Viscoelastic Behavior of Aqueous Hybrid Threadlike Micellar Solution

Kenji Nakamura and Toshiyuki Shikata*

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

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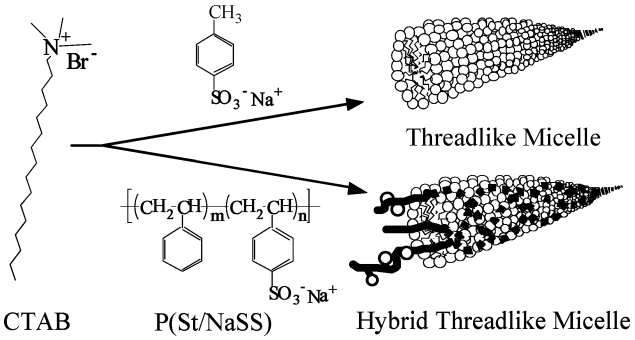
ABSTRACT: We examined the viscoelastic behavior of an aqueous hybrid threadlike micellar solution consisting of cetyltrimethylammonium bromide (CTAB) and random copolymers of styrene and sodium styrenesulfonate at the same molar concentration of total monomer units as CTAB. The micelles formed in such solutions are enormously long, flexible, stable structures that entangle so much as to exhibit profound viscoelastic behavior approximately described by the behavior of a Maxwell element with one set of relaxation time (τ) and strength (G_N). The degree of sulfonation (X_S) of the incorporated polymers affected τ and G_N values, and the concentration ([Br^-]*) of excess bromide anions in the system markedly affected τ and G_N values. Under conditions of constant [Br^-]* and X_S, τ is approximately proportional to the molecular weight of incorporated polymers, and G_N is proportional to the square of the polymer concentration in the system, as observed in ordinary entangled polymer systems.

Introduction

Micelles are simple molecular associations of surfactant molecules in aqueous solution. Their formation is mainly the result of hydrophobic interaction between the tail regions of the surfactant molecules above critical micelle concentrations (cmc's), which vary among species of surfactants. Micelles are common subjects of physicochemical research.[1] Also of interest is their potential as functional molecular assemblies for use in practical applications because water-insoluble substances (including certain medicines) can be contained in their hydrophobic interior.[2] Typically, micelles that form in aqueous solution are small and spherical, containing less than 100 surfactant molecules. However, micellar shape can be highly sensitive to solution conditions such as the concentration of the surfactant, temperature, presence of additive salts, and pH.[1] In some studies, extremely long threadlike micelles have formed in aqueous solution with and without low-molecular-weight additives (Scheme 1).[3] The cationic surfactant cetyltrimethylammonium bromide (CTAB) is one of the best known of the cationic surfactants that form ordinary threadlike micelles with additives such as sodium salicylate (NaSal)[4,5] and sodium *p*-toluenesulfonate (Na*p*TS)[6,7] and exhibit markedly viscoelastic behavior even in low-concentration aqueous solution. Physicochemical features including dynamics and micellar structure of highly viscoelastic threadlike micellar systems have been investigated using a number of relaxation techniques such as viscoelastic relaxation,[4−7] dielectric relaxation,[8,9] fluorescence anisotropy relaxation,[10,11] and nuclear magnetic resonance (NMR) measurements.[12] Structural information about threadlike micelles has been obtained using transmission electron microscopy (TEM), light microscopy,[13,14] and small-angle X-ray and neutron scattering measurements.[15]

