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Microphase Formation in Mixtures of Associating Polymers

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ABSTRACT: This paper theoretically explores possible phase diagrams of the associating polymers in which macro- and microphase separation transitions coexist. Our model binary mixture consists of long chains (A) carrying *f* associative groups and short chains (B) carrying one associative group on their ends. Comb-shaped block copolymers with A as a main chain bearing a different number of side B chains are formed in equilibrium. When A and B unfavorably interact, macro- and microphase separations compete. If the population of the formed block copolymers is sufficiently large, miscibility between A/B chains is so improved that a stable microphase appears in a restricted region on the phase plane near the stoichiometric concentration where the concentration of the mixture agrees with the molecular composition of the fully associated cluster $A \cdot B_f$. This mocrophase reveals new properties since it is formed by reversible bonds instead of covalent ones. Relation to the recently observed microphase in hydrogen-bonded polymer/surfactant systems is discussed.

I. Introduction

There has recently been growing interest in the phase formation in solutions of associating polymers. A large body of experimental data now exists on the outstanding phase behavior and rheological properties caused by the competition between phase separation and molecular association. But there is room for further experimental and theoretical study. The purpose of this paper is to study the possibility of the microphase separation transition (MST) due to association between two different species of chain molecules, one of which (referred to as A) is a polymer chain carrying a large number of associating groups, and the other (B) can be either another polymer chain with a single associating group on its chain end or a surfactant molecule with a head group capable of bonding onto the associating groups on A.

The study of MST has so far been concentrated on the block copolymers with several blocks unfavorably interacting with each other but connected by chemical bonds into linear,[1,2] comb,[3−5] and star[6−10] shapes. Formation of many new ordered phases has been reported,[7,8] and study still continues.[11,12] In solutions and blends of such chemical block copolymers, the junctions connecting two blocks do not break in any thermal processes. The similar order−disorder transition is, however, also expected in associating polymers in which junctions between unfavorable chains break and recombine in thermal motion.[13] Formation of a stable microphase requires a delicate balance between the associative force and chain repulsion. The simplest case in which an A-chain and a B-chain form a heterodimer by head association in an A/B blend was theoretically studied by us.[13] It was pointed out that in most cases an ordered phase is difficult to stay thermodynamically stable due to the tendency toward macroscopic phase separation, but also that, if the strength of the associating force is judiciously chosen, a stable ordered phase is possible near the stoichiometric concentration. We here extend this study to include an important case of polymer/surfactant complex formation.

The effect of added surfactants to the polymers is roughly classified into three categories: (i) polymer conformational transition, such as collapse or stiffening, induced by the attached surfactants, (ii) microphase separation transition due to hetero-complex formation, and (iii) modification of network-formation (gelation) by forming mixed micelles at the network junctions. We here discuss the second problem. Study of surfactant effect on the network formation will be reported in a forthcoming paper.[14]

Typical ordered phases experimentally confirmed recently in associating polymers are those found in polyelectrolyte/surfactant systems.[15] Related studies are also reported in ref 16. The ionic interaction leading to multiplets, however, is not a unique candidate for an ordered state. Hydrogen bonding works equally well if it is strong enough compared to the repulsive interaction between the polymer segments, but still weak enough to break by temperature. In fact, Ruokolainen and his co-workers[17−20] have recently observed MST in the mixture of poly(4-vinylpyridine) (P4VP) and surfactant 3-pentadecylphenol (PDP). In this sytem the hydrogen bonding between the hydroxyl group in PDP and the basic amine nitrogen in the pyridine group leads to a lamellar structure at low temperatures. The lamellar period L_p was found to decrease in proportion to the reciprocal of x, the fraction of surfactant molecules per pyridine group in P4VP. It was also found that the MST temperature takes a minimum value (microphase easiest) near the stoichiometric concentration $x = 1$.

In this paper we consider a model mixture of A-chains and B-molecules. We assume that A-chains carry f associating side groups periodically distributed along the chain and B-molecules carry a single group at their chain end. Here, a B-molecule can be a short oligomer or a surfactant molecule. In the mixture, comb-shaped copolymers ($A-B_m$) with varied $m = 1, 2, ..., f$ are formed. We call them (1, m)-clusters. In the extreme limit where B-molecules are in fact low molecular weight solvent molecules, our system reduces to the polymer solution in which hydration takes place. Polymers are partially covered by solvent molecules by hydrogen bonding. Matsuyama and one of the authors[21] showed that the miscibility gap takes either closed-loop shape or hourglass shape depending on the strength of the bonding. No MST is possible. As the length of the

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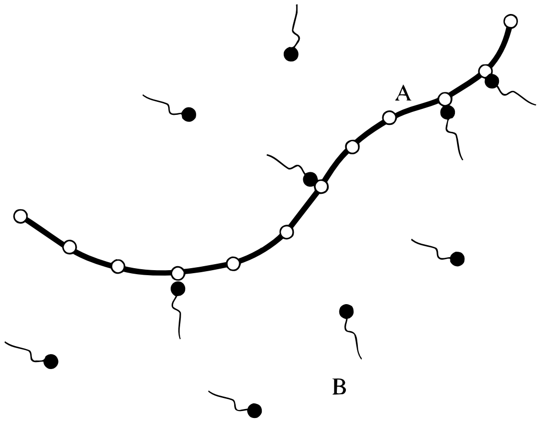

Figure 1. Model mixture of associating polymers. Short polymer chains (B) with a single associative group at their chain end associate with long polymers (A) of functionality f.

side chain becomes longer, however, associated comb block copolymers are expected to form an ordered structure. How long should the B-molecules be to form a stable mesophase? How large should the number f of the side groups be? How is the mesophase formation interfered with by the macroscopic phase separation? At what composition is the MST most easily observed? The purpose of the present paper is to answer these questions by the statistical mechanical study of the model mixture. In the following we find the MST boundary as the stability limit of the homogeneous mixture against infinitesimal concentration fluctuations with finite wave number. This limit is found from the divergence of the concentration correlation function $S(\boldsymbol{q})$ for a certain finite wave number q^* by changing the temperature and the concentration. The correlation function is derived by using the conventional random phase approximation (RPA)[1,22] applied to associating polymers. The stability limit against a macroscopic phase separation, or spinodal condition, defined by the vanishing of the second derivative of the Gibbs free energy, can also be found from the divergence of $S(\mathbf{q})$ at $q = 0$. We can thus study macro- and microphase separation from a unified picture.

