influence of changing  $\bar{M}_n$  on the spinodal in polymer mixtures is more perceivable compared with that in polymer solutions. The results obtained from eq 43 are also shown in Figure 2. It is seen that the difference does exist and is greater than that in polymer solutions. Thus, eq 43 can only produce an approximate result. Moreover, the difference between the spinodals calculated from eq 43 and from the monodisperse system is caused by using the Assumption II in eq 43. If one wants to get a more reliable result, the determinant, eq 21, should be used. In the following calculation, we use the determinant, eq 21, to continue studying the effect of polydispersity on the spinodal in a polymer mixture.

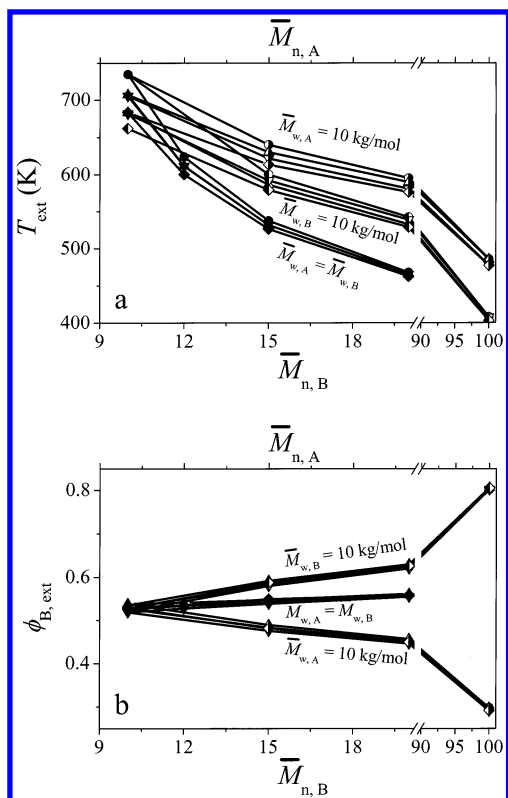
In our previous paper,<sup>1</sup> the variance of free volume in the solutions was considered to be the reason for the effect of  $\bar{M}_n$  on the spinodal. In polymer mixtures, we still can see the dependence of free volume (i.e., compressibility) on composition, temperature, and polydispersity as shown in parts a–c of Figure 3, where the free volume is defined as  $(\bar{v} - 1) \cdot v^*$ . From Figure 3b, it is seen that the dependence of free volume on the



**Figure 5.** Effects of changing  $\bar{M}_w$  on the spinodals for a model polymer A/polymer B system at  $\bar{M}_{n,A} = \bar{M}_{n,B} = 10$  kg/mol, where  $\eta_{w/n,A} = \bar{M}_{w,A}/\bar{M}_{n,A}$ ,  $\eta_{w/n,B} = \bar{M}_{w,B}/\bar{M}_{n,B}$  and  $\gamma = \eta_{w/n,A}/\eta_{w/n,B}$ . (—)  $\gamma = 1/1$ ; (---)  $\gamma = 5/5$ ; (---)  $\gamma = 50/50$ ; (—■—)  $\gamma = 2/1$ ; (—□—)  $\gamma = 1/2$ ; (—○—)  $\gamma = 1/5$ ; (—●—)  $\gamma = 5/1$ ; (—▽—)  $\gamma = 1/20$ ; (—○—)  $\gamma = 1/50$ ; (—▼—)  $\gamma = 20/1$ ; (—●—)  $\gamma = 50/1$ . a. The spinodals at different weight-average molecular weights. b. Dependence of the minimum temperature of the spinodal on the polydispersity index.

polydispersity index (the free volume increases monotonically with the polydispersity index) is different from the situation in a polymer solution (there is a maximum of free volume with the increase in the polydispersity index) when the  $\bar{M}_z$ 's are fixed. Meanwhile, the dependence of free volume on  $\bar{M}_z$  is invisible when  $\bar{M}_n$  and  $\bar{M}_w$  are unchanged at the given composition and temperature (Figure 3c); that is, the free volume only depends on  $\bar{M}_n$  and  $\bar{M}_w$  when the temperature and composition are fixed. Furthermore, the influence of the composition and molecular weight of sub-components of the polymers on the free volume of the mixture disappears at the fixed variables  $\bar{M}_n$ ,  $\bar{M}_w$ , and  $\bar{M}_z$ .

