Theory of Microphase Formation in Reversibly Associating Block Copolymer Blends

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ABSTRACT: This paper calculates the scattering functions for the associating polymer blends in which some chain segments can reversibly form bonds. From the divergence condition of the scattering function, instability against macrophase separation and microphase formation is studied from a unified point of view. Phase behavior is detailed specifically for the associating diblock copolymers whose junctions can break and recombine through a thermal process. We focus our interest on the interference between the two main transitions: macroscopic two-phase demixing and microscopic mesophase formation. Some novel aspects of the phase diagram characteristic of the reversibly associating systems are found. These include the eutectic point, the azeotrope, and the low-temperature reentrant microphase.

1. Introduction

Block copolymers have been attracting the interest of polymer researchers recently because of the abundance in the phase behavior and morphologies they exhibit. Recent experiments[1] on multiarm copolymers revealed that their ordered structures include a three-dimensional bicontinuous phase, as well as familiar lamellar, cylindrical, and spherical microdomains which had been known for diblock copolymers. Controlling their morphologies can therefore lead to the application of polymer science in numerous systems of practical interest.

The vast majority of both experimental[2-4] and theoretical[5-8] investigations on the ordered states have, however, dealt with chemically synthetic block copolymers carrying heterojunctions formed by covalent bonds. The present paper aims at studying the phase behavior of molten block copolymers whose junctions are formed by *physical bonds*.

In the case of physical bonds, the free-energy barrier between bonding and unbonding states is on the order of the thermal energy, so that the bond formation is thermally reversible, and hence enables the system to readily reach association equilibrium. The population distribution of the formed copolymers is automatically controlled by the thermodynamic variables such as the temperature and the concentration. The polydispersity of the system is intrinsic, that is, the result of the thermodynamic requirement. Hydrogen bonding, certain ionic associations, junctions formed by solvent complexation, or association by stereoregular sequences can all be a candidate of physical bonding. Because the junctions can break and recombine, the associating system can exhibit more flexibility, and hence variety, in the phase behavior and morphology compared with the chemically connected polymers.

The thermodynamics of the physically associating polymer mixtures has been studied by the present authors in a series of papers,[9-11] in which peculiar forms of the miscibility gaps and their relation to gelation or solvation were explored. The mean-field free energy was derived on the basis of the conventional Flory-Huggins lattice theory by incorporating an additional change produced during cluster formation. Gel formation, a two-phase coexistence condition, and thermodynamic stability were examined for numerous polymer systems. It was shown that a variety of higher order critical phenomena can appear as a result of the interference between two cooccurring phase transitions of a distinct nature.

We consider in this paper the effect of spatial fluctuations in the polymer concentration on the stability of the system in order to find the condition for microphase formation. We calculate the correlation function $S(\mathbf{q})$ of the concentration fluctuation, which is directly measurable in the X-ray or neutron scattering experiments, as a function of the wave vector, temperature, and concentration. When it is divergently enhanced at a certain finite wave number q, it is the precursor of the instability against the fluctuation whose spatial variations are characterized by the length q^{-1}, hence leading to the formation of an ordered state with the periodicity q^{-1}. In the case of block copolymers, q^{-1} is on the order of the radius of gyration of a single polymer chain. Divergence of $S(\mathbf{q})$ thus suggests the periodic microdomain formation,[6] that is, microphase-separation transition (MST). From the same standpoint, a macroscopic stability limit (or spinodal condition, SP) can also be found from the condition $S(\mathbf{q}=0) = \infty$, equivalent to the divergence of the osmotic compressibility. The study of $S(\mathbf{q})$ thus finds the two distinct boundaries on the temperature-concentration plane: MST and SP. Although the divergence conditions give only the stability limit rather than the true coexistence condition in either case, phase behavior on the entire temperature-concentration plane can readily be inferred from the results. The purpose of the present paper is to derive a general formula for $S(\mathbf{q})$ in associating binary blends and to apply the result to specific examples exhibiting MST. Our theory is crude in the sense that it is based on the mean-field picture but is aimed at being suitable for finding novel phase behavior characteristics of the reversibly associating polymers. We focus our attention on the new multicritical phenomena appearing as a result of the cooccurrence of MST and SP.

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2. Lattice Theory of Associating Polymer Solutions. Preliminaries

Consider a binary mixture of A chains and B chains. We assume for simplicity that polymer chains of each species consist of statistical units of the same size a. The number of statistical units on a chain are assumed to be n_A for an A chain and n_B for a B chain. We also assume that each chain carries reactive groups capable of pairwisely forming bonds. Although the following thermodynamic theory, which was developed in ref 9b, hereafter referred to as I, holds for a wider category of association, we specify our system to be the one in which polymer chains of different species associate with each other, while those of the same species do not react (category A·B shown in I). The clusters produced by association are multiblock copolymers. We assume for simplicity that the system we treat here is nongelling, that is, the cluster size remains finite.

Let V be the total volume of the system, and let $\Omega \equiv V/a^3$ be the number of the microscopic cells on which we place the polymer segments. We use a symbol (l,m) to specify the clusters made up of l A chains and m B chains. Hence the chains that remain isolated (referred to as *unimers*) are specified by the symbol (1,0) or (0,1). Let $N_{l,m}$ be the number of clusters of the (l,m) type in the system. The number concentration, $\nu_{l,m}$, is then given by $\nu_{l,m} \equiv N_{l,m}/\Omega$, giving the total number of clusters per unit volume

$$\nu^S \equiv \sum_{l,m} \nu_{l,m} \tag{2.1}$$

where superscript S indicates the quantity referring to the sol part, although it is not relevant in our present nongelling case (see I for details). By geometrical consideration, we find the volume fraction $\phi_{l,m}$ occupied by the (l,m) clusters as

$$\phi_{l,m} = (n_A l + n_B m)\nu_{l,m} \tag{2.2}$$

The nongelling assumption, together with the incompressibility constraint, gives a normalization condition

$$\phi^S \equiv \sum_{l,m} \phi_{l,m} = 1 \tag{2.3}$$

The volume fraction occupied by the total monomers of each species is given by

$$\phi_A = \sum_{l,m} (n_A l)\nu_{l,m}, \quad \phi_B = \sum_{l,m} (n_B m)\nu_{l,m} \tag{2.4}$$

Because of the condition (2.3), we take ϕ_A as an independent variable and write it simply as ϕ (hence, we have $\phi_B = 1 - \phi$) in the following of this paper.

