Phase Behavior of a Mixture of Poly(isoprene)−Poly(oxyethylene) Diblock Copolymer and Poly(oxyethylene) Surfactant in Water

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The phase behavior of a mixture of poly(isoprene)−poly(oxyethylene) diblock copolymer (PI−PEO or $C_{250}EO_{70}$) and poly(oxyethylene) surfactant ($C_{12}EO_3$, $C_{12}EO_5$, $C_{12}EO_6$, $C_{12}EO_7$, and $C_{12}EO_9$) in water was investigated by phase study, small-angle X-ray scattering, and dynamic light scattering (DLS). The copolymer is not soluble in surfactant micellar cubic (I_1), hexagonal (H_1), and lamellar (L_α) liquid crystals, whereas an isotropic copolymer fluid phase coexists with these liquid crystals. Although the PI−PEO is relatively lipophilic, it increases the cloud temperatures of $C_{12}EO_{3-9}$ aqueous solutions at a relatively high PI−PEO content in the mixture. Most probably, in the copolymer-rich region, PI−PEO and $C_{12}EO_n$ form a spherical composite micelle in which surfactant molecules are located at the interface and the PI chains form an oil pool inside. In the $C_{12}EO_5/$ and $C_{12}EO_6/PI$−PEO systems, one kind of micelles is produced in the wide range of mixing fraction, although macroscopic phase separation was observed within a few days after the sample preparation. On the other hand, small surfactant micelles coexist with copolymer giant micelles in $C_{12}EO_7/$ and $C_{12}EO_9/PI$−PEO aqueous solutions in the surfactant-rich region. The micellar shape and size are calculated using simple geometrical relations and compared with DLS data. Consequently, a large PI−PEO molecule is not soluble in surfactant bilayers (L_α phase), infinitely long rod micelles (H_1 phase), and spherical micelles (I_1 phase or hydrophilic spherical micelles) as a result of the packing constraint of the large PI chain. However, the copolymer is soluble in surfactant rod micelles ($C_{12}EO_5$ and $C_{12}EO_6$) because a rod−sphere transition of the surfactant micelles takes place and the long PI chains are incorporated inside the large spherical micelles.

Introduction

It is known that nonionic amphiphilic block copolymers form a variety of self-organized structures in water similar to the behavior of a surfactant in water. The segregation tendency of an amphiphile to form aggregates depends on each chain length, and the type of self-organized structure or the layer curvature is dictated by the compositional parameter, *f*, which represents the volume fraction of the hydrophilic part in the total amphiphile.[1−3] This parameter corresponds to the HLB (hydrophile−lipophile balance) value commonly used for surfactant fields.[4]

When a nonionic surfactant is mixed with a hydrophilic nonionic polymer [i.e., dextran and poly(ethylene glycol)] in water, a segregative phase separation takes place where one phase is surfactant-rich and the other is polymer-rich, as it is predicted by the Flory−Huggins theory.[5−8] However, there are few studies on the phase behavior and self-organization of mixtures of a nonionic amphiphilic copolymer and a nonionic surfactant in water over a wide range of compositions, mainly because it was expected that there are no special interactions and they just should mix with each other. Zheng and Davis found that nonionic surfactants form small micelles whereas nonionic copolymers form giant micelles in mixed penta(oxyethylene) dodecyl ether and poly(butadiene)−poly(oxyethylene) (PEO) copolymers in water.[9] Hence, nonionic surfactants and copolymers are not always soluble with each other in water, although the mechanism of the segregation of both amphiphiles remains to be clarified.

Kunieda et al. reported that a mixture of poly(dimethylsiloxane)−PEO diblock copolymer and nonionic surfactant forms a variety of self-organized structures in water, which are not observed in each binary water/surfactant

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or water/copolymer system.[10] They also reported that a surfactant-rich lamellar phase coexists with a polymer-rich lamellar phase in a water/nonionic surfactant/poly-(dimethylsiloxane)–PEO copolymer system. Again, this is an indication that amphiphilic nonionic surfactants and copolymers are not always miscible in self-assemblies.

Surfactants and amphiphilic copolymers have a tendency of self-segregation of the hydrophilic and hydrophobic chains in their molecules. This segregation tendency of the poly(isoprene) (PI) and PEO chains is dependent on χN, where χ is the Flory–Huggins interaction parameter and N is the total polymerization degree.[1] The segregation of both chains is enhanced in the presence of water because the hydrophilic chains are hydrated. Hence, even a short-chain surfactant forms micelles or liquid crystals in water. When a short surfactant is mixed with a long amphiphilic A–B-type copolymer, they would not form mixed micelles or liquid crystals if the interiors of the surfactant self-assemblies are not big enough to accommodate the long copolymer chain. On the other hand, although it is expected that a small surfactant can easily mix with copolymer aggregates, phase separation would take place if surfactant molecules do not cover all of the hydrophilic surface of the copolymer aggregates. However, the compatibility or miscibility of surfactant and copolymer forming aggregates with different large sizes is still not fully understood.

In this context, we have chosen a linear A–B-type PI–PEO diblock copolymer, which is insoluble in water, and a PEO-type surfactant ($C_{12}EO_n$, $n = 3, 5, 6, 7$, and 9) as a nonionic surfactant. The phase behavior of their mixtures in water was investigated by a systematic phase study, accompanied by small-angle X-ray scattering (SAXS) in the concentrated region and dynamic light scattering (DLS) in the dilute region.

