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Phase Behavior of a Mixture of Poly(oxyethylene)−Poly(dimethylsiloxane) Copolymer and Nonionic Surfactant in Water

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ABSTRACT: The A−B-type silicone copolymer, $Me_3SiO-(Me_2SiO)_{23}-Me_2SiCH_2CH_2CH_2-O-(CH_2CH_2O)_{51.6}H$ ($Si_{25}C_3EO_{51.6}$), forms only lamellar liquid crystal (L_α) in water over a whole range of concentrations. Rich phase behavior was observed upon addition of conventional nonionic surfactant, $C_{12}EO_5$, whose molecular weight is ∼1/10 of $Si_{25}C_3EO_{51.6}$. For both amphiphiles, f, the volume fraction of hydrophilic part in amphiphile, is the same, and $f = 0.5$. $C_{12}EO_5$ alone forms aqueous micellar solution (W_m), normal hexagonal (H_1), bicontinuous cubic (V_1), lamellar (L_α), and reverse micellar solution (O_m) phases in water with increasing surfactant concentration. On the other hand, W_m, discontinuous micellar cubic (I_1), L_α, reverse bicontinuous cubic (V_2), and reverse hexagonal (H_2) phases are successively formed in water at a 70/30 weight ratio of $Si_{25}C_3EO_{51.6}/C_{12}EO_5$. A reduction in the effective cross-sectional area per amphiphile at hydrophobic surface (a_S) takes place upon addition of $C_{12}EO_5$ in the mixed system. A small amphiphile, $C_{12}EO_5$, is dissolved in the copolymer L_α phase, and a relatively small amount of surfactant occupies a rather large area at an interface of aggregates, although the a_S for $Si_{25}C_3EO_{51.6}$ in the L_α phase is more than double that for $C_{12}EO_5$. Hence, the surfactant mainly dictates the morphology or amphiphile-layer curvature in the mixed system. The copolymer is practically insoluble in the L_α phase of $C_{12}EO_5$ due to the packing constraint. Hence, two L_α phases coexist in a surfactant-rich region at $W_S = 0.75$, where W_S is the weight fraction of total amphiphile in the system. On the other hand, the copolymer L_α phase changes to the I_1 phase with increasing the surfactant mixing fraction at $W_S = 0.55$. The spherical micelle in the I_1 phase has a double-layer structure in which the surface is covered by surfactant and the core is pure poly(dimethylsiloxane) chain.

I. Introduction

A−B-type block copolymer forms a variety of self-organized structures in solution or melted state depending on the A/B ratio. Since poly(dimethylsiloxane) chain is very flexible and is in a liquid state at room temperature, poly(oxyethylene)−poly(dimethylsiloxane) copolymers form various liquid crystals in water or oil.[1−6] On the other hand, conventional nonionic surfactants such as poly(oxyethylene) dodecyl ethers ($C_{12}EO_n$) also form various liquid crystals such as lamellar, hexagonal, and cubic phases.[7] Although mixtures of surfactants and polymers were extensively investigated,[8] there have not been a number of studies on the mixed systems of nonionic surfactants and nonionic amphiphilic copolymers.[9,10]

Among the various self-assemblies of amphiphilic molecules, lamellar liquid crystal (L_α) is located in the middle of the liquid-crystal sequence because the average amphiphilic layer curvature is zero. It is known that the volume fraction of A in A−B copolymer, f, and $N\chi$ dictate the morphology of self-organized structures in a copolymer melt, where χ is the Flory−Huggins segment−segment interaction parameter and N is the polymerization degree.[11] f determines the curvature of the amphiphilic layer, and $N\chi$ is related to the segregation tendency of A and B chains.

In a nonionic surfactant system, the volume fraction of the hydrophilic part in surfactant, which is the same as f, is related to classical Griffin's HLB number to evaluate hydrophile−lipophile balance of surfactant.[12,13] Even in water, the HLB number or f dictates the surfactant layer curvature in the case of poly(oxyethylene)-type nonionic surfactants.[3,13] The segregation tendency between hydrophilic and lipophilic chains increases upon addition of water, and it affects the surfactant layer curvature. For example, the both hydrophilic and lipophilic volumes of $C_{12}EO_5$ are almost the same, and the L_α phase is a dominant liquid crystal formed in water.[14,15] But, it also forms an aqueous micellar solution phase at low surfactant concentration, whereas the reverse micellar solution phase is produced at high concentration. Hence, if copolymer and surfactant are the balanced amphiphiles, we could elucidate the effect of molecular size and added water on the self-organized structures of mixed amphiphile in water. In other words, we would know the effect of mixing amphiphiles of different $N\chi$ on the phase behavior in water at constant f.

In this context, we choose $Me_3SiO-(Me_2SiO)_{23}-Me_2SiCH_2CH_2CH_2-O-(CH_2CH_2O)_{51.6}H$ ($Si_{25}C_3EO_{51.6}$) as a copolymer and $C_{12}H_{25}(CH_2CH_2O)_5OH$ ($C_{12}EO_5$) as a nonionic surfactant, and the phase behavior of their mixture in water was investigated by phase study and small-angle X-ray scattering (SAXS) measurement. Both molecules are balanced amphiphiles because the volume of hydrophilic EO part is more or less similar

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to that of hydrophobic part. The hydrophobic parts of the amphiphiles are different, but poly(dimethylsiloxane) and hydrocarbon are miscible if both chains are not extremely long.

II. Experimental Section

A. Materials. $Me_3SiO-(Me_2SiO)_{23}-Me_2SiCH_2CH_2CH_2-O-(CH_2CH_2O)_{51.6}H$ was obtained from Dow Corning-Toray Co Ltd., Japan, where Me is a methyl group attached to Si atom. It is abbreviated as $Si_{25}C_3EO_{51.6}$ and is regarded as a copolymer in the present paper, although it can be also considered as a silicone surfactant.[3,16] Its purity is greater than 94.6%. The polydispersity index, $\bar{M}_w/\bar{M}_n$, for the poly(dimethylsiloxane) chain is 1.20, and that for the poly(oxyethylene) chain is 1.13, which were confirmed by gel permeation chromatography. The main impurity is unreacted poly(dimethylsiloxane), which was removed by washing the copolymer with hexane at least three times. Homogeneous penta(oxyethylene) dodecyl ether ($C_{12}EO_5$) was obtained from Nikko Chemicals Co. The molar volumes of copolymer and surfactant are 3996 and 418 cm^3 mol^{-1}, respectively. The volume of poly(oxyethylene) part is 2011 cm^3 mol^{-1} for $Si_{25}C_3EO_{51.6}$ and 203 cm^3 mol^{-1} for $C_{12}EO_5$. Hence, the volume fraction of the EO part in total amphiphile, f, is almost 0.5 for both amphiphiles, and the molecular size of the silicone copolymer is almost 10 times bigger than the nonionic surfactant.