If we assume that the free volume in the system is independent of the composition, temperature, molecular weight, and the latter's distribution, i.e.,  $\tilde{\rho}$  is constant, then the SLLFT is similar to FH theory. For convenience, we considered  $\tilde{\rho} = 1, 0.9$ , and  $0.8$  in calculating the spinodals under this assumption. According to SLLFT,<sup>3</sup>  $\epsilon_{12}^*/k$  is adjusted to 789.9 K to obtain the reasonable spinodals. The calculated spinodals for different polydispersity indices at  $\bar{M}_{w,A} = \bar{M}_{w,B} = 20$  kg/mol are shown in Figure 4. The lower critical solution temperature (LCST) behavior has been transferred into the upper critical solution temperature (UCST) one because of the absence of free volume or the free volume independent of composition, temperature, molecular weight, and molecular weight distribution. The influence of  $\bar{M}_n$  on the spinodal disappears, which is the same as that in polymer solutions. That means the variance of free volume with composition, temperature, molecular weight, and molecular weight distribution in polymer mixtures results in the effect of  $\bar{M}_n$  on the spinodal.



**Figure 6.** Effect of polydispersities of polymers A and B on the spinodal at different number-average molecular weights.  $\eta_{w/n,B} = 1$  and 10, respectively, and  $\gamma = \eta_{w/n,A}/\eta_{w/n,B}$ . (—○—) 1/1; (—△—) 1/10; (—▽—) 10/1; (right half shaded diamond) 10/10 when  $\bar{M}_{n,A} = 10 \text{ kg/mol}$ ; (—●—) 1/1; (—▲—) 1/10; (—▼—) 10/1; (left half shaded diamond) 10/10 when  $\bar{M}_{n,B} = 10 \text{ kg/mol}$ ; (—●—) 1/1; (—▲—) 1/10; (—▼—) 10/1; (—◆—) 10/10 when  $\bar{M}_{n,A} = \bar{M}_{n,B}$ . a. Extremum temperature of the spinodal as a function of  $\bar{M}_n$  of polymer A and/or B. b. Extremum composition of the spinodal as a function of  $\bar{M}_n$  of polymer A and/or B.

**Effect of  $\bar{M}_w$  on the Spinodal at the Fixed  $\bar{M}_n$ .** In this section, we let the  $\bar{M}_n$ 's of the two polymers remain constant ( $\bar{M}_{n,A} = \bar{M}_{n,B} = 10 \text{ kg/mol}$ ), whereas the  $\bar{M}_w$ 's vary considerably. The calculated spinodals and their minimum temperatures vs the polydispersity index are shown in Figure 5 parts a and b. We can see that at different  $\bar{M}_w$ 's, the spinodals are very different from each other. Comparing Figure 5 with Figure 2, we can find that the effect of changing  $\bar{M}_w$  on the spinodal is much greater than that of changing  $\bar{M}_n$ . To show this, we fixed polymer A (or polymer B) as a monodisperse polymer and the other polymer as a polydisperse one where  $\eta = 2, 5, 20$ , and 50, respectively. The spinodals shifted from the pure polydisperse polymer side greatly when its polydisperse index increased. Moreover, the spinodals, whose ratios of polydispersity indices  $\eta_{w/n,A}/\eta_{w/n,B} = 5/5$  and 50/50, are also shown in Figure 5a. We can see that the phase separation area is enhanced greatly when both the polymers are polydisperse in mixture. This effect is much greater than that of changing the  $\bar{M}_w$  of one polymer.

**Effect of Polydispersity on the Spinodal at Different Molecular Weights.** Two different polydispersity indices ( $\eta_{w/n,A}$  and/or  $\eta_{w/n,B} = 1, 10$ ) for different molecular weights were chosen to discuss the effect of molecular weight on the spinodal. Figure 6 parts a and b show the extreme temperature of the spinodal (6a) and its corresponding polymer B composition (6b) calculated as functions of the number-average molecular weight of polymer A and/or B. We can see that with the increase of the molecular weight of the polymer the spinodal moves downward and the effect of polydispersity on the spinodal

decreases. This illustrates that when the molecular weight of the polymer reaches a certain value, the effect of polydispersity on the spinodal can be negligible. Generally speaking, the effect of polydispersity decreases when the molecular weight increases and is negligible in the end. Meanwhile, it is also seen that the effect of polydispersity on the spinodal decreases more rapidly when both the molecular weights of the two polymers increase.