Recently, there has been great progress in efforts to construct hybrid threadlike micelles containing surfactant and polymeric molecules (Scheme 1).[16−21] Two methods for formation of hybrid threadlike micelle have been developed: polymerization of preformed polymerizable threadlike micelles[18,19] and mixing of surfactant and polymeric molecules in solution.[16,17,20,21] Kline[18,19] reported the construction of hybrid threadlike micelles in aqueous solution of the polymerizable surfactant monomer cetyltrimethyl *p*-vinylbenzoate (CTAVB). He first made polymerizable threadlike micelles of CTAVB in aqueous solution and then polymerized them to obtain short hybrid threadlike micelles.[18,19] We recently found that sodium poly(*p*-vinylbenzoate) (P(NaBV)) interacts with CTAB to form fully elongated hybrid threadlike micelles in aqueous solution at pH values <4.[20] In a previous study, we found another way to make hybrid threadlike micelles consisting of CTAB and a polyelectrolyte, using CTAB as the host surfactant molecule and using a random copolymer of styrene and sodium styrenesulfonate (P(St/NaSS)) as the guest polymer. The P(St/NaSS) was prepared from anionic polymerized monodisperse polystyrene with a molecular weight of $M_n = 3.4 \times 10^5$ and a sharp molecular weight distribution of $M_w/M_n = 1.07$, using a random sulfonation technique.[22] The resulting micellar system exhibits marked viscoelastic behavior that is well described by the behavior of a Maxwell element with one set of relaxation time and strength, as observed in ordinary aqueous threadlike micellar systems[4−7] consisting of CTAB and NaSal or NapTS. These findings strongly suggest that long, stable hybrid threadlike micelles form in the system and become highly entangled as in concentrated polymer systems. The presence of enormously long threadlike micelles was also confirmed by transmission electron micrography.[21] Both P(St/NaSS)

Scheme 1



* Corresponding author: Tel/Fax +81-6-6850-5538; e-mail shikata@chem.sci.osaka-u.ac.jp.

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and PVB can form hybrid threadlike micelles with CTAB in aqueous solution, and both possess the following two properties: when the polymers form hybrid threadlike micelles, electric charges on them are effectively decreased by a pH of <4 or a degree of sulfonation (X_S) of <0.7, and they both bear phenyl rings that can generate weak intermolecular cation−π interactions with surfactant headgroup cations on the surface of micelles.

In this paper, we describe general viscoelastic properties of the aqueous hybrid threadlike micellar system consisting of CTAB and P(St/NaSS) over a wide range of molecular weight, M_n, and degree of sulfonation, X_S. The values of relaxation time and strength of this system are highly dependent on M_n and X_S of the polymers and the presence of dissociated additive bromide ions. A primary mechanism of entanglement release in this hybrid threadlike micellar system is discussed along with the modification of a phantom-crossing model that is applicable to ordinary threadlike micellar systems.

Experimental Section

Materials. CTAB was purchased from Wako Pure Chemicals (Osaka) and was purified by recrystallization from a mixture of methanol and acetone. Sodium chloride (NaCl) and sodium bromide (NaBr) were purchased from Wako Pure Chemicals and used without further purification. The polystyrenes (PSs) used as precursors for the preparation of P(St/NaSS) were anionically polymerized. A PS with the M_n of 3.3 $\times$ 10^4 and M_w/M_n of 1.03 was supplied by Polymer Source Inc. (Montreal), and a PS with the M_n of 3.4 $\times$ 10^5 and M_w/M_n of 1.07 was supplied by TOSOH (Tokyo). A PS with the M_n of 8.2 $\times$ 10^5 and M_w/M_n of 1.10 was obtained by living anionic polymerization initiated by 2-methylbutyllithium. Deuterated dimethyl sulfoxide (DMSO-d_6) was purchased from Isotec Inc. (Cambridge) and used as the solvent for NMR measurements. Highly deionized water with specific resistance of >16 MΩ cm, obtained using a Milli-Q system (Japan Millipore, Tokyo), was used as the solvent for sample preparation.

P(St/NaSS) samples were produced from the PSs using the method of partial sulfonation by acetylsulfonic acid proposed by Makowski.[22] The degree of sulfonation (X_S) of the polymer samples was controlled by adding acetylsulfonic acid. The resultant partially sulfonated polymers were obtained in acid form and were neutralized using an aqueous sodium hydroxide solution, followed by dialysis against water (pH = 9) for more than 5 days. Although one of the obtained polymers with the M_n of 3.4 $\times$ 10^5 and X_S of 0.25 was water insoluble, we forced to dialyze it against water to remove impurity as much as possible. Finally, the P(St/NaSS) samples were obtained in powder form by freeze-drying. The value of X_S was determined using proton nuclear magnetic resonance (^{1}H NMR) measurements and elementary analysis. The X_S values obtained using these two methods were in good agreement with each other, and the X_S value determined by ^{1}H NMR is used in the Discussion below (Table 1).

