

NOTE

Competition between the micellization and the liquid–liquid phase separation in amphiphilic block copolymer solutions

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We have formulated the mixing Gibbs energy density for the micelle phase of an amphiphilic block copolymer solution using mean-field lattice theory. We have found a transition between the micellization and the liquid–liquid phase separation in this solution by comparing the mixing Gibbs energy density for the micelle phase with that for the homogeneous phase.

Micellization is preferred over the liquid–liquid phase separation not only at a higher amphiphilicity of the block copolymer chain but also at a higher degree of polymerization of the copolymer.

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INTRODUCTION

Recently, thermosensitive block copolymers have attracted significant attention because they can construct and destroy micelles by changing the temperature and they are utilized in nano-carriers and nano-reactors. Many types of thermosensitive block copolymers have been synthesized, and their self-assembly behaviors have been investigated.^{1–13}

In previous studies,^{14–17} we have studied the self-assembly behavior of three different types of thermosensitive block copolymers, and found that the thermosensitive block copolymers did not necessarily form micelles, even under the amphiphilic condition of the block copolymers, but that a liquid–liquid phase separation took place instead. Although the liquid–liquid phase separation has seldom been reported for thermosensitive block copolymer solutions thus far, nanoparticles or aggregates of thermosensitive block copolymers reported to form in aqueous solutions may be colloidal droplets of the concentrated phase in the biphasic region. In fact, those nanoparticles or aggregates were often much larger than the size of the spherical micelle expected from the contour length of the block copolymer chain.^{3,8,9} Because aqueous solutions of thermosensitive block copolymers tend to form colloidal droplets of the concentrated phase in the biphasic region,^{14–16} it is rather difficult to distinguish the liquid–liquid phase separation from the micellization.

When thermosensitive block copolymers are utilized as nano-carriers and nano-reactors, it is important to clarify the conditions of the micellization and the liquid–liquid phase separation. Although some authors have theoretically examined the micellization in block copolymer solutions, they either assumed the solvent to be nonselective^{18,19} or strongly selective.²⁰ In this study, we examine the

competition between the micellization and the liquid–liquid phase separation in block copolymer solutions under weakly amphiphilic conditions, on the basis of the mean-field lattice theory using a simple spherical micelle model. Leibler *et al.*²¹ proposed a similar spherical micelle model, but they did not discuss the competition between the micellization and the liquid–liquid phase separation.

THEORY

Let us consider a solution of an amphiphilic diblock copolymer consisting of A-block (solvophilic) and B-block (solvophobic) chains of which degrees of polymerization are denoted as P_A and P_B . It is assumed that the A and B monomer units, as well as the solvent molecules S, occupy lattice sites with a common size of a . According to the Flory–Huggins theory,²² the mixing Gibbs energy per lattice site Δg_h of the homogeneous solution is given by

$$\frac{\Delta g_h}{k_B T} = \phi_S \ln \phi_S + \frac{\phi_P}{P_A + P_B} \ln \phi_P + \bar{\chi} \phi_S \phi_P \quad (1)$$

where $k_B T$ is the Boltzmann constant multiplied by the absolute temperature, ϕ_S and ϕ_P are the volume fractions of the solvent and copolymer, respectively, in the solution ($\phi_S = 1 - \phi_P$), x_A and x_B are the mole fractions of the A and B monomer unit in the copolymer chain [$x_A = 1 - x_B = P_A / (P_A + P_B)$] and $\bar{\chi}$ is the average interaction parameter between the block copolymer chain and the solvent, defined by ref. 18

$$\bar{\chi} \equiv x_A \chi_{AS} + x_B \chi_{BS} - x_A x_B \chi_{AB} \quad (2)$$

Here, χ_{AS} , χ_{BS} and χ_{AB} are the interaction parameters between the A

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monomer unit and solvent, between the B monomer unit and solvent, and between the A and B monomer units, respectively.