## Conclusion

From the above calculation and discussion, the main conclusions are summarized as follows.

Polydispersity can enhance the phase separation area, but this effect is negligible when the molecular weight becomes quite high. Moreover, either changing  $\bar{M}_w$  or  $\bar{M}_n$  can influence the shape of and extremum of the spinodal. Only when both  $\bar{M}_w$  and  $\bar{M}_n$  are fixed are the shifts of the spinodals invisible. The effect of  $\bar{M}_n$  on spinodal results from the dependence of free volume on composition, temperature, molecular weight, and molecular weight distribution for the polymer mixture. Finally, a simple expression of the spinodal for a quasibinary polymer mixture, which is similar to that in the monodisperse systems in SLLFT, was derived. This expression can be used when the molecular weight is considerably high, but it is not a good one because the effect of the number-average molecular weight on the spinodal is not visible.

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## List of Symbols

### Symbols without Superscript and Subscript

- $G$  = Gibbs energy of the mixture with volume  $V$
- $\epsilon^*$  = average interaction energy per lattice occupied
- $v^*$  = volume of a mer or a lattice of mixture
- $r$  = average number of lattice occupied by a molecule in polymer mixture
- $N$  = total number of molecules in polymer mixture
- $z$  = coordination number
- $k$  = Boltzmann's constant
- $h$  = number of the subcomponents in component 1
- $l$  = number of the subcomponents in component 2

### Symbols with Superscript or Subscript

- $\epsilon_{ij}^*$  ( $i, j = 1, 2$ ) = interaction energy of a mer belonging to component  $i$  when it is surrounded by  $z$  mers belonging to component  $j$
- $\epsilon_{ij,i'j'}^*$  ( $i, j = 1, 2$ ;  $i', j' = 1, 2, \dots, h$  or  $1, 2, \dots, l$ ) = interaction energy of a mer belonging to subcomponent  $i'$  of component  $i$  when it is surrounded by  $z$  mers belonging to subcomponent  $j'$  of component  $j$
- $r_{ij}^0$  ( $j = 1, 2, \dots, h$  when  $i = 1$ ;  $j = 1, 2, \dots, l$  when  $i = 2$ ) = number of lattice occupied by one chain of the subcomponent  $j$  of component  $i$  in the corresponding pure state
- $r_{ij}$  ( $j = 1, 2, \dots, h$  when  $i = 1$ ;  $j = 1, 2, \dots, l$  when  $i = 2$ ) = number of lattice occupied by one chain of the subcomponent  $j$  of component  $i$  in the mixture

$N_{ij}$  = number of the molecules of subcomponent  $j$  in component  $i$

$\phi_{ij}$  = close-packed volume fraction of subcomponent  $j$  of component  $i$

$\omega_{ij}$  = number of configurations available to  $r_{ij}$ -mer in the close-packed state

$\omega_{ij}^0$  = number of configurations available to  $r_{ij}^0$ -mer in the corresponding close-packed pure state

$\sigma_{ij}$  = symmetry numbers of the molecular chain of subcomponent  $j$  of component  $i$  in mixture

$\sigma_i^0$  = symmetry numbers of molecular chain of subcomponent  $j$  of component  $i$  in the corresponding pure state

$\delta_{ij}$  = flexibility parameter of subcomponent  $j$  of component  $i$  in mixture

$\delta_{ij}^0$  = flexibility parameter of subcomponent  $j$  of component  $i$  in the corresponding pure state