It was shown in I that the multiple-equilibria conditions lead to the cluster distribution

$$\phi_{l,m} = K_{l,m} x^l y^m \tag{2.5}$$

where $x \equiv \phi_{1,0}$ and $y \equiv \phi_{0,1}$ are the unimer volume fractions of each species, and $K_{l,m}$ is the association constant. Having ϕ^S or ν^S as a function of x and y after substituting (2.5) for $\phi_{l,m}$ into (2.3), the relation (2.4) can be transformed into the equivalent coupled equations

$$n_A x \frac{\partial \nu^S}{\partial x} = \phi, \quad n_B y \frac{\partial \nu^S}{\partial y} = 1 - \phi \tag{2.6}$$

which should be solved for x and y to give $x = x(\phi)$ and $y = y(\phi)$. The cluster distribution $\phi_{l,m}$ must now be regarded as a function of the total composition ϕ. The spinodal line (SP) which separates the thermodynamically unstable region from the stable one on the temperature–concentration plane can be found by the condition $\partial^2 \Delta g/\partial \phi^2 = 0$, where Δg is the Gibbs free energy (per lattice site). The SP is explicitly given by

$$\frac{\kappa_A(\phi)}{n_A \phi} + \frac{\kappa_B(\phi)}{n_B(1-\phi)} - 2\chi = 0 \tag{2.7}$$

for our lattice theoretical models (see I for details), where κ-functions are defined by

$$\kappa_A(\phi) \equiv \phi \frac{\partial \log x}{\partial \phi}, \quad \kappa_B(\phi) \equiv -(1-\phi)\frac{\partial \log y}{\partial \phi} \tag{2.8}$$

These new κ-functions appear in the position where the conventional Flory–Huggins theory[12] for nonassociating solutions gives unity. The parameter χ shows the strength of the segment contact energy.[12] It depends on the temperature: $\chi = \chi(T)$.

3. Scattering Function of Polydisperse Copolymer Blends

We have a wide spectrum of clusters whose polydispersity is controlled by the temperature T and the composition ϕ. To consider scattering strength from such polydisperse binary blends, we tentatively give a sequential number $\alpha = 1, 2, ..., N = \Omega\nu^S$ to the clusters. Let the set of the numbers (α,i) show the ith monomer on the αth cluster. The monomer density for (α,i) at lattice site $\mathbf{r}$ is then defined by

$$\rho_i^\alpha(\mathbf{r},t) \equiv \delta(\mathbf{r} - \mathbf{x}_i^\alpha(t)) \tag{3.1}$$

where $\mathbf{x}_i^\alpha(t)$ is an instantaneous position of the monomer at time t, and $\delta(\mathbf{r})$ is the Kronecker's delta. In the following we consider equal time correlations only, so that we ignore the time variable. Since the thermal average of ρ_i^α gives $1/\Omega$, we can rewrite it as

$$\rho_i^\alpha(\mathbf{r}) = 1/\Omega + \delta\rho_i^\alpha(\mathbf{r}) \tag{3.2}$$

where $\delta\rho_i^\alpha$ shows the fluctuating part of the density. The incompressibility condition leads to $\sum_{\alpha,i}\rho_i^\alpha(\mathbf{r}) = 1$, or equivalently

$$\sum_{\alpha,i} \delta\rho_i^\alpha(\mathbf{r}) = 0 \tag{3.3}$$

for any position $\mathbf{r}$.

The intensity of the scattered waves (of X-ray or neutrons) with the scattering vector $\mathbf{q}$ is most generally given by the formula

$$I(\mathbf{q}) = \sum_{\substack{\alpha,\beta \\ i,j}} b_i^\alpha b_j^\beta T_{ij}^{\alpha\beta}(\mathbf{q}) \tag{3.4}$$

in the Fourier space, where b_i^α is the scattering amplitude of the (α,i) monomer, and

$$T_{ij}^{\alpha\beta}(\mathbf{q}) \equiv \langle \delta\rho_i^\alpha(\mathbf{q})\, \delta\rho_j^\beta(-\mathbf{q}) \rangle \tag{3.5}$$

is the density correlation function for the pair (α,i) and (β,j).

Let us assume that the scattering amplitude b_i^α takes the value $b_i^\alpha = A$ for A monomers and $b_i^\alpha = B$ for B monomers. We then decompose it into the form

$$b_i^\alpha = A\tau_i^\alpha + B(1 - \tau_i^\alpha) \tag{3.6}$$

for a binary mixture, where τ_i^α is an Ising variable defined by

$$\tau_i^\alpha = \begin{cases} 1, & \text{if } (\alpha,i) \text{ is an A monomer} \\ 0, & \text{if } (\alpha,i) \text{ is a B monomer} \end{cases} \tag{3.7}$$

specifying the species of the (α,i) monomer. Substituting

(3.6) into (3.4) and using the incompressibility condition (3.3), we find

$$I(\mathbf{q}) = (A - B)^2 T(\mathbf{q}) \tag{3.8}$$

where

$$T(\mathbf{q}) = \sum_{\substack{\alpha,\beta \\ i,j}} \tau_i^\alpha T_{ij}^{\alpha\beta}(\mathbf{q}) \tau_j^\beta \tag{3.9}$$

