

Phase Behavior of Reversibly Associating Star Copolymer-like Polymer Blends

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Abstract: We theoretically consider blends of two monodisperse one-end-functionalized homopolymers (denoted by A and B) capable of forming clusters between functional groups (stickers) using weak segregation theory. In this model system resulting molecular architectures via clustering resemble star copolymers having many A- and B-arms. Minimizing the total free energy with respect to the cluster distribution, the equilibrium distribution of clusters is obtained and used for RPA (Random Phase Approximation) equations as input. For the case that polymers are functionalized by only one kind of sticker, the phase diagrams show that the associations promote the macrophase separation. When there is strong affinity between stickers belonging to the different polymer species, on the other hand, the phase diagram shows a suppression of the macrophase separation at the range of high temperature regime, as well as the phase coexistence between a disordered and a mesoscopic phase at the relatively lower temperatures.

Keywords : associating polymer blends, weak segregation theory, macrophase separation, microphase separation.

Introduction

In recent years, it has been demonstrated that noncovalent bonding can be used advantageously in constructing molecular complexes and that the concept can be applied for various applications such as the molecular construction for polymer liquid crystals and nanostructures. The complexes can involve hydrogen bonds, ionic interactions, coordination complexes, charge-transfer interactions, *etc.*¹⁻³ In the polymer mixtures involving these “physical” interactions, the phase behavior is very complicated due to the ubiquitous unfavorable interactions between unlike polymer species competed with these specifically attractive interactions between functional pairs present in the polymer molecules. In the recent experimental study investigated by Ruokolainen *et al.*,⁴ poly(4-vinyl pyridine) (P4VP) was used as a model polymer in combination with various end-functionalized oligomers. The latter consists of a long alkyl tail and a functional head group, which can form a hydrogen bond with the nitrogen of the pyridine groups of P4VP. Similar studies are reported by Russell *et al.*⁵ and Iwasaki *et al.*⁶ All these results demonstrate that the clusters resemble in many ways blocky copolymers, and the system is able to form microscopically ordered structure if the hydrogen bonding interaction is strong enough to behave like a permanent covalent bond.

The theoretical study of such systems was initiated by

Tanaka *et al.*⁷ who considered a blend of two monodisperse homopolymers capable of reversibly associating to each other to form a diblock-like cluster, which is the most basic example of molecular complex consisting of homopolymers. More recently, a slightly different description was advanced by Huh *et al.* and its theoretical results were numerically confirmed by computer simulation.^{8,9} However, although these studies of simple model system already give insight about the phase behavior of associating polymer blends, the model is oversimplified and hence, a more generalized description for the association model is required to take into account, for instance, the effect of polydispersity of cluster size and the association between the same species of polymers.

In this paper, we will consider a theoretical model for binary polymer blends capable of forming polydispersed star-like clusters using weak segregation theory. The emphasis in this approach will be placed on the phase boundaries of instability limit of homogeneous or disordered phases in the blends consisting of polydispersed clusters.

Theory

Consider a molten blend of two associating homopolymers A and B, which can form A_nB_m clusters. The total free energy change of the system, f , can be described by the sum of three parts:

$$f = f_a + f_{mix} + f_{micro} \quad (1)$$

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where f_a represents the free change due to the formation of clusters via associations between polymers, f_{mix} the free energy change of mixing between these “physically” or chemically polymerized molecular species and f_{micro} the free energy change due to the presence of the microstructure. To construct the phase diagram, the total free energy in eq. (1) has to be minimized both with respect to the distribution of the $A_l B_m$ cluster, $\{n_{l,m}\}$, and the parameters of the micro-phase separation (period, type of microstructure, amplitude):

$$\min_{\{n_{l,m}\}, \Psi} f(\{n_{l,m}\}, \Psi) = \min_{\{n_{l,m}\}, \Psi} [f_a(\{n_{l,m}\}) + f_{mix}(\{n_{l,m}\}) + f_{micro}(\{n_{l,m}\}, \Psi)] \quad (2)$$