### Appendix I: Derivation of the Second Partial Derivates of Gibbs Energy with Respect to $\phi_{ij}^0$

Equation 18 can be expressed as  $g = g(\phi_{ij}^0, \bar{\rho})$ , so

$$\frac{\partial g}{\partial \phi_{1i}^0} = \frac{\partial g}{\partial \phi_{1i}^0} \Big|_{\bar{\rho}} + \frac{\partial g}{\partial \bar{\rho}} \frac{\partial \bar{\rho}}{\partial \phi_{1i}^0} = \frac{\partial g}{\partial \phi_{1i}^0} \Big|_{\bar{\rho}} \quad (g_{\bar{\rho}} = 0, \text{ i.e., equation of state}) \quad (\text{A-1})$$

$$\frac{\partial g}{\partial \phi_{2j}^0} = \frac{\partial g}{\partial \phi_{2j}^0} \Big|_{\bar{\rho}} + \frac{\partial g}{\partial \bar{\rho}} \frac{\partial \bar{\rho}}{\partial \phi_{2j}^0} = \frac{\partial g}{\partial \phi_{2j}^0} \Big|_{\bar{\rho}} \quad (\text{A-2})$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} = \frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} \Big|_{\bar{\rho}} + \frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \bar{\rho}} \frac{\partial \bar{\rho}}{\partial \phi_{1j}^0} \quad (\text{A-3})$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} = \frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} \Big|_{\bar{\rho}} + \frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \bar{\rho}} \frac{\partial \bar{\rho}}{\partial \phi_{2j}^0} \quad (\text{A-4})$$

$$\frac{\partial^2 g}{\partial \phi_{2j}^0 \partial \phi_{2i}^0} = \frac{\partial^2 g}{\partial \phi_{2j}^0 \partial \phi_{2i}^0} \Big|_{\bar{\rho}} + \frac{\partial^2 g}{\partial \phi_{2j}^0 \partial \bar{\rho}} \frac{\partial \bar{\rho}}{\partial \phi_{2i}^0} \quad (\text{A-5})$$

where

$$\frac{\partial g}{\partial \phi_{1i}^0} = -\bar{\rho} \frac{\partial(\epsilon^*/kT)}{\partial \phi_{1i}^0} + \frac{P}{kT\bar{\rho}} \frac{\partial v^*}{\partial \phi_{1i}^0} + \left( \frac{1}{r_{1i}^0} - \frac{1}{r_{2i}^0} \right) \ln \bar{\rho} + \frac{1}{r_{1i}^0} \ln \frac{\phi_{1i}^0}{\omega_{1i}^0} + \frac{1}{r_{1i}^0} - \frac{1}{r_{2i}^0} \ln \frac{\phi_{2i}^0}{\omega_{2i}^0} - \frac{1}{r_{2i}^0} \quad (\text{A-6})$$

$$\frac{\partial g}{\partial \phi_{2j}^0} = -\bar{\rho} \frac{\partial(\epsilon^*/kT)}{\partial \phi_{2j}^0} + \frac{P}{kT\bar{\rho}} \frac{\partial v^*}{\partial \phi_{2j}^0} + \left( \frac{1}{r_{2j}^0} - \frac{1}{r_{2i}^0} \right) \ln \bar{\rho} + \frac{1}{r_{2j}^0} \ln \frac{\phi_{2j}^0}{\omega_{2j}^0} + \frac{1}{r_{2j}^0} - \frac{1}{r_{2i}^0} \ln \frac{\phi_{2i}^0}{\omega_{2i}^0} - \frac{1}{r_{2i}^0} \quad (\text{A-7})$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} \Big|_{\bar{\rho}} = -\bar{\rho} \frac{\partial^2(\epsilon^*/kT)}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} + \frac{P}{kT\bar{\rho}} \frac{\partial^2 v^*}{\partial \phi_{1i}^0 \partial \phi_{1j}^0} + \frac{\partial}{\partial \phi_{1j}^0} \left( \frac{1}{r_{1i}^0} \ln \frac{\phi_{1i}^0}{\omega_{1i}^0} \right) + \frac{1}{r_{2i}^0 \phi_{2i}^0} \quad (\text{A-8})$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} \Big|_{\bar{\rho}} = -\bar{\rho} \frac{\partial^2(\epsilon^*/kT)}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} + \frac{P}{kT\bar{\rho}} \frac{\partial^2 v^*}{\partial \phi_{1i}^0 \partial \phi_{2j}^0} + \frac{1}{r_{2i}^0 \phi_{2i}^0} \quad (\text{A-9})$$