If the solvent is a selective solvent ($\chi_{BS} > \chi_{AS} \approx 0$), the block copolymer may form a micelle. We use a simple model for the spherical micellar phase, of which radial concentration profiles of the A and B monomer units are given by

$$\phi_A = \begin{cases} 0, & 0 \leq r < R_{\text{core}} \\ \phi_{A,s}, & R_{\text{core}} \leq r < R \\ 0, & R \leq r \end{cases} \quad \phi_B = \begin{cases} \phi_{B,c}, & 0 \leq r < R_{\text{core}} \\ 0, & R_{\text{core}} \leq r < R \\ 0, & R \leq r \end{cases} \quad (3)$$

(cf. Figure 1). Here, R_{core} and R are the radii of the micelle core and the whole micelle, respectively, and the solvent volume fraction is given by $\phi_S = 1 - \phi_A - \phi_B$ at each radial point r . Furthermore, we simply assume that R_{core} and R are given parameters calculated by

$$R_{\text{core}} = aP_B^\alpha, \quad R - R_{\text{core}} = aP_A^\alpha \quad (4)$$

with an exponent α , which differs from the micellar model of Leibler *et al.*,²¹ where R_{core} and R are treated as variables in the Gibbs energy function. Actually, $\phi_{A,s}$ is not a constant but a decreasing function of r , and α in the core and coronal regions may be different, but we neglect them in the following formulation.

The average volume fraction ϕ_P of the copolymer in the micelle phase is calculated by

$$\phi_P = \frac{3a^3(P_A + P_B)N_P}{4\pi R^3} \quad (5)$$

and using R_{core} and R given by equation (4), the volume fractions $\phi_{A,s}$ and $\phi_{B,c}$ are related to ϕ_P by

$$\begin{aligned} \phi_{A,s} &= \frac{R^3}{R^3 - R_{\text{core}}^3} x_A \phi_P, \\ \phi_{B,c} &= \frac{R^3}{R_{\text{core}}^3} x_B \phi_P = \frac{(x_A^\alpha + x_B^\alpha)^3}{x_B^{3\alpha-1}} \phi_P \end{aligned} \quad (6)$$

The second equation for $\phi_{B,c}$ in equation (6) shows that ϕ_P must be equal to or less than $x_B^{3\alpha-1}/(x_A^\alpha + x_B^\alpha)^3$ because $\phi_{B,c}$ does not exceed unity.

We extended the Flory–Huggins theory to the micelle phase to formulate the mixing Gibbs energy density per lattice site Δg_m of the micelle phase, which consists of the mixing entropy ΔS_m , the mixing enthalpy ΔH_m and the interfacial Gibbs energy $4\pi R_{\text{core}}^2 \gamma$ with the interfacial tension γ between the core and shell regions of the

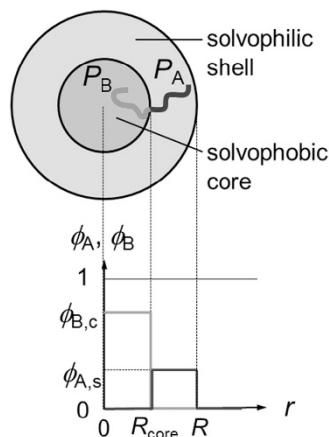


Figure 1 Radial distribution functions of A and B monomer unit concentrations in the micelle phase. A full color version of this figure is available at *Polymer Journal* online.

micelle. It should be noted that we regarded a single micelle as a thermodynamic phase, and our micelle phase should be distinguished from the micellar phase of Leibler *et al.*,²¹ which comprises many micelles. Strictly speaking, micellization is not a discontinuous phase transition when it is described by the law of mass action. However, if the aggregation number of the micelle is large enough, the micellization takes place so abruptly at the critical micelle concentration that it may be approximated as a type of phase transition.