Aqueous systems (CTAB:P(St/NaSS)/W) containing CTAB and P(St/NaSS) at several different concentrations were used to produce hybrid threadlike micellar systems with different general viscoelastic features. In these solutions, the concentrations of total monomer units (styrene and styrenesulfonate) of P(St/NaSS) (c_P) and CTAB (c_D) were equal (i.e., $c_D = c_P$) and ranged from 15 to 100 mM. Samples of CTAB:P(St/NaSS):NaBr/W and CTAB:P(St/NaSS):NaCl/W, containing additive NaBr and NaCl, respectively, were prepared with concentrations of the additive salt (c_S) ranging from 0 to 25 mM.

Methods. ^{1}H NMR measurements were performed using an NMR spectrometer (EX-270, JEOL, Tokyo) operated at a resonance frequency of 270 MHz in deuterium-locked mode. The sample temperature was kept constant at 30 °C for measurements. Gel permeation chromatography (GPC) was performed to determine the molecular weights of the precursor PSs using an LS-800 GPC system (Tosoh, Tokyo) equipped with doubly connected columns (Shodex Asahipack, Showadenko, Tokyo). The carrier solvent for GPC was tetrahydrofuran (THF), and the elution volume of the GPC system was calibrated with commercially available molecular weight standard polystyrenes.

Table 1. Degree of Sulfonation, X_S, of the Used Polymers, P(St/NaSS)s, Determined by Two Different Methods, NMR and Elementary Analysis

	X_S	
$M_n/10^3$	NMR	elementary analysis
33	0.41	0.44
	0.50	0.54
	0.55	0.55
	0.74	0.74
340	0.23	0.25
	0.38	0.40
	0.53	0.51
	0.56	0.58
	0.74	0.74
820	0.38	0.40
	0.47	0.45
	0.53	0.50
	0.83	0.84

Dynamic viscoelastic measurements were performed using a stress-controlled rheometer (DynAlyser 100, ReoLogica, Lund) equipped with a cone−plate geometry with a diameter of 40 mm and cone angle of 4°. Storage and loss moduli, G' and G'', of the linear viscoelastic regime were determined as functions of angular frequency (ω), which ranged from 2.51 $\times$ 10^{-4} to 6.28 $\times$ 10^2 rad s^{-1}, mainly at 25 °C.

The concentration of dissociated bromide ions ([Br$^-$]*) was determined using a Br$^-$-selective electrode (8005-10C, Horiba, Kyoto) and a handmade Ag−AgCl reference electrode connected to a salt bridge of aqueous 3% agar containing 1.0 M KCl. Electric potential generated between the electrodes was recorded with a pH meter (F-22, Horiba, Kyoto) and was calibrated using standard aqueous KBr solutions with different concentrations prior to [Br$^-$]* measurements.

Results

When the c_P value is kept at 25 mM, the shape of the system dramatically changes with changes in c_D, as summarized in Table 1 of a previous paper.[21] At c_D values of approximately 15 mM, which is essentially the isoelectric point between CTAB and the polymer with the X_S of 0.58 and M_n of 3.4 $\times$ 10^5, the system becomes turbid due to precipitation and has a low viscoelasticity. Increasing c_D to >15 mM causes the system to become clear and highly viscoelastic, and the system exhibits its greatest viscoelasticity and longest relaxation time at the c_D of 25 mM, whereas increasing CTAB, c_D, to >25 mM markedly decreases the viscoelasticity of the system.[21] Because precipitation is common around the isoelectric point in all CTAB:P(St/NaSS)/W systems, irrespective of the values of X_S and M_n as observed in many ionic surfactant and polyelectrolyte systems,[23−25] the above-mentioned turbidity is apparently due to neutralization of electric charges on the polymer as a result of formation of salt-like complexes with added CTA$^+$. The fact that, regardless of which polymers are used, the greatest viscoelasticity of the system always occurs at $c_P \approx c_D$ suggests the formation of long hybrid threadlike micelles and specific stoichiometric (1:1) interaction between CTA$^+$ and phenyl rings of the polymer including electrically neutral St regions, i.e., cation−π interaction.[21,26−28] Accordingly, we mainly investigated the viscoelastic behavior of the aqueous