II. Stoichiometric Definitions

Consider a model mixture consisting of the number N_A of A-chains and N_B of B-molecules. Let n_A be the total number of statistical units on an A-chain and n_B that on a B-molecule. We make a simplified assumption that both statitistical units have the same volume a^3. To cope with association, let us assume that an A-chain carries f functional groups uniformly distributed along the chain, and a B-molecule carries a single group at its end capable of forming a pairwise bond with a functional group on an A-chain. Although our theory holds for any molecular weights n_A and n_B, we assume $n_B < n_A$ in what follows to stress the case where the B-molecule is a short polymer chain, oligomer, or surfactant molecule (Figure 1). In the low molecular-weight limit of $n_B = 1$, the present model reduces to our previous one[21] for the study of the phase separation in aqueous polymer solutions. Another special case is dimer formation in which A-chains also carry a single associative group ($f = 1$) at their end. Our present study produces the previous results in these special limits.

In equilibrium, clusters made up of both species are formed. Let us introduce a symbol (l, m) to specify a cluster made up of l A-chains and m B-molecules. The symbol (1, 0) or (0, 1) therefore shows A-chains or B-molecules that remain unassociated in the mixture. While the number l must be either 1 or 0 since there is no association among A-chains, the integer m may take any value of 0, 1, 2, ..., f in the case of $l = 1$. To deal with concentrations, we choose the unit of volume to be a^3 and divide the total volume of the mixture into cells of this unit volume. Let Ω be the total number of cells, and let $N_{l,m}$ be the number of the clusters of the type (l, m) in the mixture. The number density of the (l, m) cluster is then given by $\nu_{l,m} = N_{l,m}/\Omega$, and the volume fraction occupied by them is given by

$$\phi_{l,m} = (ln_A + mn_B)\nu_{l,m} \tag{2.1}$$

The total volume fraction ϕ_A occupied by A-chains is then given by

$$\phi_A \equiv n_A \sum_{l,m} l\nu_{l,m} = n_A \sum_{m=0}^{f} \nu_{1,m} \tag{2.2}$$

Similarly, the volume fraction ϕ_B of B-molecules is given by

$$\phi_B = n_B \sum_{l,m} m\nu_{l,m} = n_B[\sum_{m=1}^{f} m\nu_{1,m} + \nu_{0,1}] \tag{2.3}$$

We assume incompressibility of the mixture so that we have

$$\phi_A + \phi_B = 1 \tag{2.4}$$

In the following we regard ϕ_A as an independent variable and write it simply as ϕ. We then have $\phi_B = 1 - \phi$ from incompressibility.

III. Lattice Theory of Reversibly Associating Polymer Solutions

To study cluster distribution and the two-phase equilibrium, we consider the free energy of the model mixture. As in our preceding papers,[23,24] and as in the conventional treatment,[25] we start from the standard reference state in which A-chains and B-molecules are prepared separately in a hypothetical crystalline state.

We first bring the system from this reference state to an intermediate fictitious state in which A-chains and B-molecules are combined into clusters whose distribution is exactly the same as that in the actual mixture. The free energy change ΔF_{rea} required in this step is given by the equation

$$\beta\Delta F_{\text{rea}} = \sum_{m=1}^{f} \Delta_m N_{1,m} \tag{3.1}$$

where $\beta \equiv 1/k_BT$ is the reciprocal temperature. The symbol Δ_m shows the free energy to form a single (1, m)-cluster from an A-chain and m B-molecules in the reference state. It is defined by

$$\Delta_m = \beta(\mu^\circ_{1,m} - \mu^\circ_A - m\mu^\circ_B) \tag{3.2}$$

in terms of the intramolecular free energy $\mu^\circ_{1,m}$ of a (1, m)-cluster, and the chemical potential μ°_A and μ°_B of an A-chain and a B-molecule in the reference state. They depend only on the temperature.

We now mix these intermediate clusters to obtain the real system. The free energy change ΔF_{mix} produced in this second step is given by

$$\beta\Delta F_{\text{mix}} = \sum_{m=0}^{f} N_{1,m} \ln \phi_{1,m} + N_{0,1} \ln \phi_{0,1} + \Omega\chi\phi(1 - \phi) \tag{3.3}$$

according to the conventional Flory–Huggins lattice theory of polymer solutions,[25,26] where $\chi = \chi(T)$ is the Flory's χ-parameter representing van der Waals type contact energy.[25,27,28]

Our total free energy change ΔF is given by the combination of these two terms:

$$\Delta F = \Delta F_{\text{rea}} + \Delta F_{\text{mix}} \tag{3.4}$$

To study phase equilibria and thermodynamic stability, let us next find the chemical potential $\Delta\mu_{1,m} \equiv \mu_{1,m} - \mu^{\circ}_{1,m}$ of a (1, m)-cluster in the mixture. They can be found by differentiating the total free energy ΔF with respect to the number $N_{1,m}$ of (1, m)-clusters with fixed temperature and the fixed number of clusters of other types. We are led to the result

$$\begin{aligned}\beta\Delta\mu_{1,m} &= \beta\left(\frac{\partial\Delta F}{\partial \text{N}_{1,m}}\right)_{T,N_{0,1},N_{1,i}(i\neq m)} \\ &= \Delta_m + 1 + \ln \phi_{1,m} - (n_{\text{A}} + m n_{\text{B}})\,\nu + \\ &\qquad \chi[n_{\text{A}}(1 - \phi)^2 + m n_{\text{B}}\phi^2]\end{aligned} \tag{3.5}$$

where

$$\nu = \sum_{l,m} \nu_{l,m} \tag{3.6}$$

is the total number density of the clusters. Specifically, we find for an A-chain that remains unassociated in the mixture

$$\beta\Delta\mu_{\text{A}} = \beta\Delta\mu_{1,0} = 1 + \ln \phi_{1,0} - n_{\text{A}}\nu + n_{\text{A}}\chi(1 - \phi)^2 \tag{3.7}$$

by substituting $m = 0$ in the above equation.