Experimental Section

Materials. PI–PEO is a linear block copolymer that was specially synthesized by Nikko Chemicals Co., Japan. Anionic polymerization of isoprene was performed in cyclohexane using *sec*-BuLi as the initiator, and then propylene oxide is attached to PI–Li to synthesize PI–OH under acidic conditions. The molecular weight distribution (M_w/M_n) of the synthesized PI–OH is 1.05 determined by HPLC. PI–PEO was produced by introducing ethylene oxide to PI–OH in diethyleneglycol dimethyl ether in the reaction autoclave. *t*-BuOK was used as a catalyst. The number-average molecular weight (M_n) was 6862 g mol^{-1}, and M_w/M_n = 1.04, as determined by gel permeation chromatography. The polymerization degree of PI–PEO is approximately $C_{250}EO_{70}$. The molar volumes of the lipophilic part of the surfactant (C_{12}–), oxyethylene units (EOs), and hydroxyl group (–OH) are 0.357 nm^3/molecule, 0.0645 nm^3/molecule, and 0.0146 nm^3/molecule, respectively.[3] The volumes of each chain are 6.41 nm^3/molecule for the PI chain and 4.59 nm^3/molecule for the PEO chain using the density of the PI chain (0.895 g/cm^3) and that of the PEO chain (1.12 g/cm^3).[11] The volume fraction of the hydrophilic part in the copolymer (f) is 0.42. The melting point of PI–PEO is 53.5 °C, as determined by differential scanning calorimetry (Seiko, DSC-6200). Homogeneous tri-, penta-, hexa-, hepta-, and nona(oxyethylene) dodecyl ethers ($C_{12}EO_n$) were obtained from Nikko Chemicals Co., Japan. All compounds were used without further purification. Throughout this study, Millipore water was used.

Phase Diagrams. The phase boundary was determined by titration of water with a mixture of surfactant and copolymer with various mixing fractions. To confirm the boundary, some samples were prepared individually in sealed glass tubes containing all the compounds. Some samples were kept at room temperature ($\sim$25 °C) for several weeks depending on their stability. Phase equilibria were determined by visual observation and by means of cross polarizers for anisotropy.

SAXS. Types of liquid crystals were confirmed by using SAXS, performed on a small-angle scattering goniometer with a 15-kW Rigaku rotating anode generator (RINT-2500; Cu Kα) at 25 °C. The samples were covered by plastic films for the SAXS experiments (Mylar seal method). Lamellar and hexagonal liquid crystalline phases were distinguished by the SAXS peaks. The ratios of interlayer spacings from the first to the second peak are 1:1/2 for the lamellar type and 1:1/$\sqrt{3}$ for the hexagonal type.

DLS and Static Light Scattering (SLS). DLS and SLS measurements were performed with a DLS-7000 (Otsuka Electronics Co., Ltd.). The DLS apparatus consists of a goniometer, a 10-mW He–Ne laser ($\lambda = 632.8$ nm) or 75-mW Ar ion laser ($\lambda = 488$ nm), and a multiple tau digital real time correlator (ALV-5000/EPP, Germany).

The experimental correlation function $g_2(t)$ was measured and fitted by a nonlinear fitting program. When aggregates of different sizes are formed in solution, $g_2(t)$ includes all the individual relaxation processes (correlation functions) and can be expressed as follows

$$g_2(t) - 1 = B + [\sum_{i=1}^{j} a_{2i-1} \exp(-\Gamma_{2i}t)]^2 \tag{1}$$

$$j = 1, 2, \ldots$$

where B is the baseline, a_{2i-1} is a fitting parameter, and Γ is the relaxation rate given by eq 2,

$$\Gamma = q^2 D \tag{2}$$

where D is the translation diffusion coefficient and q is the scattering vector as is given by eq 3,

$$q = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \tag{3}$$

where n is the refractive index of the solvent, λ_0 is the laser beam wavelength, and θ is the scattering angle. The translation diffusion coefficient D, for a spherical particle, is related to the hydrodynamic radius R_H, according to the Stokes–Einstein eq 4,

$$D = \frac{kT}{6\pi\eta_0 R_H} \tag{4}$$

where k is the Boltzmann constant, T is the absolute temperature, and η_0 is the viscosity of water (890.9 μPa·s). When 2 kinds of particles (or aggregates) are present in solution, the fitting for j=2 was applied to the experimental correlation function in eq 1, and two values of R_H were calculated from the two obtained Γ values.

The q^2 dependence predicted by eq 2 was checked by performing the experiments at five different scattering angles (45, 60, 75, 90, and 110°). The R_H values are the average values obtained for the different angles. All the measurements were made at 25 °C. All samples were kept at room temperature for at least 1 week before the DLS measurements, except for the time-dependent measurements of the aggregation process (see Figure 5).

The range for the scattering angles used for the SLS experiments is 30–120°. To determine the micellar weight, we measured the scattered intensity (Rayleigh ratio) at different amphiphile concentrations (0.2, 0.5, 1.0, and 2.0 wt %) and extrapolated to 0 wt %.

Results and Discussion

Ternary Phase Diagrams of a Water/$C_{12}EO_n$/PI–PEO System. Parts a and b of Figure 1 show the ternary

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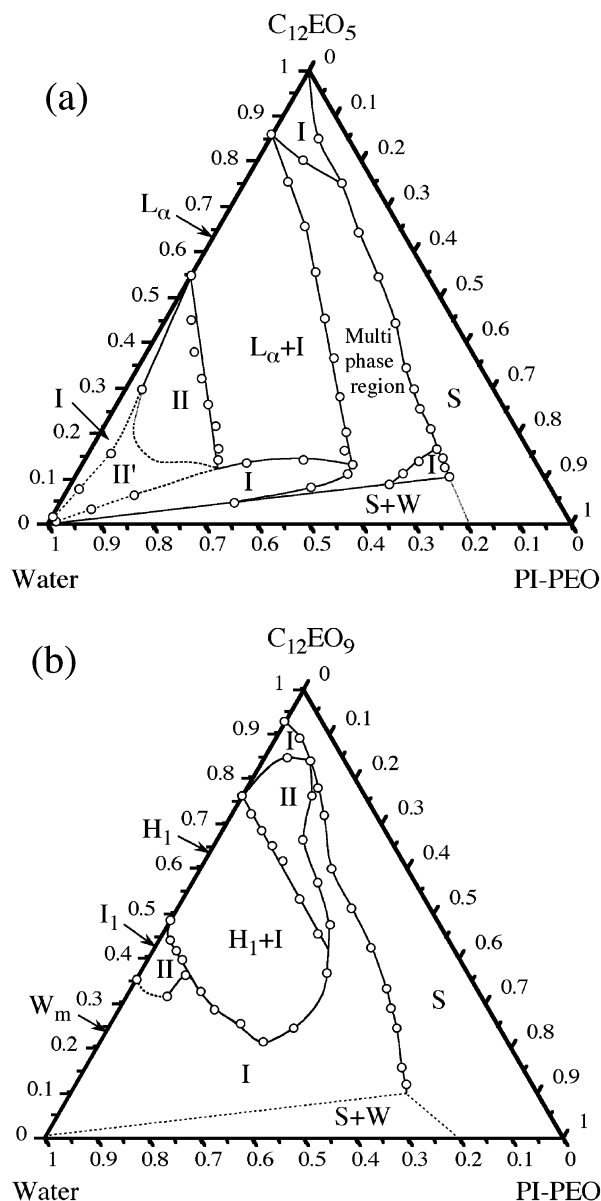
Figure 1. Ternary phase diagrams of a water/$C_{12}EO_5$/PI–PEO system (a) and a water/$C_{12}EO_9$/PI–PEO system (b) at 25 °C. The phase notation is as follows: I, isotropic liquid phase; W_m, micellar phase; II, two-liquid phase; I_1, micellar cubic phase; H_1, hexagonal liquid crystalline phase; L_α, lamellar liquid crystalline phase; S, solid phase, and W, excess water phase.