In order to obtain a specific form of $T(\mathbf{q})$, we now apply the *random-phase approximation* (RPA)[6] to our system. The RPA provides a classical treatment of concentration fluctuations for incompressible mixtures of very large molecular weight molecules. It assumes a self-consistent potential uniformly acting on all species of monomers to ensure the incompressibility condition. The details of the RPA method, as applied to our polydisperse block copolymer blend, are given in Appendix A. The result leads to

$$T(\mathbf{q}) = \frac{1}{S(q)/W(q) - 2\chi} \tag{3.10}$$

for the scattering strength, where

$$S(q) \equiv S^\circ{}_{\mathrm{AA}}(q) + S^\circ{}_{\mathrm{BB}}(q) + 2S^\circ{}_{\mathrm{AB}}(q) \tag{3.11}$$

and

$$W(q) \equiv S^\circ{}_{\mathrm{AA}} S^\circ{}_{\mathrm{BB}}(q) - [S^\circ{}_{\mathrm{AB}}(q)]^2 \tag{3.12}$$

are both related to the intracluster scattering functions (the superscript degree shows the scattering intensity coming from a single cluster). The RPA assumes Gaussian statistics for each chain, which leads to the result

$$S^\circ{}_{\mathrm{AA}}(q) = \frac{1}{\Omega} \sum_\alpha \sum_{i,j} J_{ij} \tau_i^\alpha \tau_j^\alpha \tag{3.13a}$$

$$S^\circ{}_{\mathrm{BB}}(q) \equiv \frac{1}{\Omega} \sum_\alpha \sum_{i,j} J_{ij} (1 - \tau_i^\alpha)(1 - \tau_j^\alpha) \tag{3.13b}$$

$$S^\circ{}_{\mathrm{AB}} \equiv \frac{1}{\Omega} \sum_\alpha \sum_{i,j} J_{ij} \tau_i^\alpha (1 - \tau_j^\alpha) \tag{3.13c}$$

for the intracluster scattering functions[13] with $J_{ij} \equiv \exp[-(\kappa n_{ij})]$, where n_{ij} is the distance between the ith and jth monomers along the chains measured in terms of the number of monomers, and $\kappa \equiv (aq)^2/6$ is the dimensionless squared wavenumber. This result provides a complete set for the calculation of the scattering function for the binary blends made up of the arbitrarily populated assembly of block copolymers.

For our associating blends clusters are characterized by the set of two figures (l,m), so that the sum over α can be replaced by the sum over the type (l,m). Hence, we have

$$S^\circ{}_{\mathrm{AA}}(q) = \sum_{l,m} A_{lm}(q)\, \nu_{l,m} \tag{3.14a}$$

$$S^\circ{}_{\mathrm{BB}}(q) = \sum_{l,m} B_{lm}(q)\, \nu_{l,m} \tag{3.14b}$$

$$S^\circ{}_{\mathrm{AB}}(q) = \sum_{l,m} C_{lm}(q)\, \nu_{l,m} \tag{3.14c}$$

where

$$A_{lm}(q) \equiv \sum_{i,j \in (l,m)} J_{ij} \tau_i \tau_j \tag{3.15a}$$

$$B_{lm}(q) \equiv \sum_{i,j \in (l,m)} J_{ij} (1 - \tau_i)(1 - \tau_j) \tag{3.15b}$$

$$C_{lm}(q) \equiv \sum_{i,j \in (l,m)} J_{ij} \tau_i (1 - \tau_j) \tag{3.15c}$$

are the monomer correlation functions of an isolated single cluster of the type (l,m). (The superscript τ has been omitted.)

We now consider the divergence condition for $I(\mathbf{q})$. This is equivalent to

$$\frac{S(q)}{W(q)} - 2\chi = 0 \tag{3.16}$$

within our RPA. If this condition is satisfied for finite q, the system becomes unstable against the fluctuation in the concentration whose spatial dimensions are characterized by q^{-1}. If it is satisfied for $\mathbf{q} = 0$ on the other hand, it is unstable against demixing into two coexistent macroscopic phases. In fact, as we will show explicitly in Appendix B, the RPA condition (3.16) for $\mathbf{q} = 0$ gives exactly the same equation as (2.7) for the spinodal curve. Owing to this fact, the study of the phase behavior on the entire temperature–concentration plane can start from a single equation. To search for possible new phases arising from the competition between the two opposite tendencies—MST and SP—is our central aim.

4. Phase Diagram of Associating Diblock Copolymers

Having obtained the condition to find a stability limit for both MST and SP, we now apply the theory to a dimer-forming system in which diblock copolymers are formed by end-to-end association.

Consider a mixture of A chains and B chains, each chain carrying a functional group at its one end. A pair of groups on the ends of chains of different species is capable of forming a bond through thermoreversible heteroreaction (see Figure 1). Groups on the same species are assumed to be inactive toward each other. A composite chain formed is a diblock copolymer AB with a temporal junction in the middle. The equilibrium of the system is made up of a mixture of diblock copolymers and homopolymers which remain unreacted. It is apparently the same as a mixture of chemically connected diblock copolymers with their homopolymers,[14,15] but its phase behavior is in fact much more varied because the population of the block copolymer can be shifted by the change in temperature and total concentration.

Let $n \equiv n_{\mathrm{A}} + n_{\mathrm{B}}$ be the total number of the statistical units on a block copolymer chain, and let $a \equiv n_{\mathrm{A}}/n$ ($b \equiv n_{\mathrm{B}}/n$) be the fraction of the A part (B part). We have $a + b = 1$ by definition. Furthermore, in order to simplify the notation, let $x \equiv \phi_{10}$ and $y \equiv \phi_{01}$ be the unimer volume fraction of each species. The association equilibrium condition leads to

$$z = Kxy \tag{4.1}$$

for the volume fraction z of the block copolymers, where K is the temperature-dependent association constant. A general argument developed in I gives $K = \exp(1 - \Delta)$ in terms of the free-energy difference

$$\Delta \equiv \beta(\mu^\circ{}_{\mathrm{AB}} - \mu^\circ{}_{\mathrm{A}} - \mu^\circ{}_{\mathrm{B}}) \tag{4.2}$$

which is produced when a pair of A and B chains is

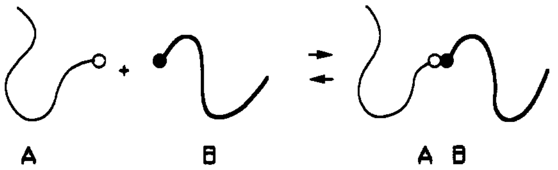

Figure 1. Dimer-forming binary blends. A chain A and a chain B are in an association equilibrium with a dimer AB, which is connected by the end-functional groups. The dimer formed is a diblock copolymer with a temporal junction, which can break and recombine.