Similarly, we find for the chemical potential $\Delta\mu_{\text{B}}$ of B-molecules that remain unassociated as

$$\beta\Delta\mu_{\text{B}} = \beta\Delta\mu_{0,1} = \beta\left(\frac{\partial\Delta F}{\partial N_{0,1}}\right)_{T,N_{1,m}} = 1 + \ln \phi_{0,1} - n_{\text{B}}\nu + n_{\text{B}}\chi\phi^2 \tag{3.8}$$

To ensure that clusters are in association equilibrium, we now impose the multiple-equilibrium conditions:

$$\Delta\mu_{1,m} = \Delta\mu_{\text{A}} + m\Delta\mu_{\text{B}} \tag{3.9}$$

These conditions lead to the cluster size distribution

$$\phi_{1,m} = K_m\phi_{1,0}[\phi_{0,1}]^m \qquad (\text{for } m = 1, ..., f) \tag{3.10}$$

in terms of the volume fraction, where

$$K_m = (m - \Delta_m) \tag{3.11}$$

is the equilibrium reaction constant. It depends only on the temperature. With the help of the multiple-equilibrium conditions, the Gibbs free energy Δg per lattice cell is expressed as

$$\begin{aligned}\beta\Delta g &= \beta\left(\frac{\phi_{\text{A}}}{n_{\text{A}}}\Delta\mu_{\text{A}} + \frac{\phi_{\text{B}}}{n_{\text{B}}}\Delta\mu_{\text{B}}\right) \\ &= \frac{\phi}{n_{\text{A}}}(1 + \phi_{1,0}) + \frac{1 - \phi}{n_{\text{B}}}(1 + \phi_{0,1}) - \nu + \chi\phi(1 - \phi)\end{aligned} \tag{3.12}$$

To proceed further and obtain more specific results for the cluster size distribution, we estimate the equilibrium reaction constant K_m as a function of the temperature and the concentration of the A-chain. The free energy change Δ_m produced in forming a (1, m)-cluster consists of three parts:

$$\Delta_m = \Delta_m^{\text{comb}} + \Delta_m^{\text{conf}} + \Delta_m^{\text{bond}} \tag{3.13}$$

The first term gives the change in entropy on combining an A-chain and m B-molecules into a (1, m)-cluster. The second term gives the change in conformational entropy of chains due to the spatial constraint introduced during cluster formation. The last term gives the free energy change in bond formation.

The combinatorial entropy comes from the number of ways to select m attaching sites out of f available ones, and takes the form

$$\Delta_m^{\text{comb}} = -\ln({}_f\text{C}_m) \tag{3.14}$$

where ${}_f\text{C}_m \equiv f!/(f - m)!m!$ is the binomial factor.

For the conformational entropy, we employ the conventional lattice-theoretical entropy of disorientation.[25,28] For a flexible linear chain with n statistical units, it takes the form

$$S^{\text{dis}} \equiv k_{\text{B}} \ln\left[\frac{nz(z - 1)^{n-2}}{\sigma \exp(n - 1)}\right] \tag{3.15}$$

where z is the lattice coordination number and σ is the symmetry number of the chain. The entropy gain $S_{1,m}^{\text{dis}}$ to bring a (1, m)-cluster from the hypothetical crystalline state to a flexible amorphous state is then given by

$$S_{1,m}^{\text{dis}} \equiv k_{\text{B}} \ln\left[\frac{(n_{\text{A}} + m n_{\text{B}})z(z - 1)^{n_{\text{A}}+m n_{\text{B}}-2}}{\sigma_{1,m} \exp(n_{\text{A}} + m n_{\text{B}} - 1)}\right] \tag{3.16}$$

where $\sigma_{1,m}$ is the symmetry number of a (1, m)-cluster; it takes 2 if the cluster has a symmetric structure, and 1 for an asymmetric structure. The configurational free energy change is then given by

$$\begin{aligned}\Delta_m^{\text{conf}} &= -\beta T(S_{1,m}^{\text{dis}} - S_{1,0}^{\text{dis}} - m S_{0,1}^{\text{dis}}) \\ &= -\ln\left\{\frac{\sigma_{1,0}}{\sigma_{1,m}}\,\frac{n_{\text{A}} + m n_{\text{B}}}{n_{\text{A}}}\left[\frac{\sigma_{0,1}(z - 1)^2}{n_{\text{B}}ze}\right]^m\right\}\end{aligned} \tag{3.17}$$

In the following we fix all the symmetry numbers at unity, *i.e.*, $\sigma_{1,0} = \sigma_{0,1} = \sigma_{1,m} = 1$, because symmetric clusters produced by random clustering are highly improbable.

Finally, the free energy change Δ_m^{bond} for bond formation is given by

$$\Delta_m^{\mathrm{bond}} = m\beta\Delta f_0 \tag{3.18}$$

where Δf_0 is the standard free energy change in binding a pair of functional groups.

From these three results we obtain the reaction constant K_m in the form

$$K_m = \frac{n_{\mathrm{A}} + mn_{\mathrm{B}}}{n_{\mathrm{A}}}\,{}_f\mathrm{C}_m\left[\frac{\lambda(T)}{n_{\mathrm{B}}}\right]^m \tag{3.19}$$

where the constant $\lambda(T)$ is defined by

$$\lambda(T) = \frac{(z-1)^2}{z}\exp(-\beta\Delta f_0) \tag{3.20}$$

It depends only on the strength of a single A–B pairwise bond and is called the *association constant*.