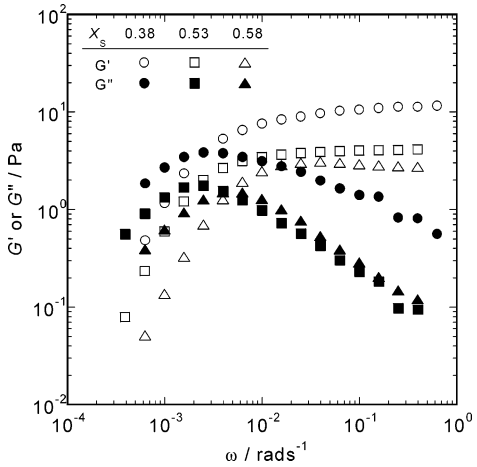


Figure 1. Dependencies of storage and loss moduli (G' and G'') on frequency ω for CTAB:P(St/NaSS)/W containing polymers with the $M_n = 3.4 \times 10^5$ and several X_S values under the condition of $c_P = c_D = 25$ mM.

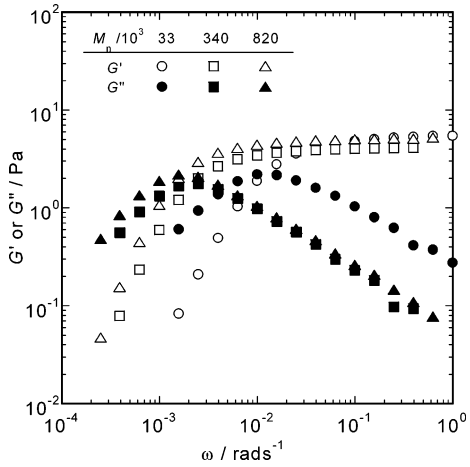


Figure 2. Dependencies of G' and G'' on ω for CTAB:P(St/NaSS)/W containing polymers with several M_n values under the condition of $c_P = c_D = 25$ mM and $X_S = 0.50-0.53$.

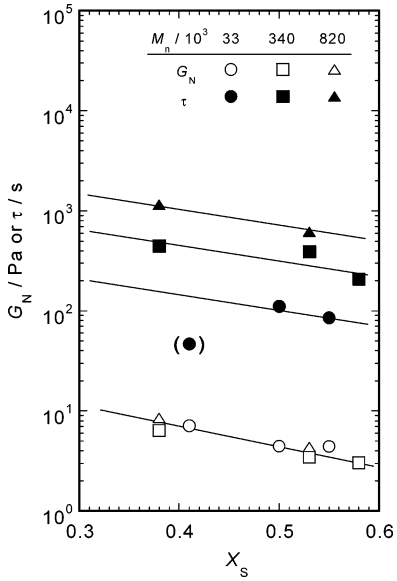


Figure 3. Dependencies of the G_N and τ values on X_S for the CTAB:P(St/NaSS)/W system containing polymers with several M_n under the condition of $c_P = c_D = 25$ mM. The parenthesized data for the solution containing a polymer with the $M_n = 3.3 \times 10^4$ and $X_S = 0.41$ has much lower activation energy for viscoelasticity than those of other solutions.

hybrid threadlike micellar system CTAB:P(St/NaSS)/W, under conditions of $c_P = c_D$.