where the order parameter, Ψ , describes the local density fluctuation of A-monomer and the parameters of the microstructures are absorbed into Ψ . The exact minimization in eq. (2) is very complicated since the parameters describing microstructures also depend on the distribution, $\{n_{l,m}\}$. However, since in the weak segregation regime, i.e. $\Psi \ll 1$, f_{micro} is small compared to the first two terms ($f_a + f_{mix}$) in eq. (1), the minimization can be approximated by

$$\min_{\{n_{l,m}\}, \Psi} f(\{n_{l,m}\}, \Psi) \cong \min_{\{n_{l,m}\}} [f_a(\{n_{l,m}\}) + f_{mix}(\{n_{l,m}\}) + f_{micro}(\{\tilde{n}_{l,m}\}, \Psi)] \quad (3)$$

where

$$f_a(\{\tilde{n}_{l,m}\}) + f_{mix}(\{\tilde{n}_{l,m}\}) = \min_{\{n_{l,m}\}} [f_a(\{n_{l,m}\}) + f_{mix}(\{n_{l,m}\})] \quad (4)$$

Thus, the minimization in eq. (2) is much simplified by the stepwise procedure of eq (3) and (4). The equilibrium cluster distribution $\{\tilde{n}_{l,m}\}$ can be understood as a molecular weight distribution of “physically” polymerized molecules. In fact, in such dynamic equilibrium a cluster has a finite lifetime (the mean lifetime of a hydrogen bond in water, for example, is of the order of 10^{-11} seconds) and its size can be changed at any time. However, the distribution, rather than individual clusters, is unchanged under the dynamic equilibrium so that “physically” polymerized molecular species are still distinguishable. In other words, the association and dissociation of molecules in such a dynamic equilibrium can be simply treated by static equilibrium distribution of clusters as if all the clusters are frozen, which is essential point to minimize the free energy of eq.(1).

Next we apply the theory to model systems. In the present work, the two kinds of binary blends of one-end-functionalized polymers (A/B) are considered. In the model system I, one of the end terminal groups of all polymers is functionalized by a sticker segment X. In the model system II, the sticker in the one of the terminal groups of homopolymers is different by homopolymer specie, i.e. homopolymers A are

functionalized by a sticker X, whereas the homopolymers B is functionalized by a sticker Y. Throughout these model systems, all homopolymers consist of an equal number of monomers, N . Also, for convenience the incompressibility is assumed and the steric effect of a sticker on the associations is neglected so that the model do not exclude the possibility of multiple associations on a single sticker.

Model I. For this model system, each contributions to the total free energy in eq. (1) are given by

$$\frac{f_a}{k_B T} = \frac{f_o}{k_B T} \sum_{l,m} \frac{\phi_{l,m}}{N} \quad (5)$$

$$\frac{f_{mix}}{k_B T} = \frac{1}{N(l+m)} \sum_{l,m} \phi_{l,m} \ln \phi_{l,m} + \chi \phi (1-\phi) \quad (6)$$

$$\frac{f_{micro}}{k_B T} = \tau \Psi^2 + \alpha \Psi^2 + \beta \Psi^2 \quad (7)$$

Here f_o is the free energy change of the formation of a single association between X-stickers, χ the Flory-Huggins interaction parameter between A- and B-monomers, and $\phi_{l,m}$ and ϕ the volume fraction of (l,m) cluster and A-monomers, respectively. The τ, α and β in the eq. (7) are the second, the third and the fourth coefficients in the Landau free energy describing the microstructure in the weak segregation regime and related to the density correlation function of A-monomer in the ideal state. According to eq. (4) the equilibrium cluster distribution can be found by

$$\left[\frac{\partial (f_a + f_{mix})}{\partial \phi_{l,m}} \right]_{\phi, \tau} = 0 \quad (8)$$

with the condition of incompressibility

$$\phi = \sum_{l,m} \frac{l}{l+m} \phi_{l,m}, \quad 1 - \phi = \sum_{l,m} \frac{m}{l+m} \phi_{l,m} \quad (9)$$