Now the equilibrium cluster distribution takes the form

$$\phi_{1,m} = (n_{\mathrm{A}} + mn_{\mathrm{B}})\,{}_f\mathrm{C}_m xy^m \qquad (m = 1, 2, ..., f) \tag{3.21}$$

for the volume fraction, and

$$\nu_{1,m} = \frac{\phi_{1,m}}{n_{\mathrm{A}} + mn_{\mathrm{B}}} = {}_f\mathrm{C}_m xy^m \qquad (m = 1, 2, ..., f) \tag{3.22}$$

for the number density, where

$$x \equiv \phi_{1,0}/n_{\mathrm{A}} \tag{3.23}$$

is the number density of the A-chains that remain unassociated, and

$$y \equiv \lambda\phi_{0,1}/n_{\mathrm{B}} \tag{3.24}$$

is the number density $\phi_{0,1}/n_{\mathrm{B}}$ (being multiplied by the association constant $\lambda(T)$) of the B-molecules that remain unassociated. Now the normalization conditions (2.2) and (2.3) give

$$\phi = n_{\mathrm{A}}x(1+y)^f \tag{3.25}$$

$$1 - \phi = n_{\mathrm{B}}[y/\lambda + fxy(1+y)^{f-1}] \tag{3.26}$$

Solving these equations with respect to x and y, we find

$$x = \frac{\phi}{n_{\mathrm{A}}(1+y)^f} \tag{3.27}$$

and

$$y = \frac{1}{2}\{Q(\phi,T) + [Q(\phi,T)^2 + 4\lambda(1-\phi)/n_{\mathrm{B}}]^{1/2}\} \tag{3.28}$$

with

$$Q(\phi,T) \equiv \lambda(1-\phi)/n_{\mathrm{B}} - f\lambda\phi/n_{\mathrm{A}} - 1 \tag{3.29}$$

Now that we have expressed the volume fraction of clusters in terms of the composition and temperature through these equations, we can express any physical quantities by these thermodynamic variables. For instance, we find

$$\nu(\phi,T) = \sum_{l,m}\nu_{l,m} = \frac{\phi}{n_{\mathrm{A}}} + \frac{y}{\lambda} \tag{3.30}$$

with y being given by eq 3.28, for the total number of clusters. The chemical potential of each species $\Delta\mu_{\mathrm{A}}$ and $\Delta\mu_{\mathrm{B}}$ can then be given by eqs 3.7 and 3.8 as functions of the composition and the temperature.

IV. Concentration Fluctuation and Its Correlation Function

To study stability against periodic concentration fluctuation, let us next derive the scattering function. We consider a small deviation of the concentration from the average value ϕ at the position $\mathbf{r}$:

$$\phi(\mathbf{r}) = \phi + \delta\phi(\mathbf{r}) \tag{4.1}$$

The scattering function $S(\mathbf{q})$ is then defined by the Fourier transform of the concentration correlation function:

$$S(\mathbf{q}) \equiv \int \mathrm{d}\mathbf{r}\,\langle\delta\phi(0)\delta\phi(\mathbf{r})\rangle \mathrm{e}^{-i\mathbf{q}\cdot\mathbf{r}} \tag{4.2}$$

Under the incompressibility condition, the intensity of the scattered wave (of X-ray, neutrons, and so forth) with the scattering vector $\mathbf{q}$ from a binary mixture is proportional to this scattering function $S(\mathbf{q})$. If this function with the finite wavenumber q^* diverges at a certain temperature or concenration, the mixture is unstable against concentration fluctuation with spatial periodicity $(q^*)^{-1}$. In the case where periodicity is of the same order of the molecular dimensions, this suggests spontaneous fomation of microdomain structure.

On the contrary, if this function diverges at infinite wavelength $q = 0$, it gives a macroscopic stability limit, or the *spinodal* condition; the mixture spontaneously separates into two phases.

To find the scattering function, we use the random-phase approximation (RPA).[1,22] The method of RPA provides a mean-field treatment of concentration fluctuations in incompressible mixtures of large molecular weight molecules. It assumes a self-consistent field uniformly acting on all species of monomers to ensure the incompressibility condition. A general scheme for applying RPA to associating polymers was described in our preceding paper.[13] The final expression for $S(q)$ is given by

$$S(q) = 1/\{G(q)/W(q) - 2\chi\} \tag{4.3}$$

with

$$G(q) \equiv S^{\circ}_{\mathrm{AA}} + 2S^{\circ}_{\mathrm{AB}} + S^{\circ}_{\mathrm{BB}} \tag{4.4}$$

$$W(q) \equiv S^{\circ}_{\mathrm{AA}}S^{\circ}_{\mathrm{BB}} - (S^{\circ}_{\mathrm{AB}})^2 \tag{4.5}$$

just the same as the conventional form, where $S^{\circ}_{\mathrm{ij}}(q)$ is the intramolecular correlation function between statistical units of the type i and j (i, j = A or B). For the associating polymers, we have to sum over all possible distributions of clusters:

$$S^\circ_{\mathrm{AA}} \equiv \sum_{m=0}^{f} (S^\circ_{\mathrm{AA}})^{1,m} \nu_{1,m} \tag{4.6a}$$

$$S^\circ_{\mathrm{AB}} \equiv \sum_{m=1}^{f} (S^\circ_{\mathrm{AB}})^{1,m} \nu_{1,m} \tag{4.6b}$$

$$S^\circ_{\mathrm{BB}} \equiv \sum_{l=0,1} \sum_{m=0}^{f} (S^\circ_{\mathrm{BB}})^{1,m} \nu_{1,m} \tag{4.6c}$$

where the superscript (l, m) on the function S indicates that it is the scattering function from a single cluster of the type (l, m). Specifically $(S^\circ_{\mathrm{A,B}}(q))^{1,m}$ is the correlation between statistical units of A -component and B -component within the same (1, m)-cluster. They are given by

$$(S^\circ_{\mathrm{A,B}}(q))^{l,m} \equiv \sum_{\mathrm{j}\in \mathrm{A}, k\in \mathrm{B}} \langle \exp(i\mathbf{q}\cdot\mathbf{r}_{jk})\rangle_0 \tag{4.7}$$

where $\mathbf{r}_{j,k}$ is the relative position vector between jth unit and kth unit on the cluster and the symbol $\langle ...\rangle_0$ indicates an average over the Gaussian distribution

$$W(\mathbf{r}_{j,k}) = \left(\frac{3}{2\pi|j-k|a^2}\right)^{3/2} \exp\left[-\frac{3(\mathbf{r}_{jk})^2}{2|j-k|a^2}\right] \tag{4.8}$$