The formulation method of Δg_m is described in the Supplementary Information. The final result is written as

$$\begin{aligned} \frac{\Delta g_m}{k_B T} &= \frac{-T\Delta S_m + \Delta H_m + 4\pi R_{\text{core}}^2 \gamma / 4\pi R^3}{k_B T} \\ &= \frac{\phi_P}{P_A + P_B} (\ln \kappa + \ln \phi_P) + \frac{R^3 - R_{\text{core}}^3}{R^3} (1 - \phi_{A,s}) \ln(1 - \phi_{A,s}) \\ &\quad + \frac{R_{\text{core}}^3}{R^3} (1 - \phi_{B,c}) \ln(1 - \phi_{B,c}) \\ &\quad + [x_A (1 - \phi_{A,s}) \chi_{AS} + x_B (1 - \phi_{B,c}) \chi_{BS} - x_A x_B \chi_{AB}] \phi_P \\ &\quad + \frac{3a R_{\text{core}}^2}{R^3} \frac{a^2 \gamma}{k_B T} \end{aligned} \quad (7)$$

where κ is defined by equation S11, including the conformational and translational entropy losses of the copolymer chains at the formation of the micelle, and $a^2 \gamma / k_B T$ is calculated by equation S15 with equation S16. In equation (7), the second and third lines come from ΔS_m , the fourth line from ΔH_m and the last line from the interfacial Gibbs energy.

RESULTS AND DISCUSSION

Using the equations of the mixing Gibbs energy densities Δg_h and Δg_m given in the above section, we discuss the phase behavior of the block copolymer solution. Let us first consider Δg_h , shown in Figure 2a. We have chosen parameters such that $P_A = P_B = 100$ and $\bar{\chi} = 0.8$. When $\bar{\chi}$ exceeds the critical value $\bar{\chi}_c = [1 + (P_A + P_B)^{1/2}]^2 / 2(P_A + P_B)$,²² Δg_h takes a W-shaped curve. One can then draw a common tangent, as indicated by the thin line in panel a, although the left part of the letter W is difficult to see. The copolymer volume fractions at the two points of contact of the common tangent (points D and C in panel a) are denoted as $\phi_{P,d}$ and $\phi_{P,c}$. If the copolymer concentration ϕ_P is between $\phi_{P,d}$ and $\phi_{P,c}$, the solution undergoes the phase separation into the dilute phase with $\phi_{P,d}$ and the concentrated phase with $\phi_{P,c}$ because the mixing Gibbs energy density of the phase-separating solution (say, indicated by the point F in panel a) is lower than that of the homogeneous solution (indicated by the point E).

Next, we consider the ϕ_P dependence of $\Delta g_m / k_B T$. In what follows, we assume α to be 0.5 (the value in the weak segregation limit).²³ In Figure 2b, the (black) solid curve and thin line are the same as those in panel a, and (red) the dotted, dashed and dot–dash curves indicate $\Delta g_m / k_B T$ values at three different pairs of χ_{AS} and χ_{BS} , where χ_{AB} is fixed at 0. (For all three of the pairs, $\bar{\chi}$ calculated by equation (2) is equal to 0.8, and the curves for $\Delta g_h / k_B T$ are common.) It is noted that the curves for $\Delta g_m / k_B T$ are restricted in the range of $0 \leq \phi_P \leq 0.25$, as mentioned above (cf. equation 6).

At $\chi_{BS} = 1.0$, the dotted curve is above the solid curve for $\Delta g_h / k_B T$, so that the micelle phase is unstable over the entire ϕ_P region. On the other hand, at $\chi_{BS} = 1.3$, the dot–dash curve is below the solid curve at $\phi_P > 0.07$, and one can draw a common tangent to the solid and dot–dash curves, as indicated by the lower (red) thin line. The copolymer volume fractions at the two points of contact of the common tangent (the points D' and M in panel b) are denoted as $\phi'_{P,d}$ and $\phi_{P,m}$. If the copolymer concentration ϕ_P is between $\phi'_{P,d}$ and $\phi_{P,m}$, the copolymer solution undergoes micellization, where the micelle phase with an average concentration $\phi_{P,m}$ coexists with the