combined to form a dimer. (μ° refers to an internal free energy of the corresponding chain.) We split Δ into the two parts: $\Delta = \beta(\Delta\epsilon - T\Delta s)$, where $\Delta\epsilon$ is the binding energy of a bond and Δs the entropy change produced during the dimerization (normally $\Delta s \leq 0$). The latter consists of two parts: $\Delta s = \Delta s_{\mathrm{dis}} + \Delta s_{\mathrm{bond}}$, where Δs_{dis} shows the change in the *entropy of disorientation*,[12] that is, the entropy arising from the flexibility of the chains, and Δs_{bond} shows the entropy loss due to the geometrical constraint in forming a bond. We assume the conventional lattice theoretical form[12] $s_{\mathrm{dis}} = k_{\mathrm{B}} \log[nz(z-1)^{n-2}/\sigma \exp(n-1)]$ for chain of n statistical units on a lattice of z coordination number (σ being the symmetricity number of a chain, i.e., which takes 1 for an asymmetric chain and 2 for a symmetric chain). We thus find $\Delta s_{\mathrm{dis}} = k_{\mathrm{B}} \log[4(z-1)^2/nabze]$ for the difference. Putting together all of these results, we find the association constant in a compact form

$$K = \frac{\lambda_0}{nab} \exp(-\beta\Delta\epsilon) \tag{4.3}$$

where the parameter λ_0 is defined by $\lambda_0 \equiv (4(z-1)^2/ze) \exp(\Delta s_{\mathrm{bond}}/k_{\mathrm{B}})$. It is related to the entropy loss during the bond formation. Specifically Δs_{bond} can be larger in the absolute value as the geometrical constraint in fitting the atoms to form a bond is stronger.

The coupled equations (2.6) now take the form

$$x(1 + aKy) = \phi \tag{4.4a}$$

$$y(1 + bKx) = 1 - \phi \tag{4.4b}$$

to be solved for x and y. The solution is given by $x = \phi - az(\phi)$ and $y = 1 - \phi - bz(\phi)$ in terms of the composition ϕ, where the dimer volume fraction is expressed by

$$z(\phi) = \frac{1}{2ab}[a(1-\phi) + b\phi + K^{-1} - [D(\phi)]^{1/2}] \tag{4.5}$$

with $D(\phi)$ being defined by $D(\phi) \equiv [a(1-\phi) + b\phi + K^{-1}]^2 - 4ab\phi(1-\phi)$. The logarithmic derivatives of x and y yield specific forms of the κ-functions for the dimerization:

$$\kappa_{\mathrm{A}}(\phi) = \frac{1 - az'}{1 - az/\phi} \qquad \kappa_{\mathrm{B}} = \frac{1 + bz'}{1 - bz/(1-\phi)} \tag{4.6}$$

We now proceed to the calculation of the scattering functions. Simple algebra gives

$$A_{10} = A_{11} = \sum_{i,j=1}^{n_{\mathrm{A}}} \exp(-\kappa|i-j|) = (na)^2 D(aQ) \tag{4.7}$$

for the AA component of the intramolecular scattering function, where $Q \equiv n\kappa = n(aq)^2/6 = (R_{\mathrm{g}}q)^2$ is the dimensionless squared wavenumber measured relative to the unperturbed gyration radius $R_{\mathrm{g}} \equiv n^{1/2}a/(6)^{1/2}$ of a diblock copolymer. The entire scattering function depends on Q, T, and ϕ. The function $D(x)$ that appeared in (4.7) is the *Debye function*[6,7] defined by $D(x) \equiv 2(\exp(-x) - 1 + x)/x^2$. It gives the scattering intensity from a single Gaussian chain. The amplitude A_{lm} is the same for both the A unimer and the copolymer.

A similar calculation leads to

$$B_{01} = B_{11} = (nb)^2 D(bQ) \tag{4.8}$$

for the BB components, and

$$C_{11} = \sum_{i\in A}\sum_{j\in B} \exp(-\kappa|i-j|) = \frac{n^2}{2}\{D(Q) - a^2D(aQ) - b^2D(bQ)\} \tag{4.9}$$

for the AB component of a block copolymer. Putting these results together, we find

$$S^\circ_{\mathrm{AA}} = A_{10}\frac{x}{na} + A_{11}\frac{z}{n} = naD(aQ)\phi \tag{4.10a}$$

$$S^\circ_{\mathrm{BB}} = B_{01}\frac{y}{nb} + B_{11}\frac{z}{n} = nbD(bQ)(1-\phi) \tag{4.10b}$$

$$S^\circ_{\mathrm{AB}} = C_{11}\frac{z}{n} = \frac{n}{2}\{D(Q) - a^2D(aQ) - b^2D(bQ)\}z \tag{4.10c}$$

and hence the function F defined by $F(Q) \equiv nS(Q)/W(Q)$ takes the form

$$F(Q) = \frac{axD(aQ) + byD(bQ) + zD(Q)}{ab\phi(1-\phi)D(aQ)\,D(bQ) - \frac{1}{4}z^2[D(Q) - a^2D(aQ) - b^2D(bQ)]^2} \tag{4.11}$$

The instability condition to be solved is given by

$$F(Q) - 2n\chi = 0 \tag{4.12}$$

This function $F(Q)$ covers the two extreme limits:

(i) nonassociating binary blends for which $K = 0$, and hence

$$F(Q) = \frac{1}{a\phi D(aQ)} + \frac{1}{b(1-\phi)D(bQ)} \tag{4.13}$$

The RPA scattering function of a binary blend was analyzed by de Gennes[16] in relation to the spinodal decomposition. The function $F(Q)$ shows no peak at finite Q.