For a single homopolymer linear chain consisting of n identical statistical units, the scattering function $S^\circ(q)$ is given by

$$S^\circ(q) = \sum_{j=1}^{n}\sum_{k=1}^{n} \exp(-\kappa|j-k|) \tag{4.9}$$

where the dimensionless squared wave number κ is defined by $\kappa \equiv (aq)^2/6$. Replacing the summation by the integrals, we find

$$\mathrm{S}^\circ(q) = n^2 D(n\kappa) \tag{4.10}$$

where the function $D(x)$ is the Debye function defined by

$$D(x) \equiv 2(\mathrm{e}^{-x} + x - 1)/x^2 \tag{4.11}$$

Quite similarly, three elements for comb block copolymers can be calculated as follows:

$$(S^\circ_{\mathrm{AA}}(q))^{1,m} = n_{\mathrm{A}}{}^2 D(n_{\mathrm{A}}\kappa) \tag{4.12a}$$

$$(S^\circ_{\mathrm{AB}}(q))^{1,m} = \frac{m n_{\mathrm{A}} n_{\mathrm{B}} E(n_{\mathrm{B}}\kappa)}{f E(n_{\mathrm{A}}\kappa/f)}[fD(n_{\mathrm{A}}\kappa) - D(n_{\mathrm{A}}\kappa/f) + E(n_{\mathrm{A}}\kappa)E(n_{\mathrm{A}}\kappa/f)] \tag{4.12b}$$

$$(S^\circ_{\mathrm{BB}}(q))^{1,m} = m n_{\mathrm{B}}{}^2 D(n_{\mathrm{B}}\kappa) + \frac{m(m-1)n_{\mathrm{B}}{}^2\, E(n_{\mathrm{B}}\kappa)^2}{(f-1)E(n_{\mathrm{A}}\kappa/f)^2} \times [fD(n_{\mathrm{A}}\kappa) - D(n_{\mathrm{A}}\kappa/f)]\mathrm{e}^{-n_{\mathrm{A}}\kappa/f} \tag{4.12c}$$

where the function $E(x)$ is defined by

$$E(x) \equiv (1 - \mathrm{e}^{-x})/x \tag{4.13}$$

In deriving these equations, we have assumed that the m sites on an A-chain for B-molecules to attach are randomly chosen from the available f sites and have taken an average over a random selection of the attaching sites. For the type (1, 0) and (0, 1) our results reduce to those of the corresponding homopolymers.

From those three elements of the intracluster scattering functions, we can obtain the scattering functions of the mixture as follows:

$$S^\circ_{\mathrm{AA}} = n_{\mathrm{A}}\phi D(n_{\mathrm{A}}\kappa) \tag{4.14a}$$

$$S^\circ_{\mathrm{AB}} = \frac{n_{\mathrm{A}}(1 - \phi - n_{\mathrm{B}}y/\lambda)E(n_{\mathrm{B}}\kappa)}{fE(n_{\mathrm{A}}\kappa/f)}\{fD(n_{\mathrm{A}}\kappa) - D(n_{\mathrm{A}}\kappa/f) + E(n_{\mathrm{A}}\kappa)E(n_{\mathrm{A}}\kappa/f)\} \tag{4.14b}$$

$$S^\circ_{\mathrm{BB}} = n_{\mathrm{B}}(1 - \phi)D(n_{\mathrm{B}}\kappa) + \frac{n_{\mathrm{A}}(1 - \phi - n_{\mathrm{B}}y/\lambda)^2\, E(n_{\mathrm{B}}\kappa)^2}{f\phi E(n_{\mathrm{A}}\kappa/f)^2}\{fD(n_{\mathrm{A}}\kappa) - D(n_{\mathrm{A}}\kappa/f)\}\mathrm{e}^{-n_{\mathrm{A}}\kappa/f} \tag{4.14c}$$

V. Phase Diagrams

In order to derive the phase diagrams, we now examine the condition of the stability limit. For spontaneous formation of a microphase with a finite wavelength, we have the instability condition

$$S(q)^{-1} = 0 \tag{5.1}$$

From the RPA formula for the scattering function, this condition takes the form

$$G(q)/W(q) = 2\chi \tag{5.2}$$

On the other hand, the spinodal condition is given by

$$S(0)^{-1} = 0 \tag{5.3}$$

From the specific forms of the scattering functions, we find that this spinodal condition is explicitly given by

$$\frac{1}{\phi}\left[\frac{1}{n_{\mathrm{A}}} + \frac{(1 - n_{\mathrm{B}}y/\lambda)^2(1 + y)}{n_{\mathrm{B}}\phi(1 - \phi + n_{\mathrm{B}}y^2/\lambda)}\right] - 2\chi = 0 \tag{5.4}$$

We can readily confirm that this equation is equivalent to the divergence of the osmotic compressibility

$$(\partial\Delta\mu_{\mathrm{A}}/\partial\phi)_T = 0 \tag{5.5}$$

by using the formula (3.7) for the chemical potential of an A-chain.

The condition for a low concentration homogeneous phase with ϕ' to coexist with a high concentration homogeneous phase with ϕ'' (*binodal curve*) is given by the coupled equations:

$$\Delta\mu_{\mathrm{A}}(\phi',T) = \Delta\mu_{\mathrm{A}}(\phi'',T) \tag{5.6a}$$

$$\Delta\mu_{\mathrm{B}}(\phi',T) = \Delta\mu_{\mathrm{B}}(\phi'',T) \tag{5.6b}$$

If one of the phases lies in the microphase-separated region, its chemical potential must be replaced by that of the corresponding ordered state. The chemical potential of the microphase depends on the ordered structure, and its precise form is unknown for the associating polymers at this moment. Therefore, in what follows we show in the phase diagrams the binodal lines calculated on the basis of eqs 5.6, together with MST boundary and spinodal lines, to examine under what conditions the microphases remain thermodynamically stable. The parts of these binodal lines lying inside the microphase-separated region should shift to some extent if the free energy of ordering is correctly taken into account. Their positions therefore only suggest the possibility of the phase equilibrium around there.