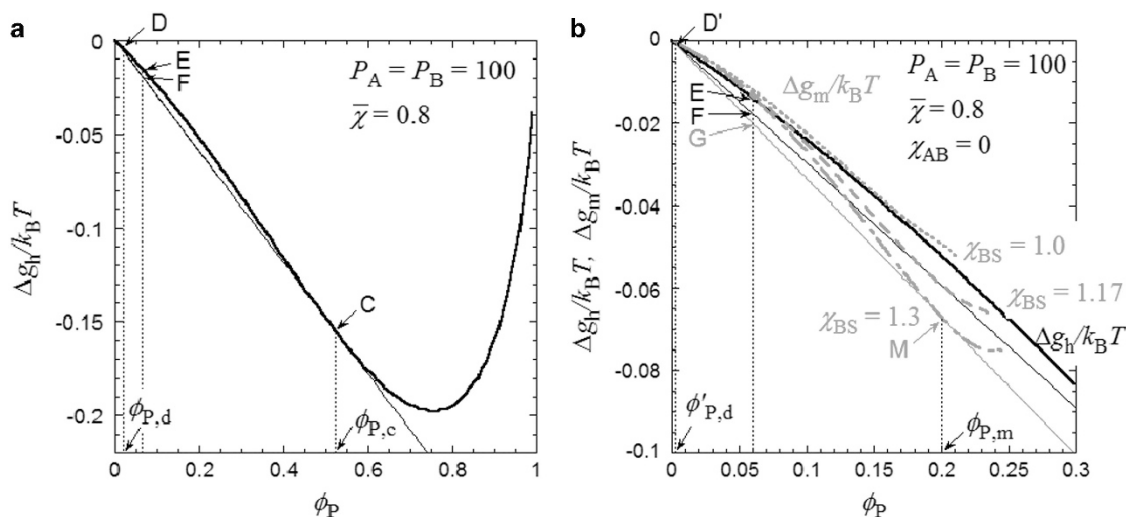


Figure 2 (a, b) Concentration dependences of Δg_l and Δg_m for block copolymer solutions with $P_A = P_B = 100$ and $\bar{\chi} = 0.8$. In **b**, the dotted, dashed and dot-dash curves indicate $\Delta g_m/k_B T$ at $\chi_{BS} = 1.0$ ($\chi_{AS} = 0.6$), $\chi_{BS} = 1.17$ ($\chi_{AS} = 0.43$), $\chi_{BS} = 1.3$ ($\chi_{AS} = 0.3$), respectively, at $\alpha = 0.5$ and $\chi_{AB} = 0$. A full color version of this figure is available at *Polymer Journal* online.

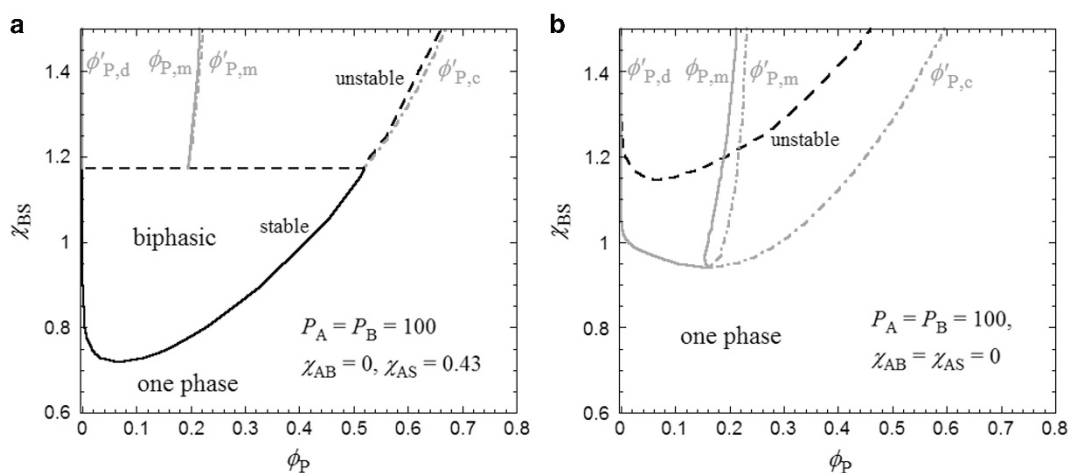


Figure 3 Phase diagram for the block copolymer solution with $P_A = P_B = 100$, $\chi_{AB} = 0$ and $\chi_{AS} = 0.43$ (a) and $\chi_{AS} = 0$ (b), at changing χ_{BS} . A full color version of this figure is available at *Polymer Journal* online.