(ii) chemically connected block copolymers for which $K = \infty$, and hence we have $a = \phi, b = 1 - \phi$, $x = y = 0$, and $z = 1$, leading to

$$F(Q) = \frac{D(Q)}{a^2b^2D(aQ)\,D(bQ) - \frac{1}{4}[D(Q) - a^2D(aQ) - b^2D(bQ)]^2} \tag{4.14}$$

The microphase formation in this limit was elaborated by Leibler.[6]

5. Results of Numerical Calculations

To show the phase diagrams obtained by a numerical calculation, we introduce the reduced temperature τ defined by the dimensionless deviation $\tau \equiv 1 - \Theta/T$ from the theta temperature Θ. The Θ temperature for the A/B mixutre is defined by the temperature where the condition $\chi(\Theta) = 1/2n_{\mathrm{B}}$ holds. For T near Θ, the Flory's interaction parameter is known to obey in most cases the formula

$$\chi(T) = 1/2n_{\mathrm{B}} - \psi_1\tau \tag{5.1}$$

where amplitude ψ_1 takes a numerical value of order unity, the precise value of which is dependent on the combination of A and B monomers. In terms of the reduced temperature, the binding energy can be written as $\beta\Delta\epsilon = -\gamma(1 - \tau)$, where $\gamma \equiv -\Delta\epsilon/k_B\Theta$ (>0) shows the bond strength measured relative to the thermal energy.

The function F defined by (4.11) now includes two physical parameters: the temperature τ and the concentration ϕ. It can either be a steadily increasing function or exhibit a single maximum at finite Q. Let Q^* (>0) be the value at which $F(Q)$ shows a minimum, if it exists. Consider a fixed concentration. At sufficiently high temperatures we have $F(Q;\tau,\phi) > 2n\chi(\tau)$ for any Q, so that the homogeneously mixed state is stable. The scattering function $T(Q)$, however, exhibits a maximum at either $Q = 0$ or $Q = Q^*$ depending on the concentration, which is a precursor of the instability. As the temperature is decreased, the condition (4.12) is first satisfied for $Q = 0$ in a certain range of the concentration where $F(Q)$ is a monotonic function, resulting in the SP;

$$F(0;\tau,\phi) - 2n\chi(\tau) = 0 \qquad (5.2)$$

This condition is met for the concentration ϕ, which is either small or large so that the population of the produced diblock copolymers is insufficient to form a microphase.

On the contrary, when the numbers of A and B chains are comparable, sufficiently many copolymers are produced to form a microphase; hence, $F(Q)$ exhibits a maximum at finite Q^*. In the latter case the instability condition is first fulfilled at this wavenumber as the temperature is lowered, which indicates that the MST takes place before SP. The condition for this situation to be realized is given by

$$\frac{\partial F(Q;\tau,\phi)}{\partial Q} = 0 \quad \text{for } Q = Q^* > 0 \qquad (5.3)$$

together with (4.12) for $Q = Q^*$. Even in this concentration region the macroinstability condition is met if one goes further down into the low-temperature region. The microphase remains stable only in the region bounded by the MST and SP.

Parts a–c of Figure 2 show typical examples of the phase diagram found by numerically solving the macro- and microinstability conditions. A symmetric system where both chains have the same length ($a = b = 0.5$) is considered. The total DP is fixed to be $n = 20$. The material parameters are chosen as $\psi_1 = 1$ and $\gamma = 3$ in the following. Although these values are rather arbitrarily chosen to show new characteristics of the phase behavior, they lie in the range that can be easily reached in the experiments. The parameter λ_0, which is related to the entropy change in the bond formation, is changed in Figure 2a–c.

Solid lines show SP, while the broken lines show MST. They meet at the two symmetric points (indicated by LP), at which the two conditions are simultaneously satisfied. They are examples of the *Lifshitz point*,[17] that is, the point where an order parameter with a finite wavenumber (Q^* in the present case) starts to appear. The whole plane is divided into several regions, each characterized by the capital letters in it. The region with letter H has a homogeneously mixed fluid phase. The regions shown by M and M′ exhibit microscopically ordered phases in which microdomains are regularly ordered, although the very structure of the domains cannot be predicted by the instability condition only. A region with two letters in the figure is a biphasic region (or *miscibility gap*) where two distinct phases indicated by the letters simultaneously coexist. For example, the letters HM indicate that the entire system is demixed into two phases in equilibrium, one of which is a homogeneously mixed phase H and the other is a microphase M. In the middle of the phase diagram we have a *eutectic point* (indicated by the letter e) where a single microphase melts into the two coexistent homogeneously mixed fluids, each having an A or a B majority in the concentration, when the temperature is lowered. As the temperature is still lowered, we observe another novel behavior characteristic of the associating systems; the miscibility gap starts to split again at the point e′ in the center of the concentration axis, and a new microphase (shown by M′) gets stabilized in between. The low-temperature microphase, which should be called *reentrant microphase*, is stabilized simply because the population of block copolymers produced becomes sufficient in this low-temperature region to homogenize the