For the numerical calculation we introduce familiar reduced temperature $\tau \equiv 1 - \Theta/T$ as the temperature measure. This is the dimensionless temperature deviation measured from the theta temperature Θ which satisfies the condition $\chi(\Theta) = {}^1/_2$. We then assume the conventional Shultz–Flory form

$$\chi(T) = 1/2 - \psi_1 \tau \tag{5.7}$$

for the χ -parameter, where ψ_1 is an entropy factor of order unity depending on the combination of the materials A and B. The association constant (3.20) can be rewritten as

$$\lambda(T) = \frac{(z-1)^2}{z} \exp(\Delta\, s_0/k_B) \exp(-\beta \Delta\epsilon) \tag{5.8}$$

where we have split the free enrgy Δf_0 of bonding into the entropy part Δs_0 and the energy part $\Delta\epsilon(<0)$. By using the reduced temperature τ, this association constant is transformed into

$$\lambda(T) = \lambda_0 \exp[\gamma(1 - \tau)] \tag{5.9}$$

with a constant prefactor

$$\lambda_0 = \frac{(z-1)^2}{z} \exp(\Delta\, s_0/k_B) \tag{5.10}$$

and the dimensionless binding energy

$$\gamma = \frac{-\Delta\epsilon}{k_B \Theta} \tag{5.11}$$

Thus, we have three material parameters: ψ_1, λ_0, and γ. In addition to these three, we must specify molecular parameters, *i.e.*, the number n_A and n_B on the primary molecules and the functionality f of an A-chain. Because the final architecture of the associated clusters can be designed by changing these parameters, phase behavior is most easily controlled by judiciously choosing them.

To specify the problem, we shall fix at $\psi_1 = 1.0$ and $n_A = 1000$ throughout the following calculation.

Parts a and b of Figure 2 compare the phase diagrams for two different binding energy parameters γ. The solid line shows the binodal, the broken line shows the MST, and the shaded areas show the unstable regions with the spinodal lines at their boundaries. The area with horizontal lines indicates a phase with microstructure. In Figure 2b, two segments of the binodal lines that lie inside the microphase region only indicate their existence near these positions, as remarked above.

The overall structure of the diagram is similar to that of A/B blends compatibilized by the addition of A•B block copolymers, but it differs in detail near the concentration that agrees with the molecular composition of the fully associated copolymers. We call this concentration *stoichiometric concentration* ϕ_{st} (vertical broken-dotted line). It is explicitly given by

$$\phi_{st} = n_A/(n_A + f n_B) \tag{5.12}$$

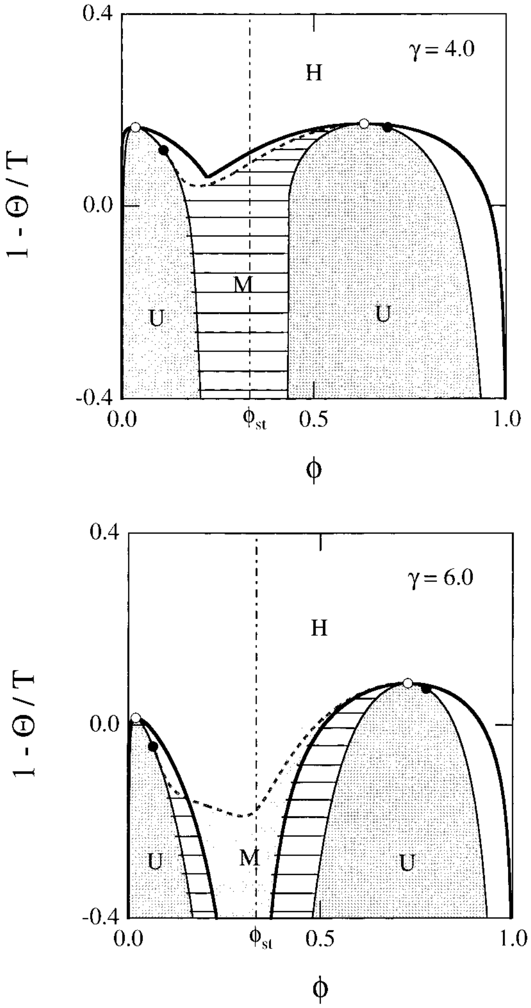

Figure 2. Phase diagrams on the temperature and concentration plane for (a) $\gamma = 4.0$ and (b) $\gamma = 6.0$. The binodal (solid line), the spinodals (borderline of the gray areas), microphase separation transition line (broken line), critical solution points (white circles), and Lifshitz points (black circles) are shown. The homogeneous mixture region, microphase region, and macroscopically unstable region are indicated by H, M, and U, respectively. Parameters are fixed at $n_A = 1000$, $f = 200$, $n_B = 10$, $\lambda_0 = 1.0$, and $\psi_1 = 1.0$. The concentration ϕ_{st} (vertical broken-dotted line) indicates the stoichiometric concentration.

Around this stoichiometric concentration, the miscibility of the mixture is sufficiently improved for the usual miscibility dome with an upper critical solution point on its top to split into two gaps, each having a critical point (white circle). The intersections (black circles) between MST and the spinodal lines are the points where the spatial periodicity of the microphase becomes infinitely long. They are called *Lifshitz points*.

As expected, the miscibility of the blend is improved with an increase of the association energy. For a weak binding energy, the microphase region is mostly included inside the metastable region between the binodal and the spinodal (Figure 2a). For a stronger binding energy, however, the two miscibility gaps are completely separated near the stoichiometric concentration, and a stable microphase appears in between (dark-shaded area in Figure 2b). This microphase differs from the conventional one formed by chemical block copolymers in that it is the result of molecular association between repulsively interacting polymers, and hence the entire phase is thermally controlled.