B. Determination of Phase Boundary. Various amounts of water and surfactant were weighed in ampules and sealed. These ampules kept in a thermostat were well shaken and left at constant temperature. Homogeneity was attained using a vortex mixer and repeated centrifugation through the narrow constriction of the sample tubes. Phase equilibria were determined by visual observation of the samples in normal light and also observed between crossed plorizers for anisotropy. The sample composition is given by the overall weight fraction of the amphiphile (or copolymer/surfactant mixture) in water $W_S = (w_1 + w_2)/(w_1 + w_2 + w_W)$, and the weight fraction of the surfactant in the surfactant/copolymer mixture $W_2 = w_2/(w_1 + w_2)$. The types of liquid crystals were identified by means of a polarized optical microscope and small-angle X-ray scattering.

C. Small-Angle X-ray Scattering (SAXS). Interlayer spacing of liquid crystal was measured using SAXS, performed on a small-angle scattering goniometer with an 18 kW Rigaku Denki rotating anode goniometer (Rint-2500) at about 25 °C. The samples of liquid crystals were lapped by plastic films for the measurement (Mylar seal method). Since the critical micelle concentration or monomer solubility of both molecules are extremely low and water enhances the segregation tendency of hydrophilic and hydrophobic parts of amphiphiles, we assume that all the amphiphilic molecules are located at an A−B interface in aggregate.

D. Calculation of the Volume Fraction of Lipophilic Part of Amphiphiles. The volume fraction of lipophilic part of amphiphile (surfactant or copolymer) was calculated by using the following equation:

$$\phi_L = \frac{V_L}{V_S + \dfrac{M_S}{\rho_W}\dfrac{1 - W_S}{W_S}} \qquad (1)$$

where V_S and V_L are the molar volumes of amphiphile and its lipophilic moiety. ρ_W is the density of water, M_S is the molecular weight of amphiphile, and W_S is the weight fraction of amphiphile in the water−amphiphile system. In the calculation of mixed amphiphile system, we assumed the following equation

$$\bar{V}_S \text{ or } \bar{V}_L \text{ or } \bar{M}_S = x_1 Y_1 + x_2 Y_2 \qquad (2)$$

where x_1 and x_2 are mole fractions and Y_1 and Y_2 are extensive properties of copolymer and surfactant, respectively. The values of V_L are 215 cm^3/mol or 0.357 nm^3/molecule for C_{12}[17] and 1985 cm^3/mol or 3.29 nm^3/molecule for $Si_{25}C_3$.[3] We assume that spherical micelles are packed in a cubic array in the I_1 phase, infinitely long rod micelles are packed in a hexagonal array in the H_2 phase, and infinitely wide bilayers are stacked in a parallel way in the L_α phase. It is also assumed that the poly(oxyethylene) chains or water molecules do not penetrate into the hydrophobic part of aggregate. According to geometrical relations, the following equations hold for the interlayer spacing, d, and the volume fraction of lipophilic part of amphiphile, ϕ_L, for each liquid crystal

$$\text{for the } H_2 \text{ phase} \qquad d = (2\sqrt{3}\pi)^{1/2}\frac{v_L}{a_S}\frac{(1-\phi_L)^{1/2}}{\phi_L} \qquad (3)$$

$$\text{for the } L_\alpha \text{ phase} \qquad d = \frac{2v_L}{a_S}\frac{1}{\phi_L} \qquad (4)$$

$$\text{for the } I_1 \text{ phase} \qquad d = (36\pi)^{1/3}\frac{{n_m}^{1/3}}{\sqrt{h^2 + k^2 + l^2}}\frac{v_L}{a_S}\left(\frac{1}{\phi_L}\right)^{1/3} \qquad (5)$$

where a_S and v_L are the effective cross sectional area and the volume of lipophilic part per amphiphile, respectively. n_m is the number of micelles in a unit cell. h, k, and l are the Miller indices. Since d values are obtained from the most intense diffraction peak $hkl = (111)$, $h^2 + k^2 + l^2$ is 3, and $n_m = 4$, for a normal face-centered-cubic structure.[18]

III. Results

A. Phase Behavior of Each Amphiphile in Water. $C_{12}EO_5$ forms an aqueous micellar solution phase in water in a dilute region,[14,15,19] in which rod micelles exist at room temperature.[20,21] With increasing surfactant concentration, normal hexagonal liquid crystal (H_1) is produced. The maximum temperature of the H_1 phase is around 20 °C. The H_1 phase is successively changed to lamellar liquid crystal (L_α) via a narrow bicontinuous cubic phase (V_1) around 60 wt % of $C_{12}EO_5$. The L_α phase is stable up to 80 °C and is a dominant phase in the binary water−$C_{12}EO_5$ system. Finally, the L_α phase is changed to surfactant liquid or reverse micellar solution phase (O_m) above 90 wt % of surfactant. Hence, with decreasing the water content, the surfactant layer curvature is gradually changed from positive to negative, where the positive curvature means the surfactant layer is convex toward water in aggregates.

In a binary water−$Si_{25}C_3EO_{51.6}$ system, the L_α phase is only one liquid crystal as is shown in Figure 1. Since poly(dimethylsiloxane) chain is in a liquid state even at low temperature, the melting temperature of the copolymer solid is mainly related to the melting temperature of the poly(oxyethylene) (EO) chain. $Si_{25}C_3EO_{51.6}$ forms an L_α phase even at 100% above the melting temperature. The melting temperature of the copolymer solid is rapidly decreased with increasing water content due to the hydration of EO chain. In the dilute region, the L_α phase coexists with excess water phase (W). Different from the water−$C_{12}EO_5$ system, the copolymer layer curvature is not changed over a whole range of composition in the water−$Si_{25}C_3EO_{51.6}$ system, although the hydrophilic/hydrophobic volume ratios of both amphiphiles are almost unity. In a short-chain $C_{12}EO_5$ system, the segregation tendency of EO chain and hydrocarbon chain increases upon addition of water, and the repulsion between the EO chains also increases with increasing its hydration. As a result, the surfactant layer curvature becomes positive with increasing water content. Although the same effect can be expected in the copolymer system, the layer curva-