The resulting solution for the equilibrium cluster distribution is then given as

$$\tilde{\phi}_{l,m} = K_{l,m} u^l v^m \quad (10)$$

where the reaction constant $K_{l,m}$

$$K_{l,m} = \exp \left[l + m - 1 - \frac{f_o}{k_B T} (l + m) \right] \quad (11)$$

and u and v are the volume fractions of unassociated free A- and B-polymer, respectively ($u \equiv \tilde{\phi}_{1,0}$ and $v \equiv \tilde{\phi}_{0,1}$). The free energy change of a single association, f_o , is expressed in terms of the association energy of a bonding, ϵ_o , and the entropic change upon formation of a bonding, s_o ,

$$f_o = \epsilon_o - T s_o \quad (12)$$

In the case of hydrogen bonds, the bonding energy lies in the range 1~10 kcal/mol and the magnitude of the entropic change is the order of 10 cal/(Kmol), which corresponds to

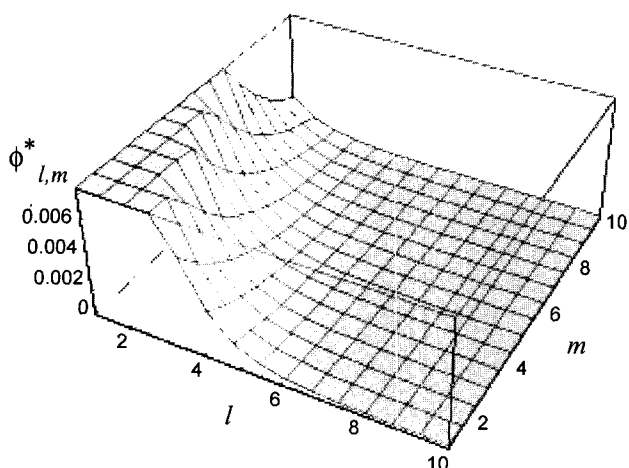


Figure 1. The equilibrium distribution of clusters as a function of l, m for $\{\phi = 0.25, \epsilon_o = -7k_B T, s_o = -5k_B\}$.

a value of $s_o \approx -5k_B$ (the negative sign stands for the loss of entropy due to directional nature of hydrogen bonding).¹⁰ Figure 1 shows an example of the cluster distribution calculated by eq. (10) with a choice of parameters, $\{\phi = 0.25, \epsilon_o = -7k_B T, s_o = -5k_B\}$.

Inserting the equilibrium distribution of clusters obtained from eq. (10) into eq. (5)-(7) gives the total free energy minimized with respect to $\phi_{l,m}$. Next, according to eq. (3) and (4), the total free energy must be minimized about the parameters describing microstructure and that is

$$\begin{aligned} \min_{\Psi} f(\tilde{\phi}, \Psi) &= f_a(\tilde{\phi}_{l,m}) + f_{mix}(\tilde{\phi}_{l,m}) \\ &+ k_B T \min_{\Psi} [\tau(\tilde{\phi}_{l,m}) \Psi^2 + \alpha(\tilde{\phi}_{l,m}) \Psi^3 + \beta(\tilde{\phi}_{l,m}) \Psi^4] \end{aligned} \quad (13)$$

Using this expression, the spinodal is found by the condition, $\tau(\tilde{\phi}_{l,m}) = 0$. For the calculation of the phase transitions other than spinodal, one should first minimize f_{micro} over the type of microstructures such as lamellar and take the common tangents in the curves of total free energy as a function of ϕ . In the present work, however, the investigation of the phase behavior is restricted to the derivation of instability boundaries, i.e. spinodal. To find this, the second order coefficient $\tau(\tilde{\phi}_{l,m})$ in eq. (13) must be evaluated. According to the Random Phase Approximation,¹¹ the second order coefficient proportional to the inverse scattering is related to the density correlation function of A monomers in a single Gaussian chain, g_{ij} :

$$\tau = \Gamma(x^*) - 2\chi, \Gamma(x) = \frac{\sum_{i,j=A \text{ or } B} g_{ij}(x)}{\|g_{ij}(x)\|} \quad (14)$$

Here Γ is often referred to as the second order vertex function. The scaled wave number x is related to the wavelength of the A monomer density fluctuation and defined by