phase diagrams of the water/$C_{12}EO_5$/PI–PEO and water/$C_{12}EO_9$/PI–PEO systems at 25 °C, respectively. The isotropic fluid phase is indicated by I. PI–PEO itself is insoluble in water because of its high melting temperature (53.5 °C) and its low f value. This temperature corresponds to the melting temperature of the long EO chain.[12,13] The melting temperature is usually reduced upon addition of water.[14] However, the melting temperature of the present copolymer is not changed even in the presence of 50 wt % water, most probably because the tightly oriented PI chains prevent the hydration of the EO chain. PI–PEO is also not soluble in water above its melting temperature, above which only a turbid dispersion was observed.

$C_{12}EO_5$ forms micellar (I), lamellar (L_α), and surfactant solution or liquid (I) phases with increasing surfactant concentration in a binary water–surfactant system.[14,15] The hexagonal phase (H_1) is formed only below 25 °C, and it does not appear in Figure 1a. $C_{12}EO_9$ forms aqueous micellar, micellar cubic (I_1), hexagonal, and surfactant solution or liquid phases in water in a binary system as is shown in Figure 1b.[16] These differences can be understood because $C_{12}EO_5$ is a balanced surfactant with an f value of 0.49, whereas the f values for the hydrophilic $C_{12}EO_9$ and lipophilic $C_{12}EO_3$ are 0.63 and 0.37, respectively.

In the water/$C_{12}EO_5$/PI–PEO system, the solubilization of copolymers in the surfactant aggregates is limited, whereas a relatively large amount of surfactant is dissolved in the isotropic copolymer phase (I) as is shown in Figure 1a. Specifically, the copolymer is practically insoluble in the surfactant L_α phase. In the dilute region, there is a two-isotropic-liquid-phase region denoted by II, in which the system is turbid. In the more dilute region (II′), the mixture is transparent at the beginning of the sample preparation, but a phase separation was observed and the solution becomes gradually turbid after a few days.

In the water/$C_{12}EO_9$/PI–PEO system, the copolymer does not dissolve in the surfactant liquid crystals [cubic (I_1) or hexagonal (H_1) phases], as it is shown in Figure 1b. When the copolymer is added to the surfactant I_1 phase, phase separation takes place and the system becomes turbid and fluid. On the other hand, surfactant and copolymer are miscible in a wide range of compositions in the isotropic-fluid-phase region (I). The aggregation in this region will be discussed later in more detail.

Cloud Temperature. The HLB or f value of the PI–PEO is lower than that of $C_{12}EO_5$ or $C_{12}EO_9$ and, therefore, is more hydrophobic. It is then expected that the surfactant cloud temperature would decrease upon addition of PI–PEO. The cloud temperatures of $C_{12}EO_5$ and $C_{12}EO_9$ aqueous solutions are 32.0 and 87.5 °C, respectively, whereas the PI–PEO aqueous systems are still turbid above the melting temperature. We investigated the change in the cloud temperature in the $C_{12}EO_n$/PI–PEO aqueous systems at a constant total amphiphile ($C_{12}EO_n$ + PI–PEO) concentration, 2 wt %, and the results are shown in Figure 2a–c. The phase diagram was constructed within 1 day of the sample preparation. It is interesting to notice that the cloud temperature of the nonionic surfactant aqueous solutions increases upon addition of the hydrophobic PI–PEO. In the $C_{12}EO_3$/PI–PEO system, the cloud temperature of $C_{12}EO_3$ does not appear above 0 °C, and the L_α phase is dispersed in water at room temperature. However, a transparent and isotropic fluid phase (I) is formed for the mixing weight fraction above 0.55, as it is shown in Figure 2a. This transparent phase becomes cloudy above 80 °C. Hence, the mixed amphiphile becomes very hydrophilic by combining two hydrophobic compounds: $C_{12}EO_3$ and PI–PEO. The same tendencies were observed in the $C_{12}EO_5$/PI–PEO and the $C_{12}EO_9$/PI–PEO systems as are shown in Figure 2b,c. In the latter systems, the cloud temperature increases very slightly at the beginning for a low mixing fraction of PI–PEO, but it increases a little more at high mixing fractions. Besides, the cloud temperature is smoothly connected from $C_{12}EO_9$–water to the mixed amphiphile systems. Hence, the