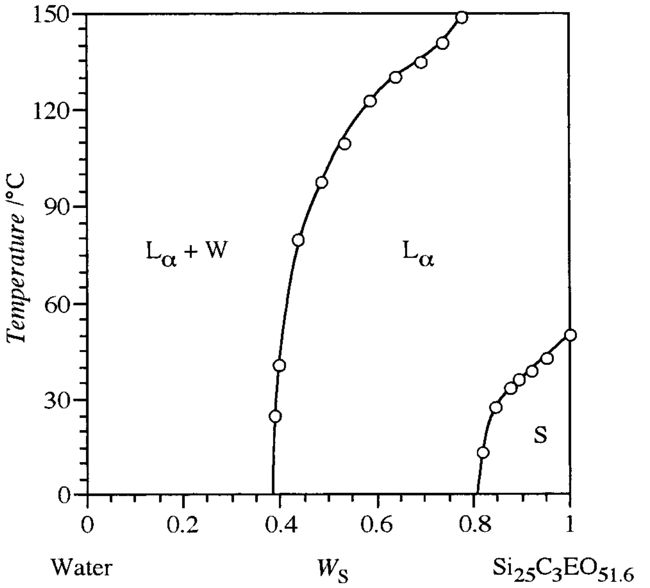


Figure 1. Phase diagram of the binary water−$Si_{25}C_3EO_{51.6}$ system as a function of weight fraction of copolymer. L_α and W indicate lamellar and excess water phases, respectively. S is a solid-present region.

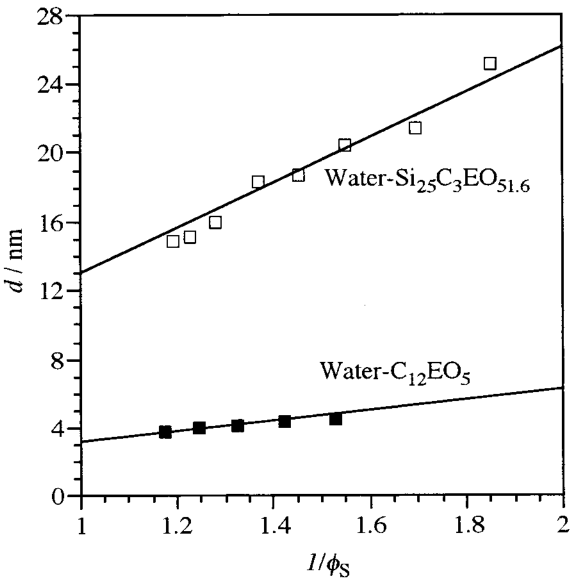


Figure 2. Change in interlayer spacing (*d*) of the lamellar phase as a function of $1/\phi_S$ in the binary water−$Si_{25}C_3EO_{51.6}$ (□) and water−$C_{12}EO_5$ (■) systems. ϕ_S = the volume fraction of amphiphile (surfactant or copolymer) in the system.

ture becomes flat because the lipophilic chain is too long to be compressed in a cone shape in the aggregate with a positive curvature.

We measured the interlayer spacing, *d*, of the L_α phase by SAXS measurement. The results are plotted against the reciprocal of the volume fraction of amphiphile, ϕ_S, in Figure 2. In the both systems, the linear relationship between *d* and $1/\phi_S$ holds, and the bilayer is just swollen by water, although *d* for both systems are very different. We obtained the *d* values for 100% amphiphiles by extrapolating the lines in Figure 2. The effective cross-sectional area per amphiphile, a_S, was calculated by eq 4 using these *d* values; 1.02 nm^2 for $Si_{25}C_3EO_{51.6}$ and 0.42 nm^2 for $C_{12}EO_5$. The half-thickness of the hydrophobic part in the L_α phase is 3.22 nm for $Si_{25}C_3EO_{51.6}$ and 0.85 nm for $C_{12}EO_5$. Although a_S remains almost constant, the hydrophobic half-thickness (d_L) is slightly suppressed upon addition of water. The half-thickness of copolymer is about 4 times bigger than that for the surfactant, although the molecular sizes are 10 times different, because the a_S for $Si_{25}C_3EO_{51.6}$ is almost 2.5 times larger than that for $C_{12}EO_5$. The effective cross-sectional area, a_S, is determined by the balance of the contraction force due to interfacial tension at A−B interface and the repulsion due to the entropy loss arising from the packing of each chain in a particular restricted volume of the aggregates. Since both hydrophilic and hydrophobic parts of $Si_{25}C_3EO_{51.6}$ are very long, the entropy loss is very large when they are completely extended or stretched.[22] Due to this effect, the a_S increases with increasing copolymer chains even if *f* is constant. Note that a short-chain silicone copolymer (or surfactant) occupying the cross-sectional area is similar to that of a conventional hydrocarbon surfactant.[2]

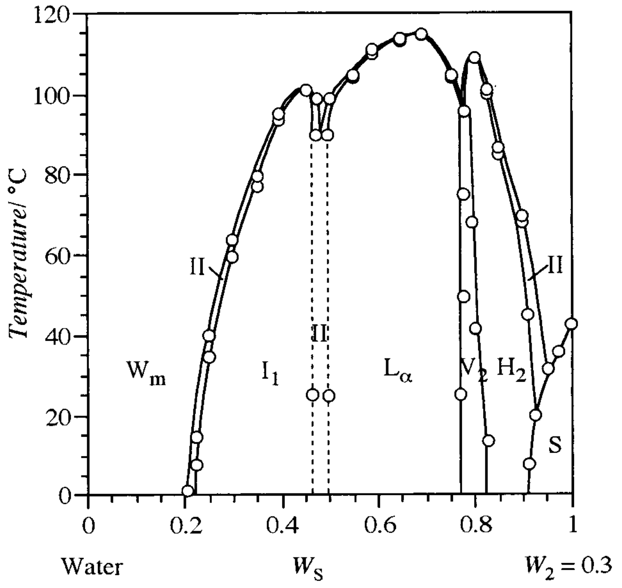


Figure 3. Phase diagram of the water/$Si_{25}C_3EO_{51.6}$/$C_{12}EO_5$ system as a function of temperature. The $C_{12}EO_5$/($C_{12}EO_5$ + $Si_{25}C_3EO_{51.6}$) weight fraction is constant (W_2 = 0.3). W_m, I_1, L_α, V_2, and H_2 are aqueous micellar solution, normal discontinuous cubic, lamellar, reverse bicontinuous cubic, and reverse hexagonal phases, respectively. II indicates a two-phase region.