$$\frac{\partial^2 g}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} \Big|_{\bar{\rho}} = -\bar{\rho} \frac{\partial^2(\epsilon^*/kT)}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} + \frac{P}{kT\bar{\rho}} \frac{\partial^2 v^*}{\partial \phi_{2i}^0 \partial \phi_{2j}^0} + \frac{\partial}{\partial \phi_{2j}^0} \left( \frac{1}{r_{2i}^0} \ln \frac{\phi_{2i}^0}{\omega_{2i}^0} \right) + \frac{1}{r_{2i}^0 \phi_{2i}^0} \quad (\text{A-10})$$

$$\frac{\partial^2 g}{\partial \phi_{1i}^0 \partial \bar{\rho}} = -\frac{\partial(\epsilon^*/kT)}{\partial \phi_{1i}^0} - \frac{P}{kT\bar{\rho}^2} \frac{\partial v^*}{\partial \phi_{1i}^0} + \left( \frac{1}{r_{1i}^0} - \frac{1}{r_{2i}^0} \right) \frac{1}{\bar{\rho}} \quad (\text{A-11})$$

$$\frac{\partial^2 g}{\partial \phi_{2j}^0 \partial \bar{\rho}} = -\frac{\partial(\epsilon^*/kT)}{\partial \phi_{2j}^0} - \frac{P}{kT\bar{\rho}^2} \frac{\partial v^*}{\partial \phi_{2j}^0} + \left( \frac{1}{r_{2j}^0} - \frac{1}{r_{2i}^0} \right) \frac{1}{\bar{\rho}} \quad (\text{A-12})$$

$$\frac{\partial \bar{\rho}}{\partial \phi_{1i}^0} = \bar{\rho}^2 \psi_{1i} \tilde{T} P^* \beta \quad \frac{\partial \bar{\rho}}{\partial \phi_{2j}^0} = \bar{\rho}^2 \psi_{2j} \tilde{T} P^* \beta \quad (\text{A-13})$$

$$\psi_{1i} = \bar{\rho} \frac{\partial(\epsilon^*/kT)}{\partial \phi_{1i}^0} + \frac{P}{kT\bar{\rho}} \frac{\partial v^*}{\partial \phi_{1i}^0} - \left( \frac{1}{r_{1i}^0} - \frac{1}{r_{2i}^0} \right) \quad (\text{A-14})$$

$$\psi_{2j} = \bar{\rho} \frac{\partial(\epsilon^*/kT)}{\partial \phi_{2j}^0} + \frac{P}{kT\bar{\rho}} \frac{\partial v^*}{\partial \phi_{2j}^0} - \left( \frac{1}{r_{2j}^0} - \frac{1}{r_{2i}^0} \right) \quad (\text{A-15})$$

$$P^* \beta = \frac{1}{\bar{\rho} \left[ \tilde{T} \left( \frac{\bar{\rho}}{1 - \bar{\rho}} + \frac{1}{r} \right) - 2\bar{\rho} \right]} > 0 \quad (\text{A-16})$$

where

$$\frac{\partial \bar{\rho}}{\partial \phi_{1i}^0} \text{ and } \frac{\partial \bar{\rho}}{\partial \phi_{2j}^0}$$

are derived from the equation of state eq 2.

From eqs 13 and 14, we have

$$\frac{\partial(\epsilon^*/kT)}{\partial \phi_{1i}^0} = [2 \sum_{j=1}^h \phi_{1j} (\epsilon_{11,ij}^* - \epsilon_{12,ji}^*) + 2 \sum_{j=1}^l \phi_{2j} (\epsilon_{12,ij}^* - \epsilon_{22,ji}^*)] / kT \quad (\text{A-17})$$

$$\frac{\partial(\epsilon^*/kT)}{\partial \phi_{2j}^0} = [2 \sum_{i=1}^h \phi_{1i} (\epsilon_{12,ij}^* - \epsilon_{12,il}^*) + 2 \sum_{i=1}^l \phi_{2i} (\epsilon_{22,ji}^* - \epsilon_{22,li}^*)] / kT \quad (\text{A-18})$$

$$\frac{\partial v^*}{\partial \phi_{1i}^0} = v_{1i}^* - v_{2i}^* \quad (\text{A-19})$$

$$\frac{\partial v^*}{\partial \phi_{2j}^0} = v_{2j}^* - v_{2i}^* \quad (\text{A-20})$$