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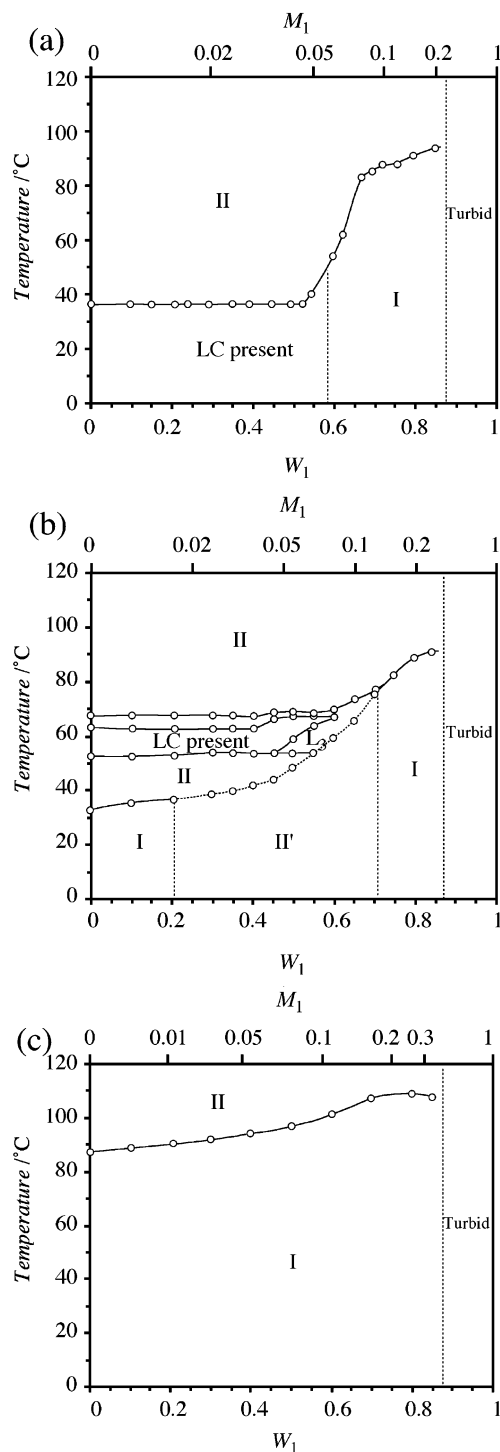
Figure 2. Cloud temperatures as a function of the weight fraction of PI−PEO, W_1, for the $C_{12}EO_3$/PI−PEO (a), $C_{12}EO_5$/PI−PEO (b), and $C_{12}EO_9$/PI−PEO (c) aqueous systems. The phase notation is as follows: I, isotropic liquid phase; II, two-liquid phase; LC, liquid crystal phase; and L_3, sponge phase.

Figure 3. SAXS diffraction patterns at the different weight fractions of PI−PEO, W_1, in a water/$C_{12}EO_5$/PI−PEO (a) and a water/$C_{12}EO_9$/PI−PEO (b) system at 25 °C. The total weight fraction of amphiphiles in the system, W_S, is fixed at 0.6.

In the case of $C_{12}EO_5$, it is already known that there is a L_α-present region above the cloud temperature. The temperature range for the LC-present region is almost unchanged in the presence of PI−PEO, and the cloud temperature is also gradually increased at a low mixing fraction of PI−PEO. The II′ region below the cloud temperature looks transparent and like a single-micellar-phase region within 1 day after the sample preparation. As described later, however, the samples look bluish with time, but a clear phase separation was not observed. The I region at a high mixing fraction of PI−PEO looks transparent and colorless for at least more than 3 months.

In the $C_{12}EO_9$/PI−PEO system, only a slight rise in the cloud temperature was observed and only an isotropic-one-phase region exists below the cloud temperatures. As described later, there are two kinds of micelles in the surfactant-rich region of the $C_{12}EO_7−$ and $C_{12}EO_9$/PI−PEO systems. Judging from the change in the cloud temperature, the surfactant-rich micelles are related to the clouding phenomenon in the surfactant-rich region in these surfactant systems. From these data, it can be suggested that the $C_{12}EO_n$ and PI−PEO mixture forms composite micelles at high mixing fractions of PI−PEO and that these micelles are more hydrophilic or more spherical than the original surfactant micelles.

Compatibility of Surfactant and Copolymer in the Liquid Crystal Region. We measured the SAXS spectra while changing the mixing weight fraction of PI−PEO in the total amphiphile (W_1) at a constant water content (W_S = the weight fraction of total amphiphile in the system = 0.6).

In the $C_{12}EO_5$/PI−PEO system (Figure 3a), the SAXS peaks for L_α phase indicated by arrows are not changed at all and only decreasing of the intensity with increasing W_1 is observed. This means that no copolymer is miscible in the surfactant bilayers. In fact, at high W_1, another peak corresponding to the isotropic copolymer solution (I)

physical−chemical meaning of the cloud temperature may be the same even in the polymer-rich region. Although the mixture of a long EO chain surfactant and PI−PEO shows a higher cloud temperature compared with the lipophilic surfactant systems, the maximum cloud temperatures attained for the studied systems are not very different, although the *f* values of the surfactants are very different. This suggests that mainly the PI−PEO dictates the cloud temperature and that the micellar shapes and sizes are similar.
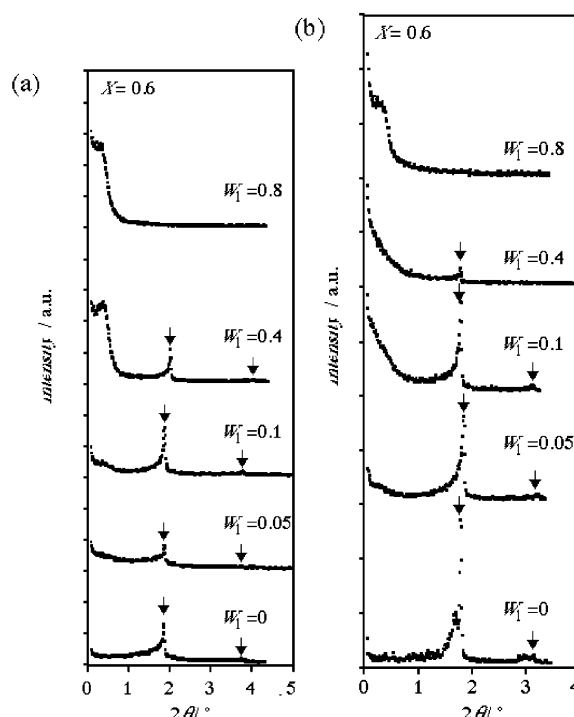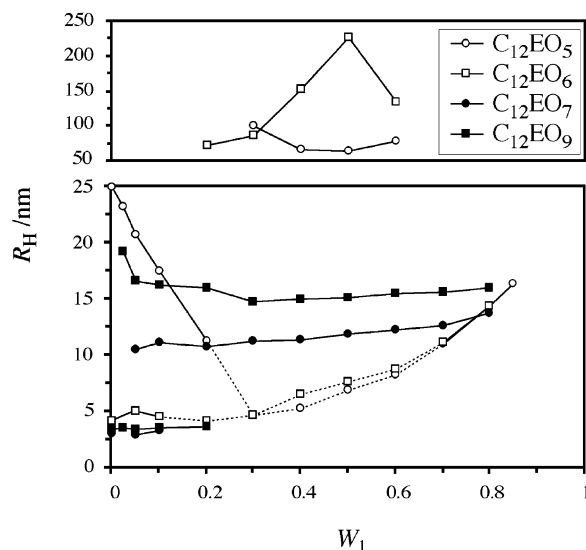
Figure 4. Change of the micellar/aggregates' hydrodynamic radius, R_H, as a function of the weight fraction, W_1, in a water/ $C_{12}EO_n$/PI−PEO system at 25 °C. The concentration of the C_{12}-EO_n + PI−PEO mixture is 0.5 wt %. $C_{12}EO_5$/PI−PEO system (○), $C_{12}EO_6$/PI−PEO system (□), $C_{12}EO_7$/PI−PEO system (●), and $C_{12}EO_9$/PI−PEO system (■).