B. Phase Behavior of Mixture in Water. Figure 3 shows the phase diagram of the water/$C_{12}EO_5$/$Si_{25}C_3EO_{51.6}$ system as a function of temperature. The $C_{12}EO_5$/$Si_{25}C_3EO_{51.6}$ weight ratio is kept constant (30/70), W_2 = 0.3. Although the H_1 and L_α phases are formed in the binary water−$C_{12}EO_5$ system and only the L_α phase is produced in the binary water−$Si_{25}C_3EO_{51.6}$ system, aqueous micellar solution (W_m), discontinuous cubic (I_1), lamellar (L_α), reverse bicontinuous cubic (V_2), and reverse hexagonal (H_2) phases are successively formed in the mixed amphiphile system. Thus, the phase behavior in the mixed amphiphile system is richer than that in each binary system. All the liquid crystals are thermally sable and melt to micellar solution phase through a narrow two-phase region with increasing temperature. The cloud temperature (T_C) phenomenon appears at a high-temperature region, and T_C = 102 °C for 2 wt % amphiphile in water. However, the T_C curve is not shown in Figure 3.

The typical SAXS spectra for different liquid crystals along with their reciprocal of the spacing ratios are

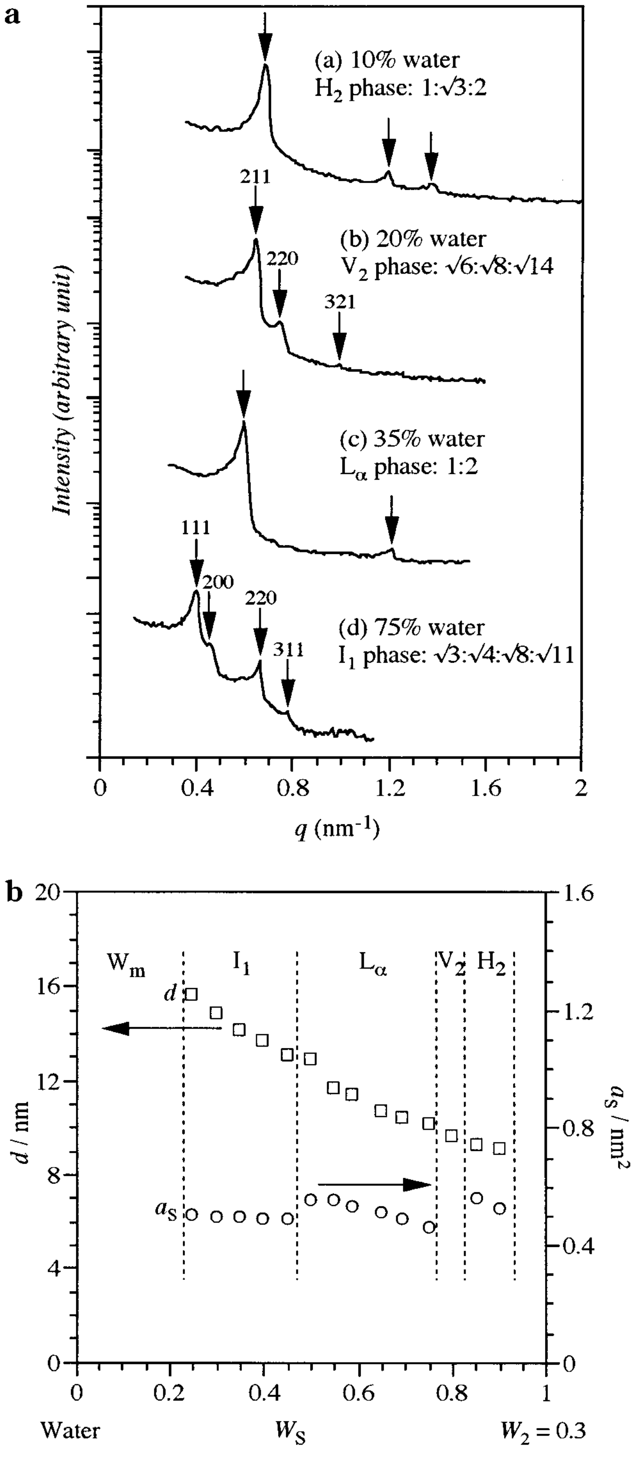


Figure 4. (a) Typical SAXS spectra for H_2, V_2, L_α, and I_1 phases and (b) change in interlayer spacing (d) and effective cross-sectional area per amphiphile (a_S) of each liquid crystal in the water–mixed amphiphile ($W_2 = 0.3$) system at 25 °C.

shown in Figure 4a. The I_1 phase is optically isotropic and highly viscous phase. The SAXS peak ratios $\sqrt{3}$:$\sqrt{4}$:$\sqrt{8}$:$\sqrt{11}$ obtained from the diffraction planes (hkl) = (111), (200), (220), and (311), respectively, for the I_1 phase suggest that this cubic phase is probably a face-centered-cubic phase belonging to $F23$ space group, which is one of the typical space group for the discontinuous micellar cubic phase.[18,23] In general, the H_1 phase is present between the I_1 and L_α phases, but the H_1 phase is missing in the present mixed amphiphile system. However, the I_1 phase directly touches the W_m phase. This also suggests that the I_1 phase consists of discrete micelles.

Another cubic phase (V_2) is located between L_α and H_2 phases. The SAXS peak ratios $\sqrt{6}$:$\sqrt{8}$:$\sqrt{14}$ obtained from the diffraction planes (hkl) = (211), (220), and (321), respectively, show that this cubic phase belongs to $Ia3d$ space group, which is a typical space group for a bicontinuous cubic structure.[24] Since the V_2 phase is located between L_α and H_2 phases, it is a bicontinuous structure in which the amphiphilic-layer curvature is slightly negative. The hexagonal phase in the concentrated region is a reverse type (H_2), because it is located between the L_α and surfactant liquid phase. The change in interlayer spacing, d, is also shown in Figure 4b. The d gradually increases with increasing water content, while a_S is not largely changed. The a_S value is in between each a_S in water–$C_{12}EO_5$ and water–$Si_{25}C_3EO_{51.6}$ systems. In each liquid crystal, a_S is slightly increased with increasing water content, and then, the a_S decreases when the type of liquid crystal is changed to another with more positive curvature as is shown in Figure 4b. With the increase in water content, the hydration of EO chain increases. It causes an increase in repulsion between EO chains and hence an increase in a_S in each liquid crystal. Since the hydrophobic part of an aggregate in the present system is a mixture of lipophilic chains of very different lengths, a_S is decreased by changing the morphology as well as the short surfactant system.