Figure 1 shows the dependencies of storage and loss moduli, G' and G'', on frequency, ω, for the CTAB:P(St/NaSS)/W system containing a polymer with the M_n of 3.4×10^5, X_S ranging from 0.38 to 0.58, and c_P and c_D of 25 mM. It clearly shows that viscoelastic spectra (G' and G'' vs ω) for solutions with X_S of 0.53 and 0.58 are approximately described by a Maxwell element possessing one set of relaxation time (τ) and strength (G_N). Because the viscoelastic spectra for the system with X_S of 0.38 are slightly dependent on sample handling (i.e., method of loading the sample on a rheometer), the stability of the resultant hybrid threadlike micelles is likely to be lower than that of solutions with higher X_S. The fact that the slope of a G'' curve at higher ω values is slightly weaker for the system with X_S of 0.38 than systems with higher X_S may be related to the lower stability of the hybrid threadlike micelles that form in the former system. Such instability of hybrid threadlike micelles was also observed in the system containing polymers with the M_n of 8.2×10^5 and X_S of 0.38 and the system containing polymers with the M_n of 3.3×10^4 and X_S of 0.41.

The relaxation time, τ, of the system is precisely determined as the reciprocal of the maximum frequency of the G'' curve. On the other hand, the value of G_N is evaluated as the plateau value of the G' curve in a higher ω range. Results indicate that with increasing c_P ($=c_D$) the value of τ decreases, whereas G_N slightly increases. Similar viscoelastic spectra were obtained for systems with different values of X_S and M_n.

Figure 2 shows viscoelastic spectra for CTAB:P(St/NaSS)/W systems of polymers with the following values: $M_n = 3.3 \times 10^4$, 3.4×10^5, 8.2×10^5; $X_S = 0.5$, 0.53, 0.53; $c_P = c_D = 25$ mM. When the value of X_S ranges from 0.50 to 0.53, the values of G_N for the system appear to be independent of M_n, whereas the values of τ increase with increasing M_n. Moreover, the shapes of ω dependencies of G' and G'' resemble those of the Maxwell model irrespective of M_n.

In Figure 3, to examine the relationship between the values of τ and G_N and the values of M_n and X_S, data obtained for the system at a c_D ($=c_P$) of 25 mM are plotted as functions of X_S. The values of τ slightly decrease with increasing X_S for all samples regardless of M_n. The finding that the solution with the X_S of 0.41 and M_n of 3.3×10^4 (data in parentheses in Figure 3) has a rather lower activation energy than other solutions suggests that the structure and relaxation mechanism of hybrid threadlike micelles that formed in this solution are slightly different from those of other solutions. Therefore, we have omitted the data for this solution from our discussion of the entanglement release mechanism of these systems. The G_N values that appear to be independent of M_n are decreased by increasing X_S (Figure 3). Because τ and G_N are highly dependent on the concentration of freely dissociated Br^- anions ($[Br^-]^*$) in the system, as described below, we will discuss τ and G_N as functions of $[Br^-]^*$. It is important to note that the system maintains a nonzero value of $[Br^-]^*$ even under conditions of $c_D = c_P$ without added salt ($c_S = 0$ mM).

The slope of the G'' curve against ω in a double-logarithmic plot can be considered a measure of the distribution of relaxation times; as the slope approaches

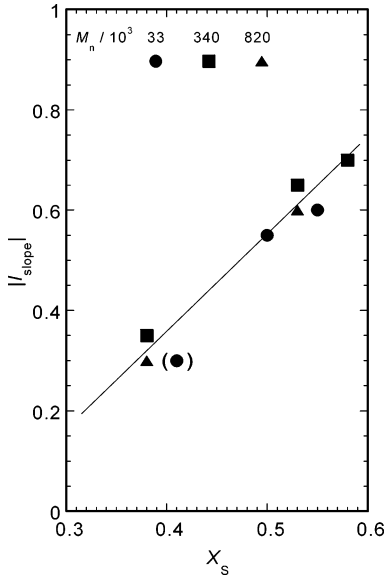


Figure 4. Relationship between a measure of the distribution of relaxation times, $|I_{slope}|$, the absolute value of a slope between G'' and ω in a high ω side in a double-logarithmic scale, on X_S for the CTAB:P(St/NaSS)/W system containing polymers with several M_n under the condition of $c_P = c_D = 25$ mM. The parenthesized data has much lower activation energy for viscoelasticity than those of other solutions.