dilute phase with $\phi'_{P,d}$. For the solution with $\phi_P = 0.06$, for example, this micellization reduces the mixing Gibbs energy density from the points E to G in panel b. This point G is lower than the mixing Gibbs energy density at the liquid–liquid phase separation indicated by the point F in panel b (or in panel a), and the micellization is more stable than the liquid–liquid phase separation. The crossover from the liquid–liquid phase separation to the micellization takes place at $\chi_{BS} = 1.17$, where the dashed curve touches the common tangent line in panel a. We may expect the simultaneous occurrence of the liquid–liquid phase separation and the micellization at $\chi_{BS} = 1.17$.

Although not shown in Figure 2b, we can draw one more common tangent to the solid and dot-dash curves in the higher ϕ_P region, corresponding to the coexistence of the micelle phase and a homogeneous concentrated phase. For example, at $\chi_{BS} = 1.3$ ($\chi_{AS} = 0.3$), the micelle phase with $\phi_{P,m} = 0.214$ coexists with the concentrated phase with $\phi'_{P,c} = 0.56$, if the copolymer concentration is between 0.214 and 0.56.

Figure 3a shows the phase diagram, drawn using the method explained above, for the block copolymer solution with $P_A = P_B = 100$, $\chi_{AS} = 0.43$, $\chi_{AB} = 0$, at changing χ_{BS} . At $\chi_{BS} < 0.72$ ($\bar{\chi} < \bar{\chi}_c$), the single-phase homogeneous solution is thermodynamically stable over the whole ϕ_P range, but at $0.72 < \chi_{BS} < 1.17$, the liquid–liquid phase separation is more stable at ϕ_P in the biphasic region. At $\chi_{BS} > 1.17$, the micellization becomes more stable than the liquid–liquid phase separation. As mentioned above, the crossover from the liquid–liquid phase separation to the micellization takes place at $\chi_{BS} = 1.17$ for this copolymer solution.

When χ_{AS} is reduced to zero (or the solvent is athermal to the A-block chain), the micellization region is expanded, and the region of the stable liquid–liquid phase separation disappears, as shown in Figure 3b. We can say that the micellization is preferred over the liquid–liquid phase separation after increasing the solvophilicity of the A-block chain or increasing the amphiphilicity of the block copolymer, which is consistent with the ionic strength

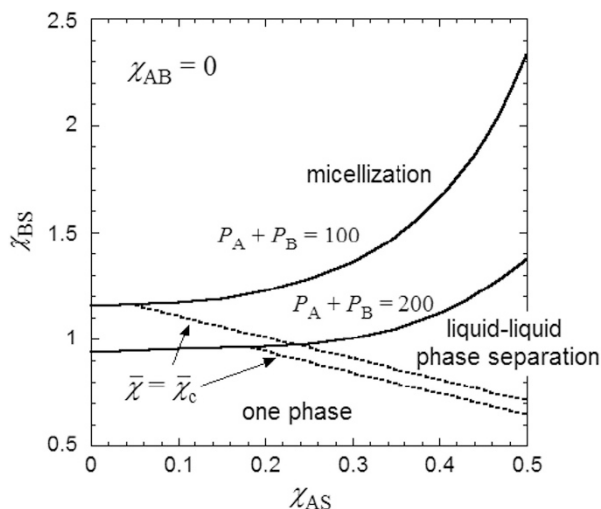


Figure 4 χ_{AS} dependence of the crossover χ_{BS} on the block copolymer solution with $P_A = P_B = 100$ and 50 at $\chi_{AB} = 0$. The region between the solid and dotted lines denotes the liquid–liquid phase separation; the region above the solid line denotes the micellization.

dependence of the phase diagram for a polyionic complex micellar system.²⁴

In both panels a and b of Figure 3, the micelle phase coexists with the dilute phase at $\phi'_{P,d} < \phi_P < \phi_{P,m}$ and with the homogeneous concentrated phase at $\phi'_{P,m} < \phi_P < \phi'_{P,c}$. In the narrow gap of ϕ_P between $\phi_{P,m}$ and $\phi'_{P,m}$, we may expect a single micelle-phase region where the average concentration of the whole solution is identical with the average concentration of the micelle. In such a concentrated micellar solution, micelles may form a lattice, but the present theory cannot address such a lattice ordering because we do not consider the intermicellar interaction in the theory.