C. Two Coexisting L_α Phases. Although both amphiphiles form the L_α phase in water, the interlayer spacings are very different due to the big difference in molecular size. To know the compatibility of both molecules in the L_α phase, the interlayer spacing of the L_α phase was measured as a function of mixing fraction of $C_{12}EO_5$ in $C_{12}EO_5 + Si_{25}C_3EO_{51.6}$ (W_2) at constant water content (25 wt % in the system, $W_S = 0.75$), and the result is shown in Figure 5a. When a small amount of $Si_{25}C_3EO_{51.6}$ is added to the L_α phase (d_1') in the water–$C_{12}EO_5$ system, the SAXS peak with a wide interlayer spacing (d_1) appears, where d_1' and d_1 are the first peaks for the surfactant lamellar (L_α') and the copolymer lamellar (L_α) phases, respectively. With increasing $Si_{25}C_3EO_{51.6}$ content, the intensity of SAXS peak for d_1 increases whereas that for d_1' decreases. Finally d_1' peak disappears at $W_2 = 0.4$. The peak ratios for both liquid crystals are d_1:d_2 = d_1':d_2' = 1:$^1/_2$, which correspond to the lamellar structure. The SAXS peaks in Figure 5a clearly show that two lamellar phases coexist in a $C_{12}EO_5$-rich region. Hence, the L_α phase in Figure 3 belongs to the copolymer L_α phase.

The interlayer spacings d and d' are plotted against the mixing fraction of $C_{12}EO_5$ (W_2) in Figure 5b. The d and the half-thickness of the hydrophobic part, d_L, are sharply decreased by replacing silicone copolymer with surfactant. It means that the silicone chains are compressed in the direction vertical to the surface because a_S is not expanded by the mixing. As is shown in Figure 5b, there is a limit for poly(dimethylsiloxane) chain to be compressed up to $d_L = 1.7$ nm, and hence, the surfactant cannot be incorporated more in the L_α phase of $Si_{25}C_3EO_{51.6}$ beyond $W_2 \approx 0.45$. $Si_{25}C_3EO_{51.6}$ is practically insoluble in the $C_{12}EO_5$ L_α' phase, because the half-thickness is too small ($d_L' = 0.82$ nm at $W_2 = 1$) to include the poly(dimethylsiloxane) chain in the surfactant bilayer. In the two-phase region, both interlayer spacings, d and d', are constant, and d' is exactly the

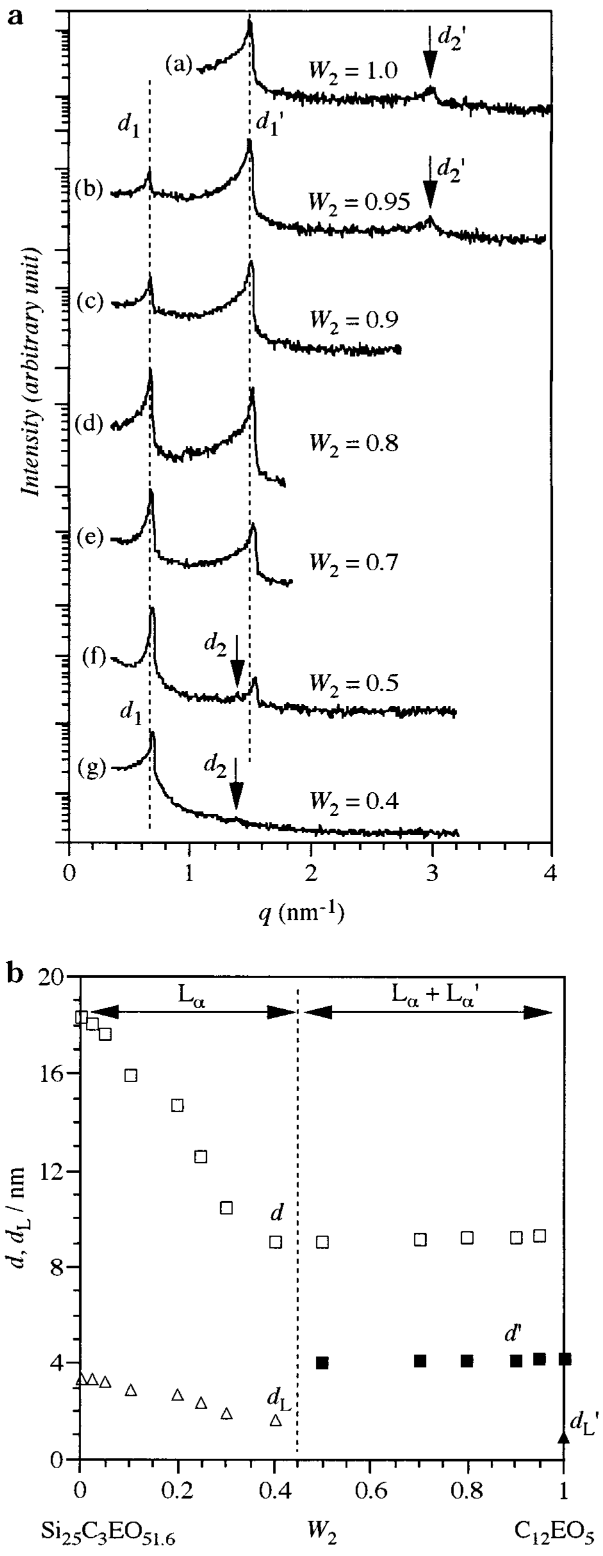


Figure 5. (a) SAXS spectra and (b) change in interlayer spacing (d or d') and half-thickness of the hydrophobic part (d_L or d_L') of two L_α phases as a function of W_2 at a constant $W_S = 0.75$ at 25 °C. The SAXS peak ratios $d_1{:}d_2 = d_1'{:}d_2' = 1{:}^1/_2$ hold for both L_α phases. The symbols without and with prime ′ represent the copolymer-rich L_α phase and the surfactant-rich L_α' phase, respectively.

same as that in the pure $C_{12}EO_5$ system. It also suggests that $Si_{25}C_3EO_{51.6}$ is completely insoluble in the $C_{12}EO_5$ L_α' phase.