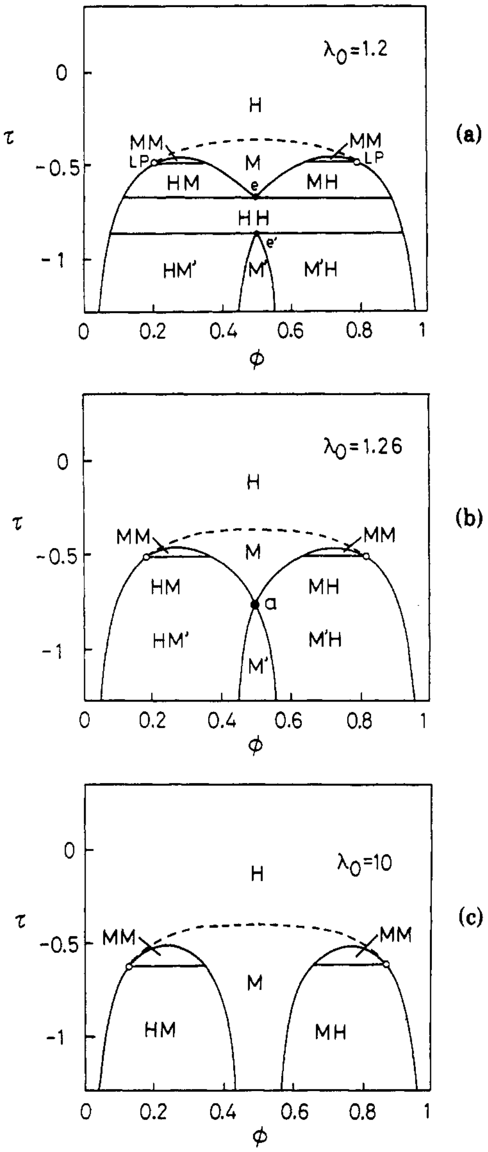

Figure 2. (a) Typical example of the phase diagrams for the associating diblock copolymer blends of relatively short chains ($n_A = n_B = 20$). MST (broken line) and SP (solid lines) are shown on the temperature–concentration plane. The entire plane is divided into several regions whose characters are indicated by capital letters (see text for details). Two points shown by (LP) are Lifshitz points, while those shown by e and e′ are eutectic points. The existence of a reentrant microphase (M′) is one of the remarkable features of the associating systems. (b) Same as in Figure 2a shown for a larger value of the entropy parameter λ_0. The two eutectic points merge into a single azeotrope (a) in this figure. (c) Same as in Figure 2a shown for a still larger value of λ_0. The miscibility gap splits completely into two separate regions at the middle of the concentration.

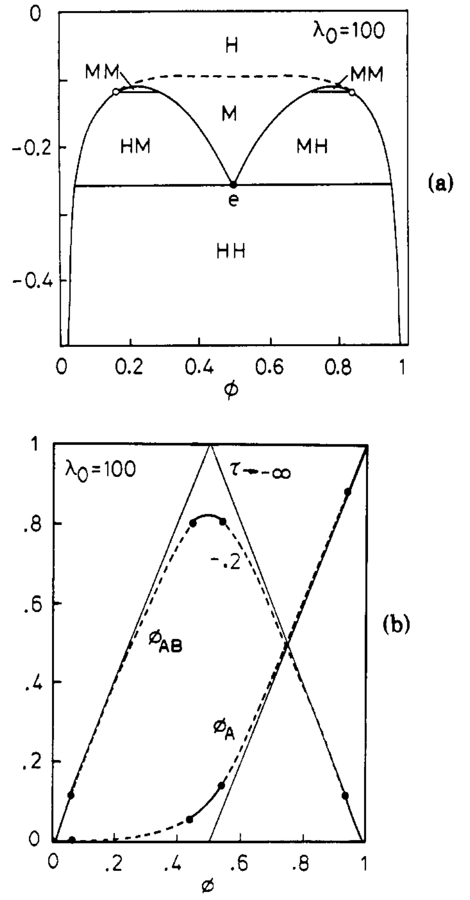

Figure 3. (a) Phase diagram of the associating diblock copolymer blends for higher molecular weight chains. The number of the statistical units on a chain is fixed as $n_A = n_B = 100$ for both species. (b) Volume fraction of the formed diblock copolymers and of the A unimers at a fixed temperature ($\tau = -0.2$) plotted against the total A composition. Material parameters are the same as in Figure 3a. The parts indicated by broken lines lie in the unstable region. The volume fraction of the copolymers approaches the triangle in a low-temperature limit.

two demixed fluid phases into a single one having microscopic ordering. At the top of the M′ region we have another eutectic point e′, where M′ melts into two homogeneous mixtures as the temperature is raised. Prediction of the existence of such a new type of reentrant phase is one of the main conclusions obtained in our theory.

Parts b and c of Figure 2 show the phase diagrams for larger values of λ_0, or equivalently, for larger values of the association constant. The tendency to form dimers is so strong that the miscibility gap tends to split completely into two separate parts. Figure 2b shows the case where two eutectic points just merge into a single one at the point shown by the letter a. This point is an example of an *azeotrope*, the point where one ordered phase transforms to another directly by the temperature change. In Figure 2c macrostability is completely recovered at concentrations near 0.5.

Figure 3a shows the phase diagram for a higher value of DP(n=100). The top of the microphase region M becomes slightly flat, but overall phase behavior is similar to the one shown in Figure 2. In order to see how the population of the block copolymers changes as the concentration changes, Figure 3b plots x ($=\phi_A$) and z ($=\phi_{AB}$) as a function of ϕ for a fixed temperature ($\tau = -0.2$). The parts shown by broken lines lie in the unstable biphasic regions. The volume fraction z of the copolymers reaches a maximum at $\phi = 0.5$. As the temperature is lowered, it approaches the limiting triangle.

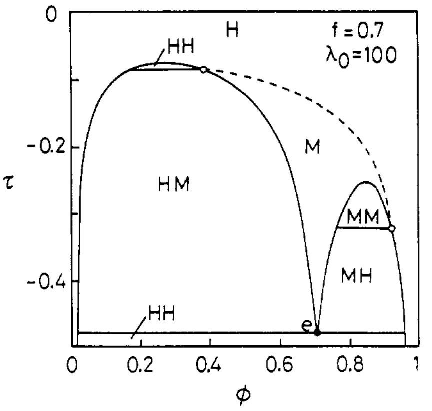

Figure 4. Phase diagram for asymmetric chains ($a = 0.7$, $b = 0.3$). The miscibility gap shifts to a low-concentration, high-temperature region, but the basic topology of the diagram remains the same.

Figure 4 shows an example of the asymmetric systems ($a > b$). As in the usual polymer solutions, the miscibility gap shifts to a low-concentration, high-temperature region, but the topological structure of the diagram is basically preserved.

The mutual interference between MST and SP is strongest around the Lifshitz point. Near a LP, where the order parameter has smaller wavenumbers, we can expand the function $F(Q)$ in powers of Q:

$$F(Q) = F_0 + F_1 Q + F_2 Q^2 + \ldots \tag{5.4}$$

Here the coefficients F_i are functions of τ and ϕ. (F_0 is identical with $F(0;\tau,\phi)$, which appeared in the SP condition.) Then LP is a point at which F_1 changes its sign from positive to negative. Combination of the condition (5.2) with $F_1(\tau,\phi) = 0$ determines the position of the LP. In the microphase region near the LP, we can write

$$F(Q;\tau,\phi) - 2n\chi = \epsilon + F_2(Q - Q^*)^2 \tag{5.5}$$

by keeping up to the second order of Q, where

$$\epsilon \equiv F_0 - \frac{F_1^{\ 2}}{4F_2} - 2n\chi \tag{5.6}$$

and

$$Q^* = -\frac{F_1}{2F_2} \ (>0) \tag{5.7}$$

The parameter ϵ measures a distance to the LP. The squared wavenumber Q^* gives the periodicity of the unstable mode. Near the LP where $\tau = \tau_L$ and $\phi = \phi_L$, F_1 is proportional to $|\tau - \tau_L|$ or $|\phi - \phi_L|$ in accordance with the direction we approach. Hence, we find $q^* \sim |\tau - \tau_L|^{1/2}$ or $\sim |\phi - \phi_L|^{1/2}$.