appears at very low angles. It is considered that the peak shows the average correlation distance between copolymer aggregates in the isotropic solution (I) and the position is also not changed with W_1. In the $C_{12}EO_9$/PI−PEO system, the positions of the SAXS peaks for the H_1 phase are also unchanged with increasing the copolymer content, as it is shown in Figure 3b. At high W_1 values, another peak for the copolymer solution also appears. The bilayer thickness of the hydrophobic part of $C_{12}EO_5$ of the L_α phase is calculated to be 1.5 nm, from its molecular volume and by using an interlayer spacing of 4.7 nm. The diameter of the hydrophobic cylindrical part of $C_{12}EO_9$ for the H_1 phase is also calculated to be 2.8 nm using an interlayer spacing of 4.8 nm. On the other hand, the extended length of the present PI chain is about 24 nm.[17] Hence, the PI chain is too big to dissolve in the surfactant H_1 or L_α phases.

Micellar Structure. We measured the hydrodynamic radii (R_H) of the aggregates formed in $C_{12}EO_n$/PI−PEO mixtures in the micellar-phase region (I) with changing W_1 at a constant amphiphile concentration (0.5 wt %) at 25 °C, and the results are shown in Figure 4. The horizontal axis shows W_1, and the vertical axis is R_H. In a binary water−surfactant system (left-hand axis), $C_{12}EO_5$ forms rather large micelles whereas $C_{12}EO_9$ forms only small micelles. The hydrophilic radii are 25.1 nm for $C_{12}EO_5$ and 3.5 nm for $C_{12}EO_9$, respectively. Because the extended length of a C_{12} chain, calculated by the Tanford equation,[18] is 1.67 nm and that of an EO unit is 0.20 nm,[19] $C_{12}EO_9$ should give almost spherical micelles whereas $C_{12}EO_5$ should form rodlike micelles because, at least, one dimension of the micelle should not exceed the surfactant length in its extended state.[20] This result is in good agreement with previous data.[20] In the same sense, C_{12}-EO_6 should form short-rod micelles and $C_{12}EO_7$ should give almost spherical micelles in water.

In the $C_{12}EO_5$/PI−PEO system, the surfactant micellar size gradually becomes small upon addition of PI−PEO up to $W_1 = 0.2$. This is the same phenomenon observed when a hydrocarbon is solubilized in rod micelles[21,22] or in the H_1 phase.[23] Because the hydrocarbon makes an oil pool, the original restriction, in which the dimension of the micelle should not exceed the extended chain length, is removed. Then, the surfactant layer curvature becomes more positive to minimize the total surface area. In the case of the $C_{12}EO_5$/PI−PEO system, the long and bulky PI chain makes a core giving rise to a rod−sphere transition in the micellar shape. At $W_1 = 0.2−0.3$, although the mixed micelle starts to grow after reaching the minimum size, the phase separation takes place at 1 day after mixing. The big aggregates of 100−200 nm in radius gradually become larger with time, and the system becomes bluish. Hence, it is considered that when the micellar size reaches the minimum, the number of surfactant molecules is not enough to cover all of the interface of the micelles. Hence, the phase separation of large aggregates takes place.

The small micelles start to grow above $W_1 = 0.3$ with increasing PI−PEO content. The big aggregates disappear before $W_1 = 0.7$, and only micelles are observed. In the $C_{12}EO_6$/PI−PEO system, the original surfactant micelles are much smaller than the $C_{12}EO_5$ micelles. But, it forms short rod micelles because the value of R_H is still bigger than the surfactant size. However, the phase behavior is similar to that of the $C_{12}EO_5$ system, and the phase separation was also observed in the middle of W_1.

On the other hand, in the $C_{12}EO_7$/ and $C_{12}EO_9$/PI−PEO systems, surfactant micellar sizes do not change upon addition of PI−PEO. Instead of that, both $C_{12}EO_7$ or C_{12}-EO_9 and PI−PEO form two kinds of micelles upon addition of a small amount of PI−PEO. The large micelles slightly decrease in size, whereas the small surfactant micelles are not changed, and the latter disappear at W_1 between 0.2−0.3. However, it is not clear that the small micelles do not really exist at high W_1. When the number of small micelles decreases, it is difficult to use the fitting at $j = 2$ for the experimental correlation function in eq 1. The micellar behavior of the $C_{12}EO_7$/PI−PEO mixture is similar to that of the $C_{12}EO_9$ system, although the copolymer micellar size is smaller than that in the C_{12}-EO_9/PI−PEO system. As was shown before in Figure 2, the cloud temperature is almost unchanged when two kinds of micelles exist. Hence, in the surfactant-rich region, the hydration of small surfactant micelles is mainly attributed to the clouding phenomenon.

