Hybrid Threadlike Micelle Formation between a Surfactant and Polyelectrolyte

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Micelles, the simplest molecular architecture formed by surfactant molecules in aqueous solution, are not only of interest for physicochemical research[1] but also interesting as functional molecular assemblies because of their hydrophobic interior which can contain and transport a number of water-insoluble substances such as medicines.[2] Most micelles formed in aqueous solution are small and spherical, containing less than 100 surfactant molecules,[1] but extremely long threadlike micelles are sometimes formed in aqueous solution with and without low-molecular-weight additives.[3,4] Cetyltrimethylammonium bromide (CTAB) is one of the best known cationic surfactants that form ordinary threadlike micelles with additives such as sodium salicylate (NaSal)[5] and sodium *p*-toluenesulfonate (Na*p*TS)[6] and show profound viscoelastic behavior even in low-concentration aqueous solution. Although great efforts[7] have been made to construct threadlike micelles that contain surfactant and polymeric molecules, called *hybrid threadlike micelles*, there has been little progress.[8,9] Hybrid threadlike micelles may have greater stability against marked changes in solution properties, and their long, flexible *nanorod* structure in aqueous media suggests many possible applications. We recently found a simple way to make hybrid threadlike micelles consisting of CTAB and a polyelectrolyte. In this paper, we report the evidence for formation of these novel hybrid threadlike micelles, obtained from viscoelastic measurements and transmission electron micrographs (TEM).

There are two methods for hybrid threadlike micelle formation: mixing surfactant and polymeric molecules in solution[7,9] and polymerization of preformed polymerizable threadlike micelles.[8] We employed the former method. CTAB was used as the host surfactant molecule, and a random copolymer of styrene and sodium styrenesulfonate (P(St/NaSS)) was the guest polymer for hybrid micelles, which was prepared from anionic polymerized polystyrene (M_w = 340 000, M_w/M_n = 1.07)[10] utilizing a partial sulfonation technique.[11] The degree of sulfonation of the polymer was determined to be 0.58, using ^{1}H NMR and elementary analysis. An aqueous system, CTAB:P(St/NaSS)/W, was prepared to test hybrid threadlike micelle formation at various polymer and detergent concentrations, c_P (monomer unit) and c_D.[12]

With c_P kept at 25 mM and c_D varied from 0 to 50 mM, the shape of the system dramatically changes with c_D, as summarized in Table 1. Around c_D = 15 mM, which is essentially the isoelectric point between P(St/NaSS) and CTAB, the system becomes turbid due to segregation of precipitation and has low viscoelasticity. Increasing c_D to >15 mM makes the system clear and highly viscoelastic, whereas increasing CTAB to >25 mM markedly decreases the viscosity and relaxation time of the system. Because segregation of precipitation is common around the isoelectric point in many ionic surfactant and polyelectrolyte systems such as an aqueous system of CTAB and sodium polystyrenesulfonate,[13] the turbidity around c_D = 15 mM is apparently due to neutralization of anionic electric charges on the polymer, owing to salt-like complex formation with added CTA$^+$. On the other hand, the behavior at c_D values of >15 mM is unique to the present system. The fact that the greatest viscoelasticity of the system always occurs under conditions of $c_P \sim c_D$ strongly suggests specific long molecular assembly formation relevant to the hybrid threadlike micelle and stoichiometric (1:1) interaction between CTA$^+$ and phenyl rings of the polymer including electrically neutral St parts, which is known as *cation-π interaction*.[14]

Table 1. Turbidity and Apparent Viscoelasticity of CTAB:P(St/NaSS)/W as a Function of the c_D Value at c_P = 25.0 mM in Monomer Unit

c_D/mM	turbidity[b]	viscoelasticity[c]
0.0	c	n
2.5	c	n
5.0	c	n
7.5	o	n
10.0	t (precipitation)	n
15.0[a]	t (precipitation)	n
17.5	t	w
20.0	o	s
22.5	c	p
25.0	c	p
27.5	c	s
50.0	c	w

[a] Isoelectric point. [b] c, clear; o, opaque; t, turbid. [c] n, none; w, weak; s, strong; p, profound.