We can calculate the aggregation number m_P of the micelle from $\phi_{P,m}$ (or $\phi'_{P,m}$) by

$$m_P = \frac{4\pi(P_A^\alpha + P_B^\alpha)^3}{3(P_A + P_B)} \phi_{P,m} \quad \text{or} \quad \frac{4\pi(P_A^\alpha + P_B^\alpha)^3}{3(P_A + P_B)} \phi'_{P,m} \quad (8)$$

In Figure 3a, $m_P = 32.5$ at $\chi_{BS} = 1.17$, and slightly increases with increasing χ_{BS} . The value of m_P increases also with increasing P_A and P_B .

The crossover χ_{BS} from the liquid–liquid phase separation to the micellization is 1.17 in Figure 3a. This crossover χ_{BS} is an increasing function of χ_{AS} , as shown in Figure 4, where the dotted line indicates the condition that $\bar{\chi}$ takes the critical value $\bar{\chi}_c$. This dependence means that the micellization requires the high amphiphilicity of the block copolymer, that is, a large difference between χ_{BS} and χ_{AS} . Furthermore, Figure 4 also shows the crossover χ_{BS} at $P_A = P_B = 50$. The micellization requires higher amphiphilicity for a lower degree of polymerization, which is consistent with experimental results reported for some thermosensitive block copolymer solutions.³

Fredrickson and Leibler¹⁹ demonstrated that a microphase transition occurs in a block copolymer dissolved in a neutral solvent at $\phi_P(P_A + P_B)\chi_{AB} > 10.495$ at $x_B = 0.5$. Because we do not consider the intermicellar interaction, we cannot address the microphase transition in our theory. Thus, the above calculation of the phase diagram was made by choosing $\chi_{AB} = 0$. However, at least for the copolymer solution with $\chi_{AS} = 0$, the intermicellar interaction (or the interaction among coronal chains) may not stabilize the microphase separating

solution, so we may discuss the competition between the micellization and liquid–liquid phase separation even at finite χ_{AB} . The present theory predicted that the incompatibility of the A- and B-block chains enhances the micellization, although not shown. The same prediction was reported by Hong and Noolandi¹⁸ for the block copolymer in a nonselective solvent.

Leibler *et al.*²¹ calculated the critical micelle concentration of a block copolymer dissolved in a melt of the homopolymer of block chain A, where $\chi_{AS} = 0$ and $\chi_{BS} = \chi_{AB}$. The present theory showed that the liquid–liquid phase separation does not occur before the micellization under the same conditions ($\chi_{AS} = 0$ and $\chi_{BS} = \chi_{AB}$) when the degree of polymerization of the homopolymer = 1, just like panel b of Figure 3 where $\chi_{BS} \neq \chi_{AB} = 0$. The left-hand side of the solid curve in Figure 3b indicates the χ_{BS} dependence of the critical micelle concentration, which qualitatively agrees with the result of Leibler *et al.*²¹

CONCLUSIONS

We have investigated the competition between the micellization and the liquid–liquid phase separation in a diblock copolymer solution under weakly amphiphilic conditions using mean-field lattice theory. Formulating the mixing Gibbs energy density of the micelle phase and comparing it with the mixing Gibbs energy density of the homogeneous phase, we have found a phase diagram containing biphasic regions of the two homogeneous liquid phases and of the micelle and homogeneous phases. The biphasic region of the micelle and the homogeneous phases enlarges after increasing not only the amphiphilicity of the block copolymer chain but also the degree of polymerization of the copolymer and the incompatibility between the two blocks.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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