Consequently, one can deduce from these measurements that the copolymer is hard to dissolve into the hydrophilic surfactant spherical micelles, whereas surfactant rod micelles dissolve the copolymer. At high copolymer weight fractions, similar copolymer micelles are formed in all the $C_{12}EO_n$−copolymer systems. The copolymer-rich micelles are spherical and more hydrophilic than surfactant or copolymer alone. We also reported the formation of spherical composite micelles in the nonionic and silicon copolymer system.[10]

Change in Morphology with Time in the II′ Region of the $C_{12}EO_5$/PI−PEO System. As described before, in the $C_{12}EO_5$/PI−PEO system, the solutions in the range from $W_1 = 0.3−0.6$ become bluish or turbid with time. We

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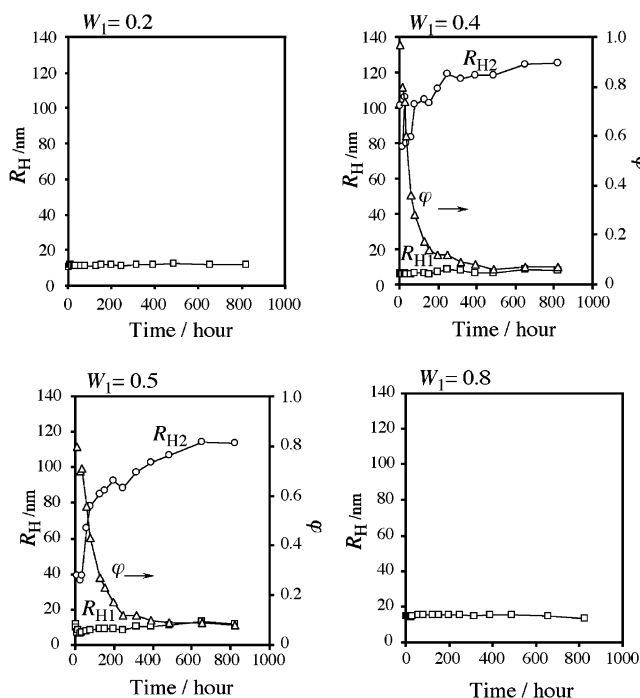(23) Kunieda, H.; Ozawa, K.; Huang, K. L. *J. Phys. Chem. B* **1998**, *102*, 831−838.

Figure 5. Change of the aggregates' size with time in the $C_{12}EO_5$/PI−PEO system at 25 °C. The micellar size, R_{H1} (○), the size of the big aggregates formed, R_{H2} (□), and the ratio of the number density of micelles to micelles + big aggregates, φ (△), are shown.

investigated the change in the aggregates' size by DLS at a constant amphiphile content (0.5 wt %) at 25 °C, as it is shown in Figure 5. The solutions at $W_1 = 0.4$ and 0.5 were prepared by mixing with solutions at $W_1 = 0.2$ and 0.8, where single transparent solutions are formed. R_{H1} and R_{H2} represent the hydrodynamic radii of the micelles and the big aggregates, respectively. φ is the ratio of the number density of micelles to micelles + big aggregates in the system. The R_{H2} values are slightly different from the hydrodynamic radii of big aggregates shown in Figure 4 because for this time-dependent study we have performed measurements only at 90°. For $W_1 = 0.4$ and 0.5, one can see that, at beginning of the experiment, both amphiphiles form homogeneous small micelles, which are not stable because the micellar size may not be big enough for PI−PEO to be dissolved into the surfactant-rich micelles, as it was described in the former section. In other words, the number of surfactant molecules is not enough to cover all of the interface of the copolymer. With increasing time, the micellar sizes remain almost constant, and the big aggregates' sizes increase at first and tend to be constant. However, the micellar size does not change in the single-phase region at $W_1 = 0.2$ and 0.8. Besides that, φ decreases while the big aggregates' size increases. Judging from the phase diagram, the separated phase (large aggregates) could be a copolymer-rich micellar phase (not a micelle itself) because the copolymer micelles of PI−PEO carrying a large EO chain should be stable in water. However, the observed aggregate size is too large to be a single copolymer micelle and, therefore, it has to be concluded that the aggregates could be formed by a dispersion of the copolymer phase including copolymer micelles.

Copolymer-Rich Composite Micelles. As described before, in the binary systems of water/$C_{12}EO_n$, the micellar shapes are long rod for $C_{12}EO_5$, short rod for $C_{12}EO_6$, and almost spherical for $C_{12}EO_7$ and $C_{12}EO_9$. The micellar

curvature is determined by the effective cross-sectional area at the interface of the hydrophobic part, a_S, the hydrophobic chain length, l_S, and the hydrophobic volume, v. a_S is determined by the balance of the hydrophilic interaction and the water−hydrocarbon interfacial tension. The hydrodynamic radii of the copolymer-rich micelles are almost similar for the four systems (see Figure 4, at $W_1 = 0.7−0.8$). The cloud temperatures are also similar and very high despite being a mixture of a hydrophobic PI−PEO with a hydrophobic surfactant. Hence, the copolymer micelles are considered to be spherical and the long EO chain of the PI−PEO should be responsible for the observed increase in the cloud temperature. In fact, around $W_1 \sim 0.8$, the measured R_H values are almost independent of the measured angles of DLS.