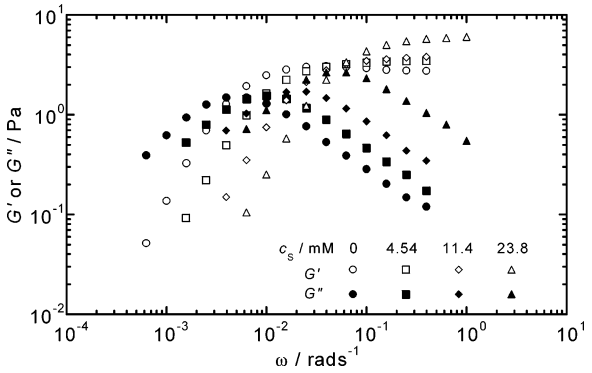


Figure 5. Dependence of G' and G'' on ω for CTAB:P(St/NaSS):NaBr/W containing a polymer with the $M_n = 3.4 \times 10^5$ and $X_S = 0.58$ under the condition of $c_P = c_D = 25$ mM.

minus unity (the value for the Maxwell element), the distribution of relaxation time becomes sharper. In Figure 4, the absolute values of slopes ($|I_{spole}|$) of G'' curves against ω in a double-logarithmic plot for the system with a c_D (=c_P) of 25 mM are plotted as functions of X_S. The figure clearly shows that the distribution of relaxation time becomes sharper as X_S increases. The highest X_S value at which hybrid threadlike micelles can form from CTAB in aqueous solution is approximately 0.7, indicating that a polymer at $X_S > 0.7$ will precipitate at CTAB concentration, c_D, around and higher than the isoelectric point which is not far from the polymer concentration, c_P.

Figure 5 shows the effects of added NaBr on the viscoelastic behavior of the CTAB:P(St/NaSS)/W system. The value of τ dramatically decreases with increasing concentration of NaBr, c_S, whereas the value of G_N increases with c_S. The c_S dependence of viscoelasticity shown in Figure 5 is similar to that of the CTAB:P(St/NaSS):NaCl/W system containing NaCl. However, NaBr has slightly greater effects on τ and G_N than does NaCl. It is clear that Na^+, Br^-, and Cl^- markedly affect the viscoelasticity of these systems. The effects of

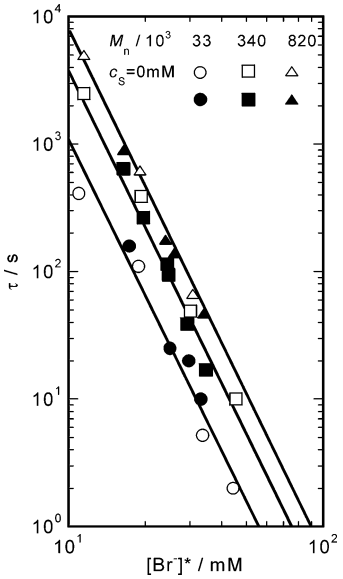


Figure 6. Relationship between τ and $[Br^-]^*$ for systems of CTAB:P(St/NaSS)/W, open symbols, and CTAB:P(St/NaSS):NaBr/W, closed symbols, containing several M_n values under the condition of $X_S = 0.50-0.53$.

specific ions on τ and G_N in these systems are described below.

Figure 6 shows the relationship between τ and $[Br^-]^*$ for CTAB:P(St/NaSS)/W (open symbols) and CTAB:P(St/NaSS):NaBr/W (closed symbols) systems with various M_n values, c_P (=c_D) ranging from 15 to 60 mM, and X_S of 0.50−0.53. The data of the CTAB:P(St/NaSS)/W system (which does not contain the contribution of Na^+ from added NaBr) forms three straight lines similar to those formed by the data obtained as a function of $[Br^-]^*$ depending on the value of M_n, indicating that the essential ion that determines τ is not Na^+ but Br^-. It appears that the slope of τ vs $[Br^-]^*$ in Figure 6 is not altered by changes in M_n or c_P (=c_D). A similar relationship between τ and $[Br^-]^* + [Cl^-]^*$, in which slopes are slightly shallower than those for CTAB:P(St/NaSS):NaBr/W (data not shown), was obtained for CTAB:P(St/NaSS):NaCl/W. Thus, we conclude that the essential ions that determine τ are the anions Br^- and Cl^-.