Dynamic viscoelastic behavior was examined for CTAB:P(St/NaSS)/W over an angular frequency (ω) range of 10^{-4}−10^{1} rad s^{-1} using a stress-controlled rheometer[15] at 25 °C. In Figure 1, storage and loss moduli (G' and G'') are plotted as functions of ω for the system at $c_D = c_P$ = 25 mM, as a typical example of the profound viscoelasticity of the system. The figure also contains viscoelastic spectra for an ordinary threadlike micellar system of CTAB:Na*p*TS/W at the same c_D and Na*p*TS concentration (c_S). Viscoelastic spectra for CTAB:Na*p*TS/W are described reasonably well by behavior of a simple Maxwell element with a set of relaxation time (τ) and strength (G_N);[5,6] the solid lines in Figure 1 show the behavior of the best fit Maxwell element, and some theoretical models for the simple viscoelasticity of ordinary threadlike micellar systems[5,6,16] have been proposed. Because the viscoelastic spectra for CTAB:P(St/NaSS)/W, which are very much greater than those of P(St/NaSS)/W at the same c_P as seen in Figure 1, are also described well with a Maxwell element (dotted lines in Figure 1) with a G_N value identical to that of CTAB:Na*p*TS/W[6] at the same c_D and τ much longer than that of the CTAB:Na*p*TS/W system, it is likely that both the structure of micelles and a mechanism for viscoelastic relaxation in the CTAB:P(St/NaSS)/W system are not much different from those of the ordinary threadlike micelles formed in CTAB:Na*p*TS/W.

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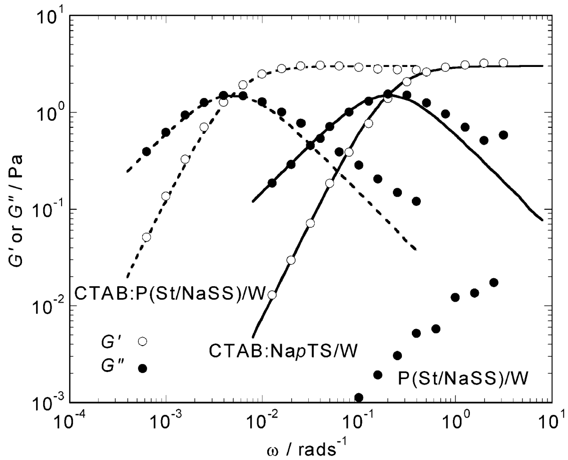

Figure 1. Dependence of storage and loss moduli (G' and G'') on frequency ω for CTAB:P(St/NaSS)/W at $c_P = c_D = 25$ mM, CTAB:Na*p*TS/W at $c_D = c_S = 25$ mM, and P(St/NaSS)/W at $c_P = 25$ mM (G'; negligibly small). Solid and dotted lines represent the best fit curves for G' and G'' calculated assuming the behavior of the Maxwell element.

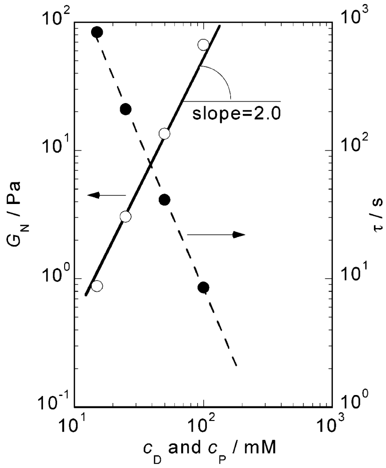

Figure 2. Relationship between relaxation strength (G_N) and time (τ) and c_P for CTAB:P(St/NaSS)/W at $c_P = c_D$.

Figure 2 shows the relationship between the values of τ and G_N, and c_D for CTAB:P(St/NaSS)/W at $c_P = c_D$, determined by the fit of the behavior of the Maxwell element. The G_N value for the system appears to be proportional to c_D,[2] as observed in CTAB:Na*p*TS/W; the solid line represents the behavior observed in CTAB:Na*p*TS/W. Because the relationship between the plateau modulus and polymer concentration found in concentrated flexible polymer systems[17] is essentially the same as observed in Figure 2, entanglement between long threadlike micelles is the cause of the profound viscoelasticity in both the CTAB:P(St/NaSS)/W and CTAB:Na*p*TS/W systems. On the other hand, the value of τ dramatically decreases with increasing c_D ($= c_P$), as seen in Figure 2; this kind of c_D dependence of τ is frequently observed in ordinary threadlike micellar systems such as CTAB:Na*p*TS/W.[6] In contrast, the longest relaxation time always increases with increasing polymer concentration in concentrated polymer systems;[17] therefore, the behavior of τ in Figure 2 is not explained by a reptation mode,[18] which seems valid for concentrated polymer systems. These findings suggest that CTAB:P(St/NaSS)/W contains highly developed entanglement networks of long hybrid threadlike micelles and that entanglement release is governed by a mechanism similar to that of ordinary threadlike micellar systems.[5,6]