$x = q^2 \langle R^2 \rangle$, where q is the magnitude of the scattering vector and $\langle R^2 \rangle$ the mean square radius of gyration of A(B)-polymer. The x^* stands for the dominant wave number that minimize τ . The density correlation function, g_{ij} , appearing in this equation, for the model system are given by

$$\begin{aligned} g_{AA}(x) &= \frac{2N}{x^2} (x + e^{-x} - 1) \left(u + \sum_{l,m} \frac{l}{l+m} K_{l,m} u^l v^m \right) \\ &+ \frac{N}{x^2} (1 - e^{-x})^2 \sum_{l,m} \frac{l(l-1)}{l+m} K_{l,m} u^l v^m \end{aligned} \quad (15)$$

$$\begin{aligned} g_{BB}(x) &= \frac{2N}{x^2} (x + e^{-x} - 1) \left(v + \sum_{l,m} \frac{m}{l+m} K_{l,m} u^l v^m \right) \\ &+ \frac{N}{x^2} (1 - e^{-x})^2 \sum_{l,m} \frac{m(m-1)}{l+m} K_{l,m} u^l v^m \end{aligned} \quad (16)$$

$$g_{AB}(x) = \frac{N}{x^2} (1 - e^{-x})^2 \sum_{l,m} \frac{lm}{l+m} K_{l,m} u^l v^m \quad (17)$$

An important point in these equations is that unlike systems consisting of permanent bonds, the vertex function itself in eq. (14) is also temperature dependent (see eq.11), i.e. $\Gamma = \Gamma(x, \phi, T)$ and hence, the spinodal condition, $\tau(\tilde{\phi}_{l,m}) = 0$, for a fixed ϕ should be found by solving the following equation,

$$2\chi(T_S) = \Gamma(x^*, \phi, T_S) \quad (18)$$

where T_S is the spinodal temperature. Eq. (18) is general for both of the microphase separation ($x^* \neq 0$) and the macrophase separation ($x^* = 0$). For $x^* = 0$ when the g_{ij} 's cannot be calculated by the eq. 15-17, the vertex function should be obtained by taking the limit of $x \rightarrow 0$. Since the both sides in eq. (18) have the temperature dependence, i.e. χ and $f_o/k_B T$ in Γ , the eq. (18) can only be solved by taking an explicit expression for the relation between χ and $f_o/k_B T$. By introducing a parameter r , f_o is given as

$$\frac{f_o}{k_B T} = \frac{\epsilon_o}{k_B T} - \frac{s_o}{k_B} = -rN\chi - \frac{s_o}{k_B} \quad (19)$$

The parameter r is, roughly speaking, the ratio between the association energy (ϵ_o) and the dispersive interaction energy of the whole chain ($N\chi k_B T$), and so it depends not only on the type of A- and B-monomers and the character of the association, but also on the number of monomers per chain.

Figure 2 presents the spinodals for the model system I with different choices of the association parameters, compared to the case of the binary blend without stickers. Figure 2 shows that the instability of homogeneous phase is always attributed to a macroscopic separation and there are no microscopic separations. Furthermore, as the affinity between X-stickers increases (larger r or smaller s_o), the macrophase separation is promoted and the critical points are lower than that in the case of the binary blend without

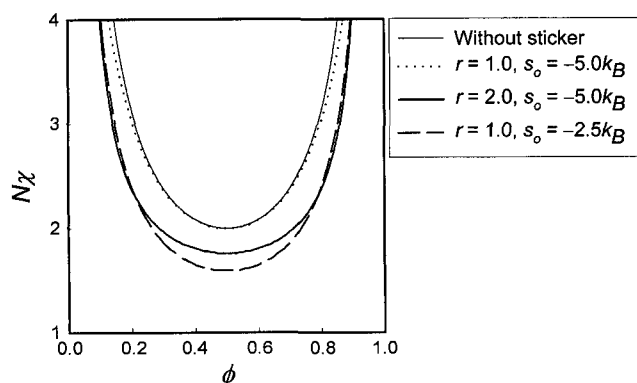


Figure 2. The spinodal values of $N\chi$ vs. the fraction of the A-monomer for model I.