Figure 3 shows the inverse periodicity q^* as a function of the concentration along the MST line. The binding

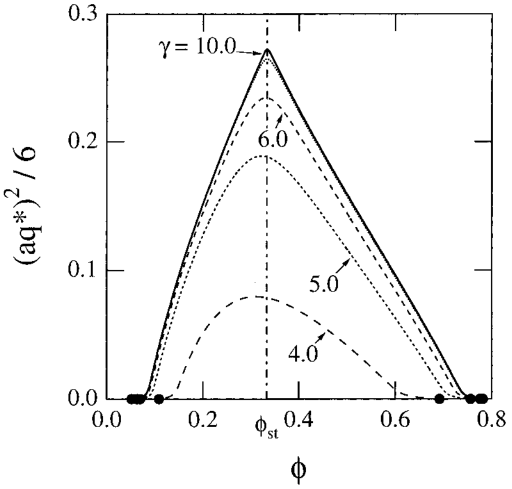

Figure 3. Dimensionless squared wave number q^* along the MST curve as a function of the polymer concentration. The binding energy γ relative to the thermal energy is changed from curve to curve. For a given γ the wave number takes a maximum value near the stoichiometric concentration. It increases with γ at all concentrations and approaches a triangular curve in the limit of infinite γ. Black circles show the Lifshitz points where periodic structure starts to appear.

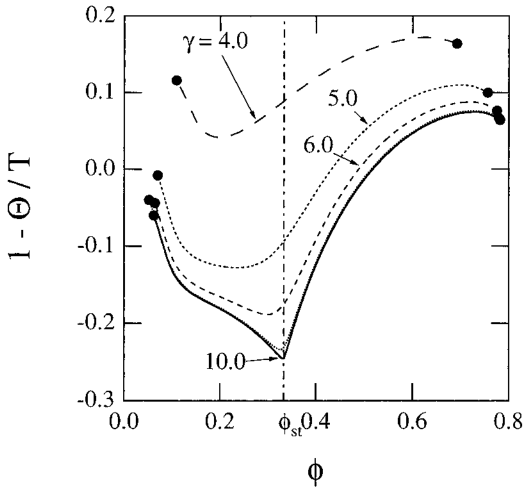

Figure 4. MST boundaries on the phase plane. The binding energy is changed from curve to curve. As γ is increased, the MST curve shifts to higer temperature; *i.e.*, the microphase formation becomes easier. For a given γ, the transition temperature takes the lowest value near the stoichiometric concentration. Black circles at the ends show the Lifshitz points.

energy γ is varied from curve to curve. At the stoichiometric concentration the periodicity of the microphase is smallest (q^* largest). Also, as the binding energy is increased, the periodicity is reduced. In the limit of the infinite binding energy $\gamma \to \infty$, the periodicity approaches the limiting value. Off the stoichiometric concentration, the excess unassociated chains swell the periodic structure formed by the saturated (1, *f*)-clusters and modify its periodicity. In Figure 4 we replot MST curves only on the phase plane with γ varied. These curves shift to a lower temperature region with an increase of the binding energy and approach the limiting curve. This limiting curve shows the MST by chemically connected comb block copolymers mixed with homopolymers of both components.

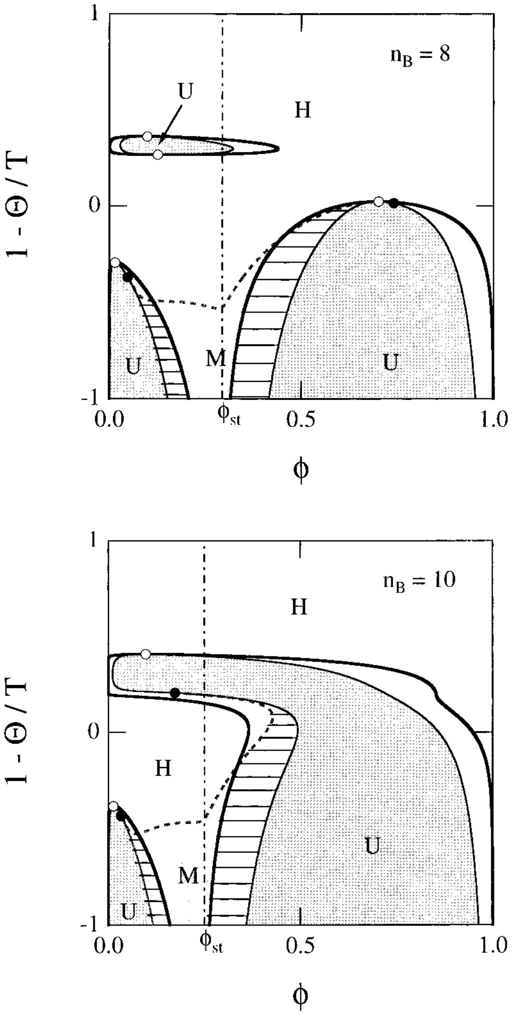

Figure 5. Phase diagrams with the length n_B of the side chain varied. Parameters are fixed at $n_A = 1000$, $f = 300$, $\lambda_0 = 0.002$, $\gamma = 10.6$, and $\psi_1 = 1.0$. (a) $n_B = 8$. For short side chains, a miscibility loop at high temperatures appears. (b) $n_B = 10$. It merges with the miscibility dome on the right as n_B increases, and a reentrant homogeneous phase appears near the Θ temperature.