Given the above findings, when we consider the relationship between τ and M_n for the systems of CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W, we should compare data at a constant $[Br^-]^*$ value such as 10 mM. Figure 7 shows the relationship between τ and M_n for systems with a $[Br^-]^*$ of 10 mM. It appears that τ is approximately proportional to M_n, with an intercept that is highly dependent on $[Br^-]^*$. The presently observed proportionality between τ and M_n is quite a unique relationship and has never previously been observed in entangled systems. The present finding that τ is function of only M_n, irrespective of c_P (=c_D) at a constant $[Br^-]^*$, is one of the unique characteristics of this hybrid threadlike micellar system.

The magnitude of efficiency of $[Br^-]^*$ on τ, which can be evaluated from the slope (T_{slope}) of the relationship between τ and $[Br^-]^*$ in a double-logarithmic scale for polymers with the X_S of 0.50−0.53, is a function of X_S (Figure 6). Figure 8 shows the relationship between the absolute value of T_{slope}, $|T_{slope}|$, and X_S for the hybrid threadlike micellar systems CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W, containing polymers with different M_n. The efficiency, $|T_{slope}|$, appears to decrease

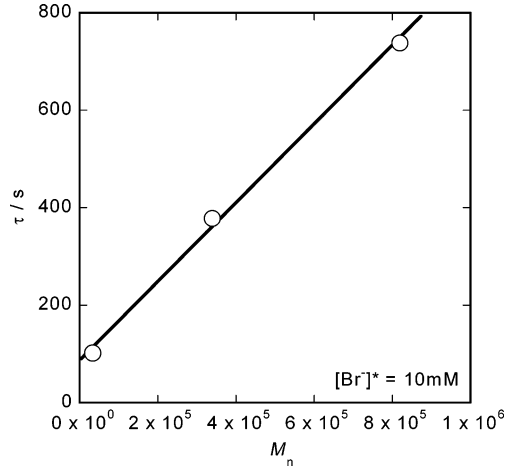


Figure 7. Dependence of τ on M_n at $[Br^-]^* = 10$ mM for systems of CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W under the condition of $X_S = 0.50-0.53$.

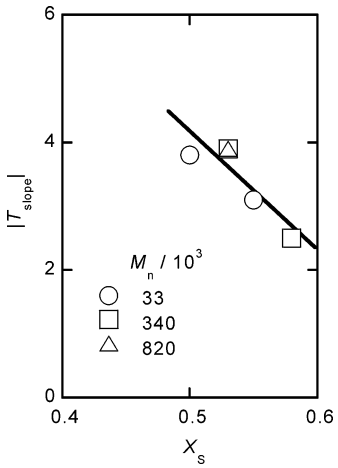


Figure 8. Dependence of $|T_{slope}|$ on X_S for the systems of CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W under the condition of $c_P = c_D$.

when X_S is increased. A possible reason for this behavior, which is discussed below, is interaction exchange between cation$-\pi$ and electrostatic interaction caused by the presence of freely dissociated Br^-. In sample solutions of the system containing polymers at lower X_S values such as 0.41, segregation was precipitated at additive salt concentrations of $c_S > 5$ mM. Thus, we were not able to determine the $|T_{slope}|$ for the system at $X_S < 0.41$.

The magnitude of the plateau modulus, G_N, is also a marked function of the concentration of freely dissociated Br^-, $[Br^-]^*$, even with constant M_n and X_S (Figure 5). The relationship between G_N and $[Br^-]^*$ is shown in Figure 9a for CTAB:P(St/NaSS)/W (open symbols) and CTAB:P(St/NaSS):NaBr/W (closed symbols) systems containing polymers with varying M_n at X_S values of 0.50−0.53. All data obtained with the same c_P ($=c_D$) value forms distinct straight lines that depend on c_P, with similar slopes irrespective of the presence of Na^+ and the M_n value (Figure 9a). Because we obtained G_N data only for a c_S value of 0 mM for the system at the c_P ($=c_D$) ≥ 40 mM, the lines with the same slope as that of the system at the c_P ($=c_D$) of 15 and 25 mM are drawn. These findings show that, with constant X_S and $[Br^-]^*$ values, the magnitude of G_N is mainly dependent on the value of c_P ($=c_D$). Figure 9b shows the relationship between G_N and c_P ($=c_D$) for systems with a $[Br^-]^*$ of