6. Conclusion and Discussion

The microscopic theory of the scattering function presented in this paper and the interpretation of the calculation based on it are profitable for finding the stability limit against both macroscopic separation and microscopic ordering. The picture we have presented here on the concentration fluctuations provides a starting point to develop the study on the phase behavior of physically associating polymer mixtures covering a variety of categories. These include a long linear chain formed with alternating AB blocks (-[AB]$_n$-) (*equilibrium heteropolymerization*), comblike block copolymers (AB$_f$) formed by several shorter chains sticking on a long A chain by end-functional groups, and starlike block copolymers (BA_f) with several long A chains connected by a shorter B chain at their chain ends. Chemically synthetic counterparts of all of these block copolymers have already been confirmed experimentally to form microphases corresponding to their molecular architectures. Hence, it is plausible that physically associated block copolymers can also undergo MST, although systematic experiments to find their phase behaviors have not been reported. One advantage in dealing with associating copolymers is that they exhibit more variety in phase behavior and morphology, because of their flexibility in changing molecular architecture. The presence of the reentrant ordered phases, for example, encourages research along this line.

It is also straightforward to study, within the scheme of our theory, the scattering properties of physical gels[9a,10,18,19] in which macronetworks are formed by reversible cross-linking. Some experimental evidences for the existence of the singular behavior near gelation transition (enhanced low-angle scattering) in the anisotropic scattering have been reported[19] in relation to the physical gels of atactic polystyrene. It would be very effective if the sol-to-gel transition point can be identified by scattering measurements.

Our theory on the other hand is severely limited by the lack of the method to account for the spatial structure of the microphase. We must compare the free energy to find what kind of structure is actually stabilized in a given region on the temperature–concentration plane. One candidate of the free energy to be considered may be expressed by the Landau type formula

$$\mathcal{F} = \int \mathrm{d}\mathbf{r} \left\{\frac{1}{2n}\phi(\mathbf{r})\,[F(-i\nabla;\tau,\phi(\mathbf{r})) - 2n\chi]\phi(\mathbf{r}) + \Delta g(\phi(\mathbf{r}))\right\} \tag{6.1}$$

where replacement of $\mathbf{q}$ in F by the operator $-i\nabla$ is indicated, and $\Delta g(\phi)$ is the nonlinear part of the lattice theoretical free energy, details of which were given in our preceding paper I. The inhomogeneous free energy (6.1) is designed to produce an RPA scattering function when linearized. For practical purpose, however, the function F must be replaced by its power expansion (5.5) to get specific conclusions.

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Appendix A. Derivation of the RPA Scattering Function for Polydisperse Polymer Blends

To derive the RPA scattering function in a compact form, we here introduce vector notations. Let τ be an Ω-component columnar vector whose (α,i)th component is defined by τ_i^α given in the eq 3.7, so that we can write $\tau = [\tau_i^\alpha]$. Similarly let $\mathbf{e}$ be the columnar vector whose components are all unity. We have by definition

$$\mathbf{e}^{\mathrm{T}}\cdot\tau = \sum_{\alpha,i} \tau_i^\alpha = \Omega\phi \tag{A.1}$$

where $\mathbf{e}^{\mathrm{T}}$ is a transposed vector of $\mathbf{e}$. The monomer density (3.2) can be expressed as

$$\rho = \frac{1}{\Omega}\mathbf{e} + \delta\rho \tag{A.2}$$

by the use of this notation. According to the conventional lattice theory, the monomer–monomer contact energy takes the value χ when the neighboring pair is (A,B), while it is zero for the (A,A) for (B,B) pair. We must therefore introduce a matrix χ defined by

$$\hat{\chi} = \chi[\tau{:}(\mathbf{e} - \tau)^{\mathrm{T}} + (\mathbf{e} - \tau){:}\tau^{\mathrm{T}}] \tag{A.3}$$

where $\mathbf{a}{:}\mathbf{b}^{\mathrm{T}}$ shows a diadix formed by the two vectors. Specifically we have a relation

$$\mathbf{e}^{\mathrm{T}}\cdot\hat{\chi}\cdot\mathbf{e} = 2\chi\Omega^2\phi(1 - \phi) \tag{A.4}$$

We now consider the linear response $\langle\delta\rho_i^\alpha\rangle$ of the density to an arbitrary external field acting on each monomer with strength U_i^α. Linear response theory gives

$$\langle\delta\rho(\mathbf{q})\rangle = -\hat{\mathbf{T}}\cdot\mathbf{U}(\mathbf{q}) \tag{A.5}$$

where $\hat{\mathbf{T}}$ is a matrix whose components are given by the correlation (3.5). The RPA assumes that (A.5) is approximately equivalent to

$$\langle\delta\rho\rangle = -\hat{\mathbf{S}}\cdot(\mathbf{U} + \delta\mathbf{U}^{\mathrm{eff}} - \hat{\chi}\cdot\langle\delta\rho\rangle) \tag{A.6}$$

if the effective potential $\delta\mathbf{U}^{\mathrm{eff}}$ is judiciously chosen, where $\hat{\mathbf{S}}$ is a correlation function of monomers belonging to the *same* single cluster. Gaussian statistics gives[13]

$$S_{ij}^{\alpha\beta}(\mathbf{q}) = \delta_{\alpha,\beta}J_{ij} \tag{A.7}$$

in terms of $J_{ij} = \exp(-\kappa n_{ij})$ defined below (3.13). The effective potential $\delta\mathbf{U}^{\mathrm{eff}}$ is a self-consistent potential to ensure the incompressibility condition (3.3) or equivalently

$$\mathbf{e}^{\mathrm{T}}\cdot\delta\rho = 0, \quad \text{and hence } \mathbf{e}^{\mathrm{T}}\cdot\hat{\mathbf{T}} = 0 \tag{A.8}$$