If it is assumed that  $\epsilon_{11,ij}^* = \epsilon_{11}^*$ ,  $\epsilon_{21,ij}^* = \epsilon_{12}^*$ ,  $\epsilon_{22,ij}^* = \epsilon_{22}^*$ ,  $v_{1i}^* = v_1^*$  and  $v_{2j}^* = v_2^*$ , then

$$\frac{\partial(\epsilon^*/kT)}{\partial\phi_{1i}} = [2\phi_1(\epsilon_{11}^* - \epsilon_{12}^*) + 2\phi_2(\epsilon_{12}^* - \epsilon_{22}^*)]/kT = \lambda_{12} \quad (\text{A-21})$$

$$\frac{\partial(\epsilon^*/kT)}{\partial\phi_{2j}} = 0 \quad (\text{A-22})$$

$$\frac{\partial v^*}{\partial\phi_{1i}^0} = v_1^* - v_2^* \quad (\text{A-23})$$

$$\frac{\partial v^*}{\partial\phi_{2j}^0} = 0 \quad (\text{A-24})$$

According to eqs 8 and 9 and the combining rule of SLLFT, we have

$$\phi_{ij} = \phi_{ij}^0 \frac{v_i^*}{v_{ij}^*} \quad (\text{A-25})$$

So

$$\frac{\partial(\epsilon^*/kT)}{\partial\phi_{1i}^0} = \sum_j^h \frac{\partial(\epsilon^*/kT)}{\partial\phi_{1j}} \frac{\partial\phi_{1j}}{\partial\phi_{1i}^0} + \sum_j^{l-1} \frac{\partial(\epsilon^*/kT)}{\partial\phi_{2j}} \frac{\partial\phi_{2j}}{\partial\phi_{1i}^0} = \lambda_{12} \frac{v_1^* v_2^*}{v^{*2}} \quad (\text{A-26})$$

$$\frac{\partial(\epsilon^*/kT)}{\partial\phi_{2i}^0} = \sum_j^h \frac{\partial(\epsilon^*/kT)}{\partial\phi_{1j}} \frac{\partial\phi_{1j}}{\partial\phi_{2i}^0} + \sum_j^{l-1} \frac{\partial(\epsilon^*/kT)}{\partial\phi_{2j}} \frac{\partial\phi_{2j}}{\partial\phi_{2i}^0} = 0 \quad (\text{A-27})$$

$$\frac{\partial^2(\epsilon^*/kT)}{\partial\phi_{1i}^0 \partial\phi_{1j}^0} = \frac{\partial}{\partial\phi_{1j}^0} \left( \frac{\partial(\epsilon^*/kT)}{\partial\phi_{1i}^0} \right) = \frac{2v_1^* v_2^*}{v^{*3}} \left[ \frac{\chi v_1^* v_2^*}{v^*} - \lambda_{12}(v_1^* - v_2^*) \right] = \Theta \quad (\text{A-28})$$

$$\frac{\partial^2(\epsilon^*/kT)}{\partial\phi_{1i}^0 \partial\phi_{2j}^0} = \frac{\partial}{\partial\phi_{2j}^0} \left( \frac{\partial(\epsilon^*/kT)}{\partial\phi_{1i}^0} \right) = 0 \quad (\text{A-29})$$

$$\frac{\partial^2(\epsilon^*/kT)}{\partial\phi_{2i}^0 \partial\phi_{2j}^0} = \frac{\partial}{\partial\phi_{2j}^0} \left( \frac{\partial(\epsilon^*/kT)}{\partial\phi_{2i}^0} \right) = 0 \quad (\text{A-30})$$

$$\frac{\partial^2 v^*}{\partial\phi_{1i}^0 \partial\phi_{1j}^0} = 0, \frac{\partial^2 v^*}{\partial\phi_{2i}^0 \partial\phi_{2j}^0} = 0, \frac{\partial^2 v^*}{\partial\phi_{1i}^0 \partial\phi_{2j}^0} = 0 \quad (\text{A-31})$$

$$\chi = \frac{1}{2} \frac{\partial\lambda_{12}}{\partial\phi_{1i}} = (\epsilon_{11}^* - 2\epsilon_{12}^* + \epsilon_{22}^*)/kT \quad (\text{A-32})$$