For a further discussion, we assumed that all the surfactant and polymer molecules form aggregates (the solubility of the monomers is neglected), the micellar size distribution is neglected, and all the micelles formed by the $C_{12}EO_n$, at high W_1 values, are assumed to be spherical. Besides, it is also assumed that the mixing of surfactant and copolymer is an ideal mixing. Then, we obtain

$$\bar{a}_S = a_{S,S}(1 - M_1) + a_{S,P}M_1 = \frac{4\pi r^2}{N_{agg}} \qquad (5)$$

$$\bar{v} = v_S(1 - M_1) + v_P M_1 = \frac{4\pi r^3}{3N_{agg}} \qquad (6)$$

where $\bar{a}_S$ and $\bar{v}$ are the average effective sectional area/amphiphile and the molecular volume of the hydrophobic parts of the amphiphile and $a_{S,S}$ and $a_{S,P}$ are the effective cross-sectional area/surfactant and /copolymer, which are maintained constant. v_S and v_P are the molecular volumes of the hydrophobic parts of the surfactant and copolymer, respectively. M_1 is the mole fraction of the copolymer in the amphiphile mixture. N_{agg} is the surfactant and copolymer total aggregation number. $a_{S,S}$ for $C_{12}EO_5$ is taken from that of the L_α phase, and that for the $C_{12}EO_9$ is calculated using the assumption that $C_{12}EO_9$ forms spherical micelles with a radius similar to the extended hydrocarbon chain length, $l_S = 1.67$ nm. The N_{agg} values are calculated from the micellar weight obtained by SLS experiments for all $C_{12}EO_n$ systems. Then, $a_{S,P}$ is calculated to be 2.1 ± 0.3 nm² at $W_1 = 0.8$ using eq 5. The radius of the hydrophobic parts of the spherical micelles is ~5.6 nm for all the mixed systems.

The radius of the copolymer-rich micelles is much larger than the surfactant hydrocarbon chain. Although the copolymer-rich micelles contain a large amount of PI−PEO, the mole fraction of the copolymer is still much lower than that of surfactant. Therefore, these copolymer-rich micelles are composite micelles in which the surface is mainly covered by surfactant molecules and there are PI-chain pools inside of the micelles, as it is shown in Figure 6a.

Change in the Micellar Size and Shape ($C_{12}EO_5$ and $C_{12}EO_6$ Systems). Although there is a macroscopic phase separation at the middle of W_1 for $C_{12}EO_5$/ or $C_{12}EO_6$/PI−PEO mixtures, at least, at the beginning of the sample preparation, only one type of micelles are present over a wide range of mixing fractions. We assume that in the copolymer-rich side the micelles are spherical in shape. Then, we calculate the radius of the hydrophobic part of the micelles keeping constant $a_{S,S}$ and $a_{S,P}$. The results are shown by the solid curve, c−d, in Figure 7a. It is impossible for a spherical micelle to exist in the low-W_1
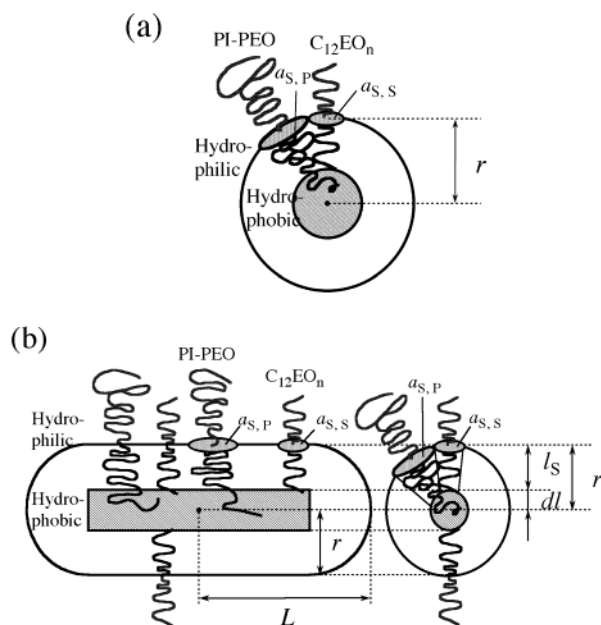
Figure 6. Schematic representation of the composite copolymer-rich micelle (a) and the rodlike micelle and its cross section (b). The inner core represents an oil pool of pure PI.
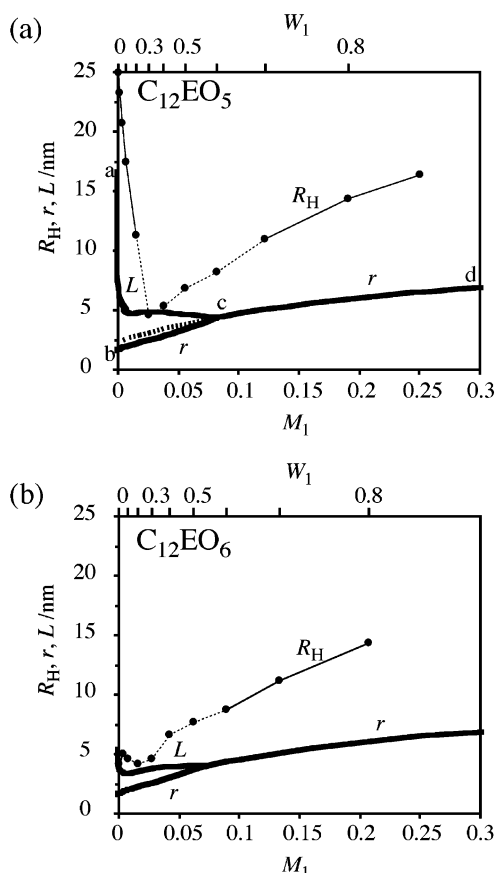

Figure 7. Change of the micellar hydrodynamic radius, R_H, as a function of the copolymer mole fraction, M_1, in a water/$C_{12}EO_5$/PI−PEO system (a) and a water/$C_{12}EO_6$/PI−PEO system (b) at 25 °C. The heavy line represents the calculated values of L and r (see Figure 6 for details).

region, because in this region of low copolymer content the radius of the micelles still exceeds the hydrocarbon chain length of the surfactant in its extended state. In the extreme case, at $W_1 = 0$, we have already noted that surfactant micelles consist of long or short rods. Hence,

in the surfactant-rich side, the rod-shaped-micelle model is applied, as it is shown in Figure 6b. In the original surfactant micelles, the radius of the cylindrical micelles, r, is assumed to be the hydrocarbon chain length in its extended state, $l_S = 1.67$ nm, derived from the Tanford equation.[18] When the copolymer is solubilized, the radius will increase because $r > l_S$ and the inner part should be filled with pure copolymers. From a simple geometrical relation of rod micelles with semisphere parts, we obtain

$$\frac{r}{L} = 3 - \frac{6\bar{v}}{\bar{a}_S r} \qquad (7)$$

where L and r are the long and short lengths of the rod micelles, respectively. The shaded area in Figure 6b is the inner pure copolymer core, whose radius is indicated by dl. Hence, $r = l_S + dl$ holds and l_S is considered to be constant. If the hydrophobic volume of the copolymer in the surfactant palisade layer is proportional to the cross-sectional area, $a_{S,S}$ or $a_{S,P}$, the radius of the inner core, dl, can be calculated from

$$dl = r\sqrt{[v_P - v_S(a_{S,P}/a_{S,S})]M_1} \qquad (8)$$

By combining eqs 7 and 8, we obtain

$$\frac{r}{L} = 3 - \frac{6\bar{v}}{\bar{a}_S l_S}\{1 - \sqrt{[v_P - v_S(a_{S,P}/a_{S,S})]M_1}\} \qquad (9)$$