It is assumed to act uniformly on all species of monomers in a bulk system

$$\delta\mathbf{U}^{\mathrm{eff}} = \mathbf{e}\delta U \tag{A.9}$$

where δU is a scalar. To find δU, we substitute (A.5) and (A.9) into (A.6) and multiply $\mathbf{e}^{\mathrm{T}}$ from the left. Solving the result for δU, we find

$$\delta U = -\frac{\mathbf{e}^{\mathrm{T}}\cdot\hat{\mathbf{S}}\cdot(\hat{\mathbf{1}} + \hat{\chi}\cdot\hat{\mathbf{T}})\cdot\mathbf{U}}{(\mathbf{e}^{\mathrm{T}}\cdot\hat{\mathbf{S}}\cdot\mathbf{e})} \tag{A.10}$$

Comparing (A.5) and (A.6), we finally find

$$\hat{\mathbf{T}} = \frac{1}{\hat{\mathbf{1}} - \hat{\mathbf{Q}}\cdot\hat{\chi}}\cdot\mathbf{Q} \tag{A.11}$$

where

$$\hat{\mathbf{Q}} \equiv \hat{\mathbf{S}} - \frac{(\hat{\mathbf{S}}\cdot\mathbf{e}){:}(\mathbf{e}^{\mathrm{T}}\cdot\hat{\mathbf{S}})}{(\mathbf{e}^{\mathrm{T}}\cdot\hat{\mathbf{S}}\cdot\mathbf{e})} \tag{A.12}$$

The true correlation function $\hat{\mathbf{T}}$ is thus expressed in terms of the intracluster correlation function $\hat{\mathbf{S}}$; this is the fundamental idea of the RPA. Now simple algebra gives

$$\tau^{\mathrm{T}}\cdot\hat{\mathbf{T}}\cdot\tau = \frac{1}{S(q)/W(q) - 2\chi} \tag{A.13}$$

which is equivalent to (3.10).

Appendix B. Spinodal Condition as the $q \rightarrow 0$ Limit of the Scattering Function

In this appendix we prove that the RPA condition (3.16) is equivalent to the spinodal (2.7) when the wavenumber is set to zero. To simplify the notation, we define $n \equiv n_A + n_B$ for the sum of the DP of both species and write $n_A \equiv na$ and $n_B \equiv nb$ with $a + b = 1$. For $\mathbf{q} = 0$ we have $J_{ij} = 1$, and hence $A_{lm}(0) = (nal)^2$, $B_{lm}(0) = (nbm)^2$, and C_{lm}

$= n^2ablm$, leading to $S^\circ_{AA} = n^2a^2\langle l^2\rangle\nu^S$, $S^\circ_{BB} = n^2b^2\langle m^2\rangle\nu^S$, and $S^\circ_{AB} = n^2ab\langle lm\rangle\nu^S$, where a bracket $\langle\ \rangle$ shows the number-weighted average. By definition we obtain

$$\frac{S(0)}{W(0)} = \frac{\langle(al+bm)^2\rangle}{(nab)^2(\langle l^2\rangle\langle m^2\rangle - \langle lm\rangle^2)\nu^S} \qquad \text{(B.1)}$$

By use of the number-average quantities, the relation (2.6) can be expressed as

$$n_A\langle l\rangle = \phi, \quad n_B\langle m\rangle = 1-\phi \qquad \text{(B.2)}$$

We next proceed to express the κ-functions in terms of the average quantities. For this purpose we take the derivative of the two relations (2.6) with respect to ϕ and find

$$na[x'\nu_x + x(\nu_{xx}x' + \nu_{xy}y')] = 1 \qquad \text{(B.3a)}$$

$$nb[y'\nu_y + y(\nu_{yx}x' + \nu_{yy}y')] = -1 \qquad \text{(B.3b)}$$

where a prime indicates the derivative with respect to ϕ and ν_{xy}, etc., are the partial derivatives of ν^S. By use of the identities $x^2\nu_{xx} = \sum l(l-1)\nu_{l,m} = (\langle l^2\rangle - \langle l\rangle)\nu^S$, $y^2\nu_{yy} = (\langle m^2\rangle - \langle m\rangle)\nu^S$, and $xy\nu_{xy} - \langle lm\rangle\nu^S$, we eliminate the partial derivatives in favor of the number-average quantities. By use of the definitions of κ_A and κ_B in (2.8), the relations in (B.3) are transformed into

$$\frac{\langle l^2\rangle}{\langle l\rangle}\kappa_A - \frac{a}{b}\frac{\langle lm\rangle}{\langle m\rangle}\kappa_B = 1 \qquad \text{(B.4a)}$$

$$\frac{b}{a}\frac{\langle lm\rangle}{\langle l\rangle}\kappa_A - \frac{\langle m^2\rangle}{\langle m\rangle}\kappa_B = -1 \qquad \text{(B.4b)}$$

which, when solved with respect to κ's, give

$$\kappa_A(\phi) = \frac{a\langle lm\rangle + b\langle m^2\rangle}{b(\langle l^2\rangle\langle m^2\rangle - \langle lm\rangle^2)}\langle l\rangle \qquad \text{(B.5a)}$$

$$\kappa_B(\phi) = \frac{a\langle l^2\rangle + b\langle lm\rangle}{a(\langle l^2\rangle\langle m^2\rangle - \langle lm\rangle^2)}\langle m\rangle \qquad \text{(B.5b)}$$

The κ-functions have thus been expressed in terms of the average cluster sizes. Substituting the result into (2.7) and with the help of the relations in (B.2), we actually confirm that it is equivalent to $T(\mathbf{q}=0)^{-1} = 0$. The RPA scattering function has thus been most generally proven to give the lattice theoretical spinodals in the limit of vanishing wavenumber.

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