From the above equations, we have

$$\frac{\partial^2 g}{\partial\phi_{1i}^0 \partial\phi_{1j}^0} = \begin{cases} -\tilde{\rho}\Theta + \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta\psi_{1i}\psi_{1j} & (i \neq j) \\ -\tilde{\rho}\Theta + \frac{1}{r_{2l}^0 \phi_{2l}^0} + \frac{1}{r_{1l}^0 \phi_{1l}^0} - \tilde{\rho}\tilde{T}P^* \beta\psi_{1i}^2 & (i = j) \end{cases} \quad (\text{A-33})$$

$$\frac{\partial^2 g}{\partial\phi_{1i}^0 \partial\phi_{2j}^0} = \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta\psi_{1i}\psi_{2j} \quad (\text{A-34})$$

$$\frac{\partial^2 g}{\partial\phi_{2i}^0 \partial\phi_{2j}^0} = \begin{cases} \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta\psi_{2i}\psi_{2j} & (i \neq j) \\ \frac{1}{r_{2l}^0 \phi_{2l}^0} + \frac{1}{r_{2l}^0 \phi_{2l}^0} - \tilde{\rho}\tilde{T}P^* \beta\psi_{2i}^2 & (i = j) \end{cases} \quad (\text{A-35})$$

## Appendix II: Derivation of Spinodal under the Condition of Assumptions I and II

Substituting  $J_{11}$ ,  $J_{22}$ ,  $L_{1i}$ , and  $L_{2j}$  into eq 42, the following are given:

$$1 + \left[ (-2\tilde{\rho}\chi - \tilde{\rho}\tilde{T}P^* \beta\psi^2) + \frac{1}{r_{2l}^0 \phi_{2l}^0} \sum_{i=1}^k r_{1i} \phi_{1i} + \frac{1}{r_{2l}^0 \phi_{2l}^0} \sum_{j=1}^{l-1} r_{2j} \phi_{2j} + \frac{1}{r_{2l}^0 \phi_{2l}^0} (-2\tilde{\rho}\chi - \tilde{\rho}\tilde{T}P^* \beta\psi^2) \sum_{i=1}^k r_{1i} \phi_{1i} \sum_{j=1}^{l-1} r_{2j} \phi_{2j} \right] = 0 \quad (\text{A-36})$$

that is

$$1 - (2\tilde{\rho}\chi + \tilde{\rho}\tilde{T}P^* \beta\psi^2) \sum_{i=1}^h r_{1i} \phi_{1i} + \frac{1}{r_{2l}^0 \phi_{2l}^0} \sum_{i=1}^h r_{1i} \phi_{1i} + \frac{1}{r_{2l}^0 \phi_{2l}^0} \sum_{j=1}^l r_{2j} \phi_{2j} - 1 - \frac{1}{r_{2l}^0 \phi_{2l}^0} (2\tilde{\rho}\chi + \tilde{\rho}\tilde{T}P^* \beta\psi^2) \sum_{i=1}^h r_{1i} \phi_{1i} \sum_{j=1}^l r_{2j} \phi_{2j} + (2\tilde{\rho}\chi + \tilde{\rho}\tilde{T}P^* \beta\psi^2) \sum_{i=1}^h r_{1i} \phi_{1i} = 0 \quad (\text{A-37})$$

that is

$$\frac{1}{r_{2l}^0 \phi_{2l}^0} \left( \sum_{i=1}^h r_{1i} \phi_{1i} + \sum_{j=1}^l r_{2j} \phi_{2j} - (2\tilde{\rho}\chi + \tilde{\rho}\tilde{T}P^* \beta\psi^2) \sum_{i=1}^h r_{1i} \phi_{1i} \sum_{j=1}^l r_{2j} \phi_{2j} \right) = 0 \quad (\text{A-38})$$

Multiplying

$$r_{2l}^0 \phi_{2l}^0 \left( \sum_{i=1}^h r_{1i} \phi_{1i} \sum_{j=1}^l r_{2j} \phi_{2j} \right)^{-1}$$

into the above equation, the spinodal is written as follows:

$$\frac{1}{r_{w,1} \phi_1} + \frac{1}{r_{w,2} \phi_2} = \tilde{\rho}(2\chi + \tilde{T}P^* \beta\psi^2) \quad (\text{A-39})$$

## References and Notes

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