stickers ($N\chi = 2$). This can be explained as follow. Since the model system I has only one type of sticker X, all the pairwise associations between polymer species, i.e. AA, AB and BB, are equally probable and therefore, the fraction of a cluster does not depend on the polymer species but only on the total number of polymers in the cluster. Obviously, clusters consisting of same polymer species (AA, BB) contribute to promote demixing of the mixture whereas AB-type clusters can act as compatibilizers for the mixture when the degree of heterogeneity of cluster exceeds a certain criteria. Therefore, two opposing effects compete each other but in the case of model system I, the former contribution always dominates over the latter. This can be shown more rigorously. According to the eq. (18), the resulting spinodal condition for the macrophase separation for this case is in the form of

$$N\chi = \frac{2}{n\phi} \quad (20)$$

where n is the average number of molecules in a cluster and ϕ the fraction of heteroclusters that contribute to suppress the macrophase separation, i.e. compatibilizer. In all cases in the model system I, we found that $n\phi > 1$ and therefore, the association promotes the macrophase separation.

Model II. As described previously, this model system of binary blend consists of A-polymers functionalized by X-sticker and B-polymers functionalized by Y-stickers. In this case, unlike the model system I, the degree of the association between polymers depends not only on the number of polymers per a cluster but also on the pair of the association. Taking into account the pairwise association between stickers, the formula for f_a is expressed as

$$\frac{f_a}{k_B T} = \sum_{l,m} \frac{\phi_{l,m}}{N k_B T (l+m)} [n_{XX} f_{XX} + n_{XY} f_{XY} + n_{YY} f_{YY}] \quad (21)$$

where n_{ij} is the mean number of the physical bonding between the sticker i and j in a (l,m) cluster and f_{ij} the free

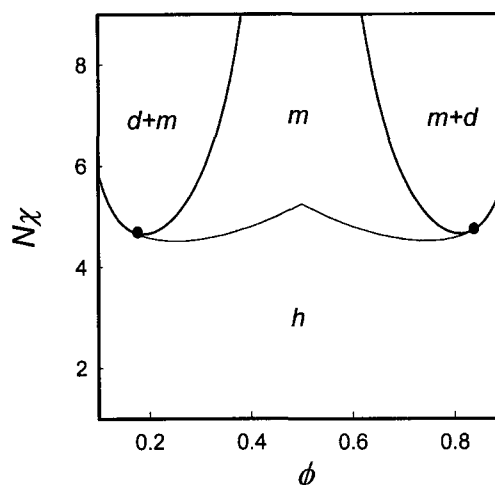


Figure 3. The spinodal values of $N\chi$ vs. the fraction of the A-monomer for model II with $\{r_{XX} = r_{YY} = 0.1, r_{XY} = 2.0, s_o = -5k_B\}$. “h”, “d”, and “m” represent the homogeneous, disordered, and mesoscopic phase, respectively and “+” stands for the phase coexistence.

energy change of a single association between the sticker i and j . The other contribution to the total free energy, f_{mix} and f_{micro} are the same as in the model I (eq. (6) and (7)). Also, the free energy changes of the pairwise association free energy, f_{ij} , are defined in similar way:

$$\frac{f_{ij}}{k_B T} = -r_{ij} N\chi - \frac{s_o}{k_B} \quad (22)$$

Using the same procedure described in the model I, the spinodal can be calculated and the result is presented in the following.

Figure 3 presents the spinodal for the model system II with the choice of association parameters $\{r_{XX} = r_{YY} = 0.1, r_{XY} = 2.0, s_o = -5k_B\}$, which corresponds to a symmetric association with a preferential affinity between sticker X and Y ($r_{XY} > r_{XX} = r_{YY}$). Unlike the phase diagram in the model system I where only the macrophase transitions appear, the spinodal in figure 3 shows not only the macrophase separation but also the microphase separation. In particular, if $\phi \neq 0.5$, the phase of the mixture undergoes from a homogeneous phase to a microscopically ordered phase followed by the phase coexistence between a disordered and a microscopically ordered phase, as $N\chi$ increases (the temperature decreases).