D. L_α−I_1−W_m Phase Transition. At a high water content, the L_α phase in the $Si_{25}C_3EO_{51.6}$ system changes to aqueous micellar solution phase via the I_1 phase upon addition of $C_{12}EO_5$. We also measured the interlayer spacing as a function of W_2 at 45 wt % water (W_S = 0.55), at which $C_{12}EO_5$ alone forms an aqueous solution phase (W_m) at 25 °C. The result is shown in Figure 6. As well as in Figure 5b, d decreases with increasing $C_{12}EO_5$ content up to $W_2 \approx 0.45$. However, both amphiphiles are still miscible with each other, and the L_α−I_1 phase transition takes place. The radius of hydrophobic part of micelles in the I_1 phase, r_I, is very large, ~4 nm. As is shown in Figure 3, the W_m phase is present in a dilute region of the I_1 phase; i.e., this large micelle is soluble in water.

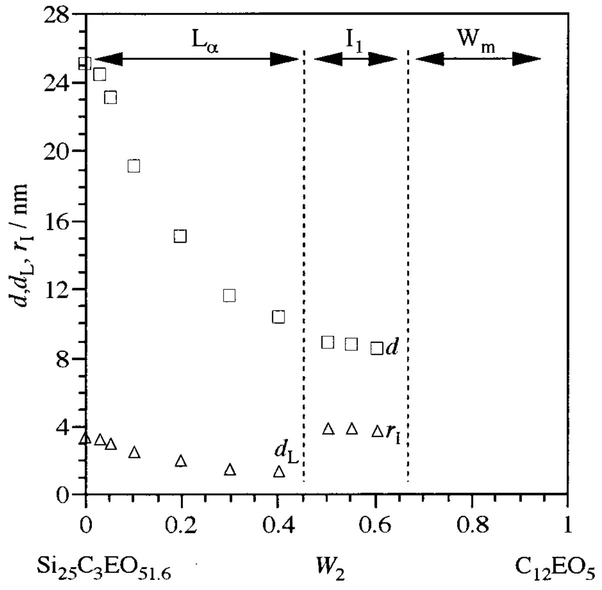


Figure 6. Change in interlayer spacing (d) of the L_α and I_1 phases as a function of W_2 at a constant $W_S = 0.55$ at 25 °C. d_L is the half-thickness of the hydrophobic layer in the L_α phase, and r_I is the radius of the hydrophobic core of micelle in the I_1 phase.

With the further increase in $C_{12}EO_5$ content at a constant $W_S = 0.55$, the I_1 phase is also changed to the W_m phase. Since rod micelles are present in the W_m phase in the binary water−$C_{12}EO_5$ system,[20] the sphere−rod transition takes place. It is not known whether the large spherical micelle is continuously changed to the surfactant rod micelle or both spherical and rod micelles coexist in the W_m phase. In the more dilute region, W_S = 0.45, $C_{12}EO_5$ forms the H_1 phase at temperatures below 25 °C. $Si_{25}C_3EO_{51.6}$ is immiscible and coexists with the surfactant H_1 phase up to ~23 °C and W_2 = 1−0.75 at constant W_S = 0.45. At room temperature, the H_1-present phase is changed to an aqueous solution phase. Probably, this isotropic solution phase consists of two kinds of micelles, namely small surfactant micelle and big composite micelle (surfactant−copolymer mixed micelle).[9,10] The population of the composite micelle increases with increasing copolymer weight ratio and forms the I_1 phase beyond W_2 < 0.6, and finally, the I_1 phase is changed to the copolymer lamellar phase.

IV. Discussion

A. Change in a_S. If each molecule occupies the same area as that in nonmixing state, the average $\bar{a}_S$ should be linearly changed according to the following equation obtained from eq 2,

$$\bar{a}_S = x_1 a_{S(1)} + x_2 a_{S(2)} \qquad (6)$$

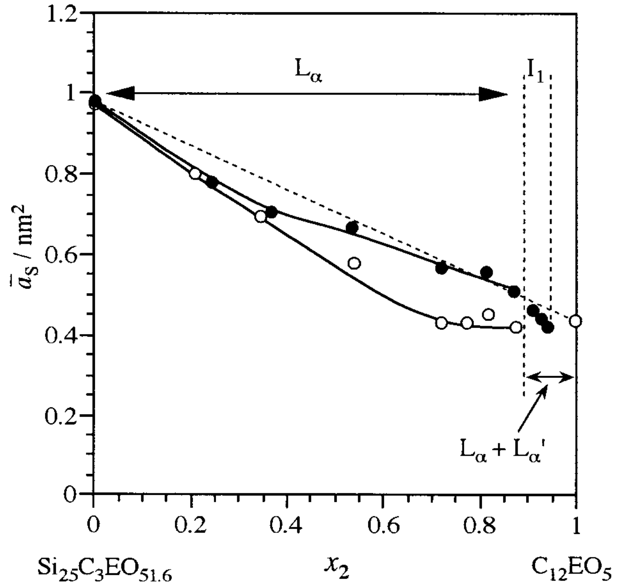
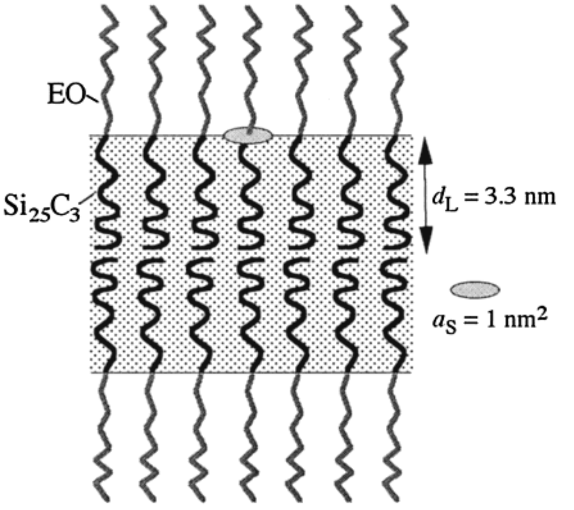


Figure 7. Change in $\bar{a}_S$ as a function of mole fraction of $C_{12}EO_5$ in $C_{12}EO_5$ + $Si_{25}C_3EO_{51.6}$ (x_2) at constants $W_S = 0.75$ (○) and $W_S = 0.55$ (●).