Parts a and b of Figure 5 show the phase diagrams by varying the degree of polymerization n_B of the B-molecule. As shown in Figure 5a, for sufficiently small values of n_B, a miscibility loop appears at high temperatures in addition to the ordinary miscibility domes. In fact, in the limit of $n_B = 1$, our mixture can be regarded as a polymer solution in a solvent in which low molecular weight solvent molecules are attached to the polymer chains. If the solvent is water and the associative force is hydrogen bonding, this phenomenon is called *hydration*. Our preceding study of poly(ethylene oxide) in water[21] demonstrated that hydration is the main cause of the observed peculiar phase separation with miscibility loop at high temperatures in this solution. As the side chain becomes longer, the miscibility loop expands and eventually merges into the miscibility dome on the right, as shown in Figure 5b. A reentrant homogeneous phase appears in the intermediate temperature near the Θ temperature. The lower critical point on the bottom of the loop, together with the upper critical point on the top of the dome, forms a double critical point when the two gaps exactly come into contact. In both cases of the phase diagram, a microphase near the stoichiometric concentration can remain thermodynamically stable. As the degree of polymerization of the side chain is increased, the periodicity of the microdomains along the MST line becomes larger in the high concentration region, while it becomes smaller in the low concentration region.

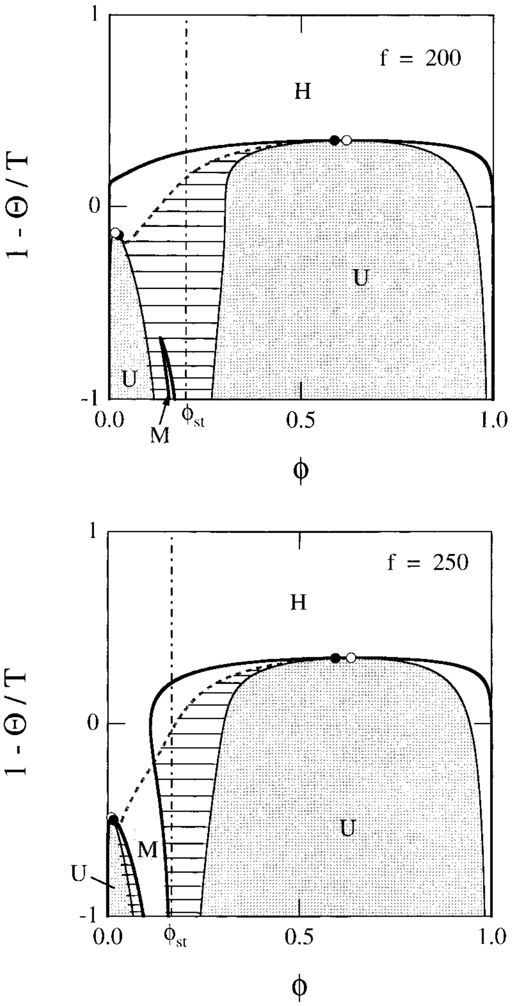

Figure 6. Phase diagrams with the functionality *f* of the main chain varied. Parameters are fixed at $n_A = 1000$, $n_B = 20$, $\lambda_0 = 1.0$, $\gamma = 5.0$, and $\psi_1 = 1.0$. (a) $f = 200$. A narrow reentrant microphase appears below the metastable region. (b) $f = 250$. A stable microphase can exist near the stoichiometric concentration between the two gaps.

Parts a and b of Figure 6 show how the phase behavior depends on the number of functional groups carried by A-chains. For $f = 200$, the two-phase region on the right hand side has a large metastable region extending to the extremely low concentration at intermediate temperature. This overhang of the metastable region overlaps with the two-phase region on the left. As a result, a narrow stable microphase indicated by the letter M appears at low temperatures as shown in Figure 6a. As the temperature is lowered from a sufficiently high one, the homogeneous liquid phase separates into two phases and again mixes into one phase with the microstructure in region M. Hence this may be called a reentrant homogeneous phase. For larger *f* (see Figure 6b), the block copolymers improve miscibility and the two-phase region completely separates into two domes, between which a stable microphase appears. Functionality can therefore be an efficient parameter for controlling the phase behavior.

VI. Conclusions and Discussion

We have derived the phase diagrams of associating polymer mixtures to examine how microphase separation transition is caused by association between the different chains. We aimed at studying the effect of the molecular architecture of the formed clusters in the limit of full association, paying special attention to the length and the number of side chains and the functionality of the main chain.

As the association energy increases, the periodicity q^{*-1} becomes smaller and approaches the limiting values at each concentration. In this limit the stoichiometric concentration is most important. The periodicity becomes the smallest at this concentration. We predict that, for a small association energy, the microdomains swell with penetrating free homopolymers in the entire concentration region. However, if the association energy is large enough (the infinite limit being a chemical bond), no unassociated homopolymers remain at the stoichiometric concentration; the microdomain is formed only by the fully associated copolymers.

We predict also that the miscibility is markedly reduced as the side chains become longer, even if the association force is strong. In such a situation, the repulsive interaction between the statistical units of A-chains and B-molecules dominates the attractive associative interaction. Thus, the side chains can not be too long to realize a stable microphase.

Recently, Ruokolainen *et al.*[17−20] reported that, in the mixture of poly(4-vinylpyridine) and 3-pentadecylphenol, the period of the lamellar microphase is inversely proportional to the number of side chains at a fixed temperature. In this mixture complexes (P4VP−(PDP)$_x$) are formed by hydrogen bonds and their spatial ordering drives the mixture into a lamellar structure. Their *x*, the fraction of surfactant molecules per pyridine group, corresponds to

$$x = fN_A/N_B = fn_A(1 - \phi)/n_B\phi$$

in our notation. Therefore, our result on q^* as a function of the functionality *f* may be compared with the experimental data, but calculations must be done not along the MST line but *under a fixed temperature*. The free energy in the ordered lamellar phase in associating polymers is required for this. However, at this moment, we are not aware of any general prescription that allows calculation of the ordered phase.

Our theoretical study also suggests that the periodicity of the microdomain structure is greatly influenced by the remaining free chains and, hence, by the concentration of the mixture. Measurement of the periodicity as a function of the concentration will greatly be helpful for understanding the microphases in associating polymers.

The realization of a stable microphase in associating polymer mixtures will require a balance in the combination of constituent molecules, in their degrees of polymerization, and in the functionality of constituent molecules. Studies of the phase diagrams provide a pathway to modeling the microphase structure by the modification of the molecular architecture.

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