Figure 4 shows the scattering function for the case of $\{r_{XX} = r_{YY} = 0.1, r_{XY} = 2.0, s_o = -5k_B, \phi = 0.5\}$. The scattering function is obtained from the inverse of $\Gamma - 2\chi$. In this plot of scattering, the position of the dominant fluctuation x^* moves from $x^* = 0$ toward a larger value of x^* as $N\chi$ increases, indicating that the characteristic length scale of A-monomer density fluctuation becomes smaller and hence the mixture is microscopically separated if the transition is

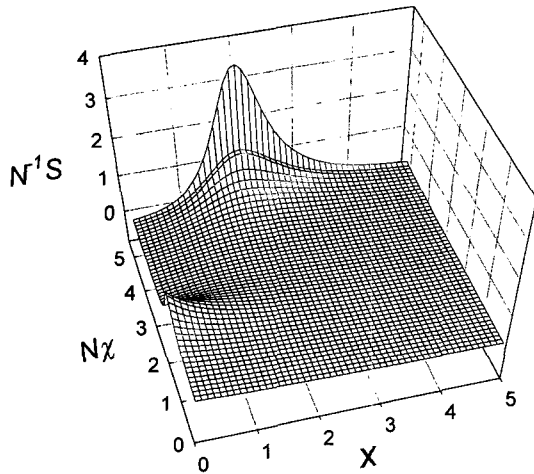


Figure 4. The scattering function, S , as a function of the scaled wave number x and $N\chi$ for model II with $\{r_{XX} = r_{YY} = 0.1, r_{XY} = 2.0, s_o = -5k_B, \phi = 0.5\}$.

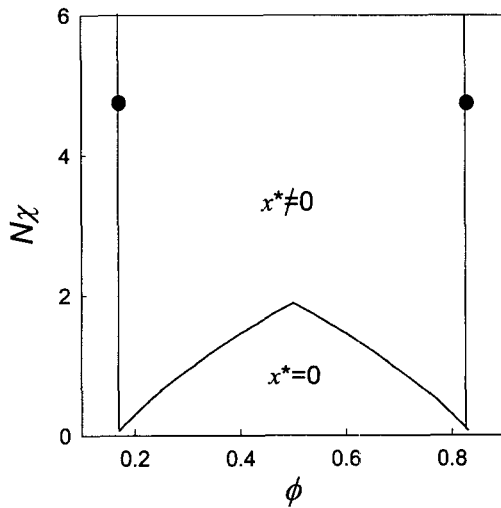


Figure 5. The boundary between $x^* = 0$ and $x^* \neq 0$ in $(\phi, N\chi)$ space for model II with $\{r_{XX} = r_{YY} = 0.1, r_{XY} = 2.0, s_o = -5k_B\}$.

reached. The condition for the change of the dominant fluctuation from $x^* = 0$ to $x^* \neq 0$ is found from:

$$\left[\frac{\partial \Gamma(x \rightarrow 0)}{\partial x} \right]_{x=0} = 0 \quad (23)$$

The solution of the eq. (23) with respect to χ and ϕ is shown in Figure 5 with the same association parameters used in Figure 3. The solid circle represents the Lifshitz point at which both of the eqs. (18) and (23) are satisfied, corresponding to a multicritical point connecting the homogeneous, the macroscopically ordered, and the microscopically ordered phase transition.

Figure 6 shows the spinodal for the case of $\{r_{XX} = r_{YY} = 0.1, r_{XY} = 1.5, s_o = -5k_B\}$. The weaker bonding energy

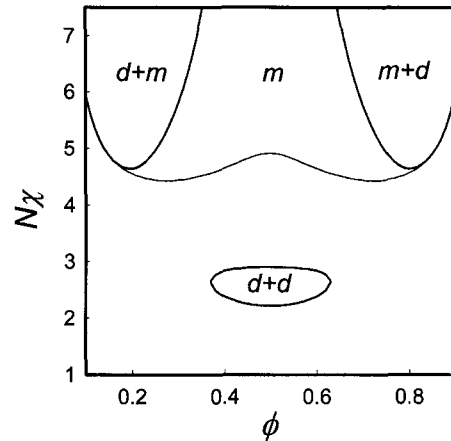


Figure 6. As in figure 3, but now with $\{r_{XX} = r_{YY} = 0.1, r_{XY} = 1.5, s_o = -5k_B\}$.