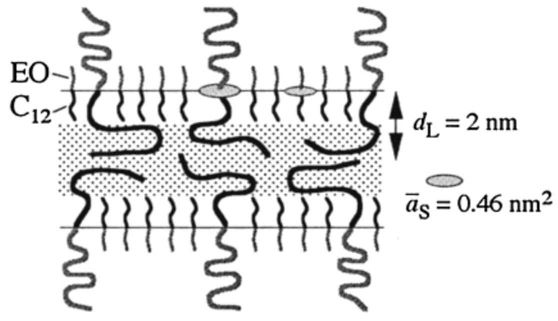
where $a_{S(1)}$ and $a_{S(2)}$ are the effective cross-sectional area for $Si_{25}C_3EO_{51.6}$ and $C_{12}EO_5$ in the nonmixing state, respectively. However, as is shown in Figure 7, $\bar{a}_S$ is considerably lower than the molar average (dotted line). We assume that all the surfactant molecules are located at an interface. Since the segregation tendency between surfactant and poly(dimethylsiloxane) chain of copolymer is enhanced in the presence of water, the monomeric solubility of surfactant in the poly(dimethylsiloxane) part must be very low. Hence, the reduction of $\bar{a}_S$ implies that $a_{S(1)}$ and/or $a_{S(2)}$ are decreased in the mixture.

In nonionic surfactant systems, if the EO chain length is the same, the a_S values are similar for both hydrocarbon and poly(dimethylsiloxane) surfactants of the same volume.[2] Therefore, the reduction of $\bar{a}_S$ is mainly attributed to the reduction in repulsion of copolymer chains on the both sides of A−B interface due to the mixing of amphiphiles with different chain lengths. As is schematically shown in Figure 8, when amphiphiles with different chain lengths are mixed, the long chain has more space than that in pure copolymer system. The entropy loss decreases, and the reduction in repulsion takes place on the both sides of the A−B interface. The reduction in $\bar{a}_S$ is also known in the mixed nonionic surfactant system.[25] The reduction in $\bar{a}_S$ is large when the surfactants of very different chain lengths are mixed. Hence, probably, the a_S for $Si_{25}C_3EO_{51.6}$ is mainly reduced in the mixture in comparison with the a_S for $C_{12}EO_5$.

B. Phase Transition. When $C_{12}EO_5$ content increases in the L_α phase, $\bar{a}_S$ and d_L decrease as is shown in Figures 5b, 6, and 7. Then, the long poly(dimethylsiloxane) chain has to be confined in the narrow length in the direction vertical to the surface as is schematically shown in Figure 8. The same thing happens for the long EO chain in the hydrophilic part. At the surfactant/(surfactant + copolymer) weight fraction $W_2 = 0.4$, the d_L reaches a minimum, 2 nm for $W_S = 0.55$ and 1.7 nm for $W_S = 0.75$; beyond this concentration the surfactant is not dissolved more in the copolymer L_α phase. In other words, the half-thickness cannot be reduced more because the reduction in d_L is energetically unfavorable for both lipophilic and hydrophilic chains of the copolymer. In the dilute region ($W_S = 0.55$, filled circle), the $\bar{a}_S$ is larger than that in a concentrated region ($W_S = 0.75$, open circle) close to the boundary of the L_α phase in Figure 7. Although the amphiphile mixing fraction is almost the same ($W_2 \approx 0.45$) at the boundary of L_α phase at $W_S = 0.75$ and 0.55, the hydrophilic part (water + EO chain) is larger and has more space for the EO chain in the dilute region ($W_S = 0.55$). Then, this large $\bar{a}_S$ is attributed to the increase in repulsion of EO chain due to the increase in hydration in the dilute region. At the high surfactant concentration ($W_S = 0.75$), the pure surfactant L_α' phase is separated from the copolymer L_α phase. If the copolymer L_α phase is changed to a spherical micelle, the volume fraction of mixed amphiphile + hydrated water exceeds the critical volume fraction of the closest packing spheres. Hence, the surfactant L_α' phase coexists with the copolymer L_α phase.



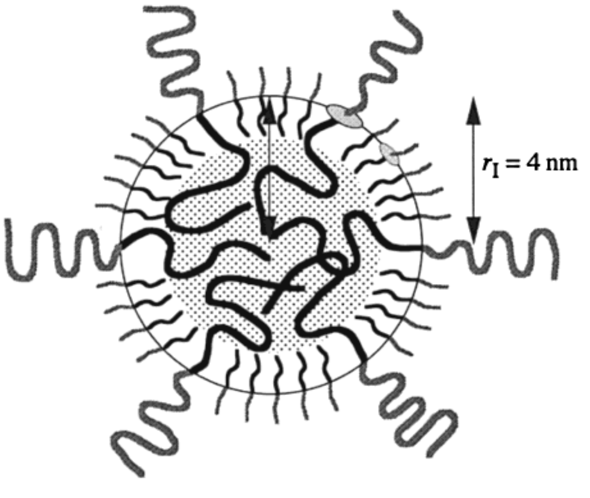
(a) Copolymer L_α phase



(b) Mixed amphiphile L_α phase

Figure 8. Schematic representation of copolymer L_α phase (a) and L_α phase in the mixed amphiphile system (b).

On the other hand, in the dilute region ($W_S = 0.55$), by changing from L_α to I_1 phases, the distance between EO chains can separate, and the EO chain has more space in the direction normal to the surface as is schematically shown in Figure 9. Simultaneously, the poly(dimethylsiloxane) chain has more freedom because the half-thickness d_L in the L_α phase is changed to the large radius of spherical micelle, r_I, in the I_1 phase. For these changes, the amphiphiles can form the mixed aggregate even in the surfactant-rich region without change in $\bar{a}_S$. At the boundary between the L_α and I_1 phases at $W_2 \approx 0.45$, the mole fraction of $C_{12}EO_5$ in $C_{12}EO_5$ + $Si_{25}C_3EO_{51.6}$ is $x_2 = 0.9$ or more. Since the a_S for



Spherical micelle in the I_1 phase

Figure 9. Schematic representations of spherical micelle in the I_1 phase in the mixed amphiphile system.

$Si_{25}C_3EO_{51.6}$ is almost double that for $C_{12}EO_5$, the short surfactant molecules approximately cover the 80% surface of aggregate. The aggregation number of the micelle in the I_1 phase is 430, in which 30 copolymer molecules are included. Hence, as shown in Figures 8b and 9, bilayer in the L_α phase or spherical micelle in the I_1 phase has double-layer structure in which surfactant mainly occupies the surface and the core is almost pure poly(dimethylsiloxane) part. The extended length of poly(dimethylsiloxane) is $l_{max(1)} = 6.7$ nm, whereas it is $l_{max(2)} = 1.55$ nm for the dodecyl group. Hence, the $l_{max(1)} - l_{max(2)}$ parts have rather free space and can be easily distributed to make a purely siloxane oil pool, unless there is any monomeric solubility of the $C_{12}EO_5$.