Then, we can calculate the change in L and r as a function of the mole fraction of copolymer. Using eqs 5, 6, and 9, the results are shown by the curves a−c and b−c in Figure 7a. We also calculated the change in r and L in the $C_{12}EO_6$ system, and the results are shown in Figure 7b.

It is very clear that the surfactant rod micelles become spherical upon addition of a small amount of copolymer. On the surfactant-rich side, L is smaller than the hydrodynamic radius. In the real system, especially in the $C_{12}EO_5$ system, the radius of the cylinder may be shorter than $l_S = 1.67$ nm. When R_H becomes minimal, the short-rod micelles are not stable because the phase separation takes place after a while. Maybe the short axis, r, is still too short to incorporate the bulky PI chain. We need further investigation for this phase-separation phenomenon. With increasing W_1, L and r become equal and spherical micelles are formed. Then, the bulky PI chain can be incorporated into the spherical micelles and the macroscopic phase separation is prevented. It is not surprising that the difference between R_H and r increases at high W_1, because the copolymer has a very long EO_{70} chain and this part of the copolymer is not considered for the calculation (see Figure 6).

Change in the Micellar Size and Shape ($C_{12}EO_7$ and $C_{12}EO_9$ Systems). Different from the $C_{12}EO_5$ and $C_{12}EO_6$ systems, the copolymer is not solubilized into the small spherical micelles formed in the $C_{12}EO_7$ and C_{12}-EO_9 systems, and it forms its own giant micelles even at very low W_1 values, as it is shown in Figure 4, although the system is transparent and single-phase. Surfactant micelles consist of only surfactant molecules, whereas the giant micelles contain copolymer and surfactant. With increasing W_1, a decrease in the number of small micelles was observed. However, it is very difficult to detect at what mixing fraction the small micelles disappear. We assume that the small micelles coexist with the giant spherical micelles and that the micellar compositions are not changed until the small ones disappear. At higher M_1 or W_1, only giant spherical micelles seem to exist. Then,
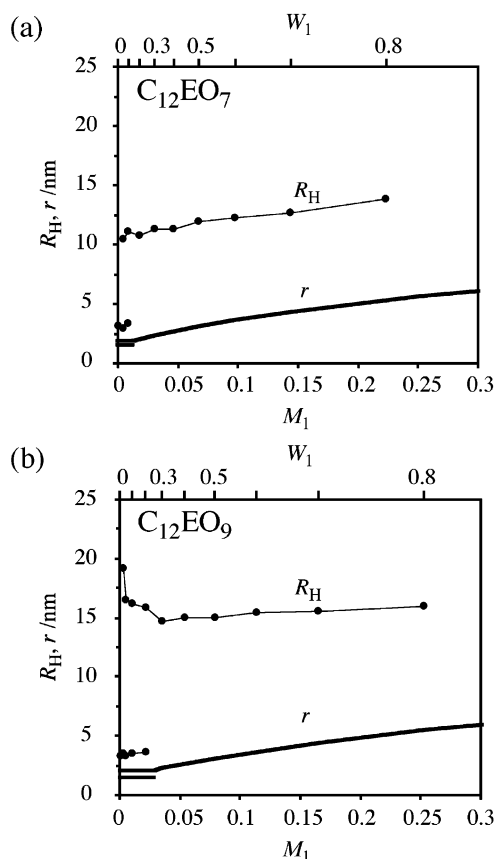
Figure 8. Change of the micellar hydrodynamic radius, R_H, as a function of the copolymer mole fraction, M_1, in a water/$C_{12}EO_7$/PI−PEO system (a) and a water/$C_{12}EO_9$/PI−PEO system (b) at 25 °C. The heavy line represents the calculated values of r (see Figure 6 for details).

we calculate the radii of both micelles, and the results are shown in Figures 8a,b.

The thick solid curves show the radii of the hydrophobic parts of the surfactant- and copolymer-rich micelles. Although there is a big difference between the observed R_H and the calculated r as a result of the neglection of the EO chain, the calculated values show a tendency similar to that of the experimental data. Hence, it is considered that the copolymer cannot dissolve the small spherical surfactant micelles, whereas surfactant dissolves in the copolymer and the composite micelles are formed even in the surfactant-rich region.

Conclusions

The ternary phase diagrams of the water/$C_{12}EO_5$/PI−PEO and the water/$C_{12}EO_9$/PI−PEO systems were constructed. PI−PEO is not soluble in the surfactant hexagonal (H_1) and lamellar (L_α) liquid crystals, which were also confirmed by SAXS measurements. PI−PEO is also insoluble in spherical micelles in aqueous solutions of $C_{12}EO_7$ and $C_{12}EO_9$, and two kinds of surfactant and copolymer micelles coexist. On the other hand, long-rod and short-rod micelles of $C_{12}EO_5$ and $C_{12}EO_6$ incorporate PI−PEO, and a rod−sphere transition takes place. In the copolymer-rich region, the copolymer forms composite micelles with the surfactant, in which the surfactant layer is formed at the interface and the long PI chain forms a core like an oil pool. Because the copolymer forms hydrophilic composite micelles with the surfactant, cloud temperatures of $C_{12}EO_{3−9}$ aqueous solutions increase upon addition of PI−PEO. In the $C_{12}EO_5$/ or $C_{12}EO_6$/PI−PEO systems, a slow macroscopic phase separation was observed in the dilute region of middle values of W_1.