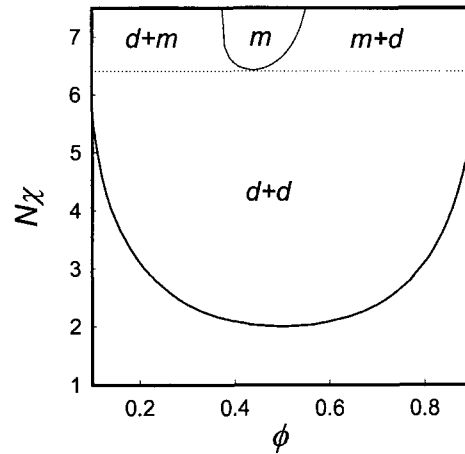


Figure 7. As in figure 3, but now with $\{r_{XX} = 1.0, r_{YY} = 0.1, r_{XY} = 1.5, s_o = -5k_B\}$.

between unlike stickers, $r_{XY} = 1.5$, in this case leads to two-phase coexistence between disordered phases at the relatively low values of $N\chi$. This phase coexistence disappears and the mixtures are homogenized when the temperature is low enough to create more heteroclusters acting as compatibilizers for the mixture. At the even lower temperatures corresponding to larger $N\chi$, the phases are microscopically ordered ($\phi \approx 0.5$) or two-phase coexistence between a disordered and a microscopically ordered phase occurs ($\phi \neq 0.5$) as similar to that in Figure 3.

In Figure 7, the spinodal is calculated for the case that the bonding energy between X-stickers increases to $r_{XX} = 1.0$, while the other association parameters are the same as that in Figure 6. The resulting phase diagram is dominated by various types of two-phase coexistence, which is due to the increase in the number of the formation of AA-type clusters.

Concluding Remarks

In this paper, the phase behavior of reversibly associating star-like A/B homopolymer blends was investigated theoretically in the weak segregation limit. Our theoretical treatment based on the stepwise minimization procedure greatly simplifies the calculation of phase transitions in this complicated blends involving complexes. The correct procedure would be to minimize the total free energy with respect to all parameters. However, as long as the weak segregation limit is validated so that $f_a + f_{mix} \gg f_{micro}$, the stepwise minimization can be justified and becomes fairly good approximation.

The main result in the model system I, where polymers are functionalized by only one kind of sticker, is that the association always promotes the macrophase separation and the wavelength of the dominant density fluctuation is infinite over the entire range in the ϕ - T space. A suppression of such undesirable macrophase separation is observed only in the model system II when the energy of the bonding between unlike species is stronger than that between the same species. The model system II exhibits more variety in morphologies including the phase coexistence between a disordered and a macroscopically ordered phase. However, in order to construct a full phase diagram including the first order transition between microstructures with different symmetries (lamellar, hexagon, BCC, etc), one should include the expansion terms of f_{micro} higher than the second order in the total free energy. The main difficulty in calculating a full phase diagram for such a polydisperse system like the mixture in the present study arises from the presence of additional nonlocal term, which is attributed to the polydispersity and vanishes in a monodisperse system. For instance, in the case of a random copolymer, Shakhnovich and Gutin derived the nonlocal term which accounts for the chain connectivity.¹² They found that the nonlocal term is a dominant contribution in the vertex functions since only self-correlations survive in the regular vertex function repre-

senting local interaction and the correlation other than the self-correlations are all cancelled out. Therefore, the nonlocal term for a random copolymer system is only difference from a corresponding low molecular mixture of disconnected monomers. Within the Landau free energy, such nonlocal term appears in the fourth order term and does not modify the second order term, i.e. spinodal instability is not affected by the nonlocal term, which is investigated in the present study. The full phase diagrams including the nonlocal term will be calculated in the future work.

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