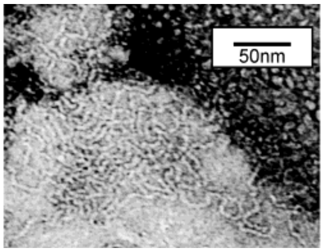

Figure 3. TEM image of CTAB:P(St/NaSS)/W at $c_P = c_D = 3.0$ mM obtained by the conventional negative staining method. Scale indicates 50 nm.

One useful method for confirmation of hybrid threadlike micelle formation in CTAB:P(St/NaSS)/W is direct observation using a cryogenic TEM technique[19] without staining and drying of specimens. At present, we only have preliminary micrographs obtained using a conventional TEM technique[20] including negative staining with an aqueous solution of uranyl acetate. Figure 3 shows a typical image of the hybrid threadlike micelles in CTAB:P(St/NaSS)/W at $c_D = c_P = 3.0$ mM. The image clearly shows flexible threadlike structures about 4−6 nm in width (roughly the micellar cross-sectional diameter similar to those of ordinary threadlike micelles[20]). The number of surfactants, CTA$^+$, included in the micellar cross section is roughly estimated to be more than 15 on the basis of argument for the structure of ordinary threadlike micelles.[21] Long length of the threadlike structures seen in Figure 3 strongly sustains hybrid threadlike micelle formation in this system.

One important reason for the successful hybrid threadlike micelle formation in CTAB:P(St/NaSS)/W without precipitation is adequate reduction of electrostatic interaction between the surfactant and polyelectrolyte using the partial sulfonation technique.[22] However, an aqueous solution of cetyltrimethylammonium chloride and a random copolymer of *n*-butylvinyl ether (BVE) and sodium styrenesulfonate does not form hybrid threadlike micelles as in CTAB:P(St/NaSS)/W at any BVE fraction, although electric charges of the polymer are controlled by the neutral BVE.[23] This suggests that the presence of St instead of BVE is another important reason for the hybrid threadlike micelle formation. Cation-π interaction between CTA$^+$ and phenyl rings of St (and SS$^-$) functions effectively to construct hybrid threadlike micelles in CTAB:P(St/NaSS)/W. Increasing CTA$^+$ to a level greater than the isoelectric point disassembles precipitated complexes, which form between CTA$^+$ and the polymer at an electrically neutral composition, via specific cation-π interaction with phenyl rings that dissolves them in water in the shape of hybrid threadlike micelles similar to that of ordinary threadlike micelles. It is obvious that a hybrid threadlike micelle in CTAB:P(St/NaSS)/W is not formed by a polymer but a great number of polymers because the length of the micelle is much longer than that of a fully extended polymer from both viscoselastic data (Figures 1 and 2) and TEM images (Figure 3). Moreover, the formed hybrid threadlike micelle seems to be a bundle of some polymers stabilized by the presence of CTA$^+$ since the cross section of micelles includes more than 15 CTA$^+$ cations, and each phenyl ring of polymers interacts with a cationic headgroup of CTA$^+$ via cation-π interaction on the surface of micelles. A partner phenyl ring of one CTA$^+$ ion due to cation-π interaction on the surface of hybrid threadlike micelles is exchanged frequently because the cation-π interaction is not as strong as the electrostatic interaction. This dynamic structural feature is apparently essential for stability of hybrid threadlike micelles in aqueous media without segregation[9] and allows polymers included in hybrid threadlike micelles to migrate randomly within the micelles. The migrational motion of each polymer within hybrid threadlike micelles will be one of the most important factors controlling a mechanism of entanglement release.

We are currently investigating the dependence of the viscoelasticity in CTAB:P(St/NaSS)/W on the molecular weight and degree of sulfonation of the polymer and also on additive salt concentrations to clarify the precise condition of the hybrid threadlike micelle formation and the essential mechanism of entanglement release in this hybrid threadlike micellar system.

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