The I_1 phase is changed to the W_m phase at $W_S = 0.55$ with the further increase in $C_{12}EO_5$ fraction. It is known that rod micelles exist in the dilute region of the water−$C_{12}EO_5$ system.[20] Hence, the rod−sphere transition of micelle takes place in the W_m phase from the surfactant side. The surfactant rod micelle is changed to a spherical micelle upon addition of hydrocarbon because the hydrocarbon is solubilized in the lipophilic part and makes an oil pool inside the micelle.[26] In this case, since the volume of the hydrophobic part increases whereas total surface area is not largely changed, the rod−sphere transition takes place. In the present system, although copolymer is an amphiphile, the same phenomenon takes place because the long poly(dimethylsiloxane) chain makes an oil pool inside the micelle.

V. Conclusion

The poly(oxyethylene)−poly(dimethylsiloxane) copolymer, $Si_{25}C_3EO_{51.6}$ with equal volumes of hydrophilic and lipophilic parts ($f = 0.5$), forms only lamellar liquid crystal in water. A large amount of surfactant is dissolved in the copolymer aggregate, whereas copolymer is hard to dissolve in the surfactant ($C_{12}EO_5$) aggregate because of the large size of the copolymer. The considerable reduction in an average effective cross-sectional area per amphiphile, $\bar{a}_S$, takes place in the copolymer L_α phase because the long lipophilic and hydrophilic chains of the copolymer have a space in the mixture much more than that in pure state, and the reduction of repulsion between chains occurs. The half-thickness of the bilayer is rapidly decreased with increasing the surfactant content. As a result, the copolymer L_α phase containing a large amount of surfactant coexists with the pure surfactant L_α' phase at a high amphiphile concentration ($W_S = 0.75$). On the other hand, the copolymer L_α phase is changed to the discontinuous micellar cubic phase at $W_S = 0.55$. Since the molecular weight of surfactant is low, it covers most of the surface of the copolymer aggregates even when the weight fraction of surfactant in the mixture is not very large. Although both amphiphiles have similar $f = 0.5$, the surfactant layer curvature in the water−$C_{12}EO_5$ system gradually changes from negative to positive with increasing water content. In the mixed amphiphile system, the layer curvature is also changed from negative to positive upon addition of water, and rich phase behavior was observed. Hence, surfactant molecules mainly dictate the layer curvature of the mixed aggregate. However, in the mixed amphiphile system, the self-organized morphlogies are different from that in the pure $C_{12}EO_5$ system.

References and Notes

(1) Yang, J.; Wegmer, G.; Koningsveld, R. *Colloid Polym. Sci.* **1992**, *270*, 1080.
(2) Kunieda, H.; Taoka, H.; Iwanaga, T.; Harashima, A. *Langmuir* **1998**, *14*, 5113.
(3) Kunieda, H.; Uddin, Md. H.; Horii, M.; Furukawa, H.; Harashima, A. *J. Phys. Chem. B* **2001**, *105*, 5419.
(4) Uddin, Md. H.; Rodriguez, C.; Watanabe, K.; Lopez-Quintela, A.; Kato, T.; Furukawa, H.; Harashima, A.; Kunieda, H. *Langmuir* **2001**, *17*, 5169.
(5) Rodriguez, C.; Uddin, Md. H.; Watanabe, K.; Furukawa, H.; Harashima, A.; Kunieda, H. *J. Phys. Chem. B*, in press.
(6) In *Silicone Surfactants*; Hill, R. M., Ed.; Surfactant Science Series 86; Marcel Dekker: New York, 1999.
(7) Huang, K. L.; Shigeta, K.; Kunieda, H. *Prog. Colloid Polym. Sci.* **1998**, *110*, 171.
(8) Zhang, K.; Lindman, B.; Coppola, L. *Langmuir* **1995**, *11*, 538.
(9) Zheng, Y.; Davis, H. T. *Langmuir* **2000**, *16*, 6453.
(10) Couderc, S.; Li, Y.; Bloor, D. M.; Holzwarth, J. F.; Wyn-Jones, E. *Langmuir* **2001**, *17*, 4818.
(11) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(12) Griffin, W. C. *J. Soc. Cosmet. Chem.* **1954**, *5*, 249.
(13) Kunieda, H.; Shigeta, K.; Ozawa, K.; Suzuki, M. *J. Phys. Chem. B* **1997**, *101*, 7952.
(14) Mitchell, D. J.; Tiddy, G. J. T.; Waring, L.; Bostock, T.; McDonald, M. P. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 975.
(15) Strey, R.; Schomacker, R.; Roux, D.; Nallet, F.; Olsson, U. *J. Chem. Soc., Faraday Trans. 1* **1990**, *86*, 2253.
(16) Kumar, A.; Uddin, Md. H.; Kunieda, H.; Furukawa, H.; Harashima, A. *J. Dispersion Sci. Technol.* **2001**, *22*, 245.
(17) Kunieda, H.; Ozawa, K.; Huang, K.-L. *J. Phys. Chem. B* **1998**, *102*, 831.
(18) Rodriguez, C.; Uddin, Md. H.; Furukawa, H.; Harashima, A.; Kunieda, H. *Prog. Colloid Polym. Sci.*, in press.
(19) Jonsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solution*; John Wiley & Sons: Chichester, U.K., 1998; Chapter 4.
(20) Nilsson, P.-G.; Wennerström, H.; Lindman, B. *J. Phys. Chem.* **1983**, *87*, 1377.
(21) Kato, T.; Anzai, S.; Takana, S.; Seimiya, *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 2499.
(22) Matsen, M. W.; Bates, F. S. *J. Chem. Phys.* **1997**, *106*, 2436.
(23) Li, X.; Washenberger, R. M.; Scriven, L. E.; Davis, H. T.; Hill, R. M. *Langmuir* **1999**, *15*, 2267.
(24) Alexandridis, P.; Olsson, U.; Lindman, B. *J. Phys. Chem.* **1996**, *100*, 280.
(25) Kunieda, H.; Kabir, H.; Aramaki, K.; Shigeta, K. *J. Mol. Liq.* **2001**, *90*, 157.
(26) Hoffmann, H.; Ulbricht, W. *J. Colloid Interface Sci.* **1989**, *129*, 388.

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