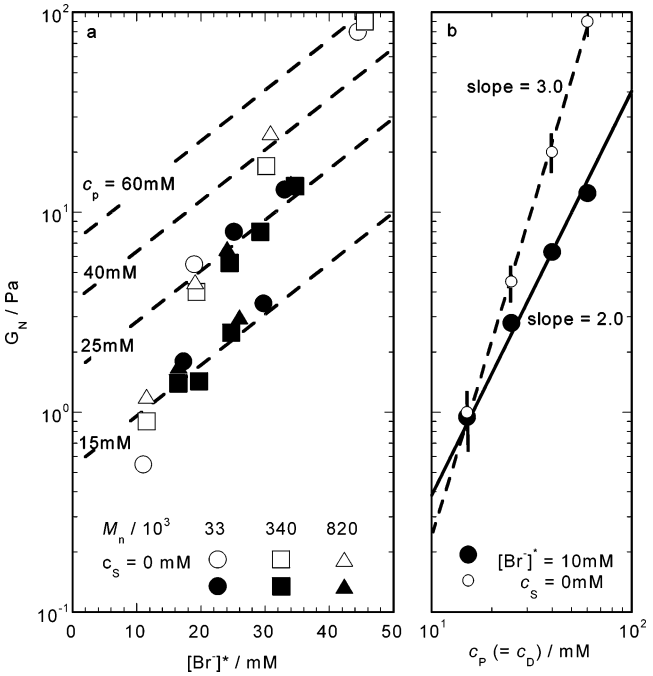


Figure 9. (a) Dependence of G_N on $[Br^-]^*$ for the systems of CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W under the condition of $X_S = 0.50-0.53$. (b) Relationship between G_N and c_P ($= c_D$) at $[Br^-]^* = 10$ mM and $c_S = 0$ mM for the system seen in Figure 9a.

10 mM in a double-logarithmic scale. The G_N values for the system at the c_S of 0 mM (i.e., CTAB:P(St/NaSS)/W) are also plotted in Figure 9b as references without considering the contribution of the presence of Br^- in the bulk aqueous phase. The slope of the line plotting G_N data at the $[Br^-]^*$ of 10 mM in Figure 9b is 2.0, which is equal to the value observed previously for ordinary entangled polymer systems.[29] These findings strongly suggest that the main mechanism of the elasticity of the CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W systems is entanglement between the long hybrid threadlike micelles, which is also the main mechanism of the elasticity of entangled polymer systems and ordinary threadlike micellar systems. Because the slope of G_N data for the c_S of 0 mM is much higher than 2.0, precise determination of the effects of c_P on G_N requires maintenance of a constant $[Br^-]^*$ value (Figure 9b).

The magnitude of efficiency of $[Br^-]^*$ to G_N for the hybrid threadlike micellar system is also a function of the value of X_S. The slope of the line (M_{slope}) in Figure 9a appears to be a measure of the magnitude of the efficiency of $[Br^-]^*$ to G_N. Figure 10 shows the relationship between the absolute value of M_{slope}, $|M_{slope}|$, and X_S for CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W systems at several different M_n values. It appears that the $|M_{slope}|$ value decreases as X_S increases, which is similar to the relationship between $|T_{slope}|$ and X_S in Figure 8. In a previous study, the slope of G_N for the system containing a polymer at the X_S of 0.58 and c_S of 0 mM appears to be close to 2.0.[21] This previous finding is relevant to the present finding that the efficiency of $[Br^-]^*$ to G_N in the system containing the polymer at the $X_S > 0.58$ is much lower than that in the system with the X_S of 0.5−0.53. As described above, in systems containing polymers at the $X_S < 0.41$, segregation occurred when NaBr was added. Thus, the value of $|M_{slope}|$ could not be determined for samples

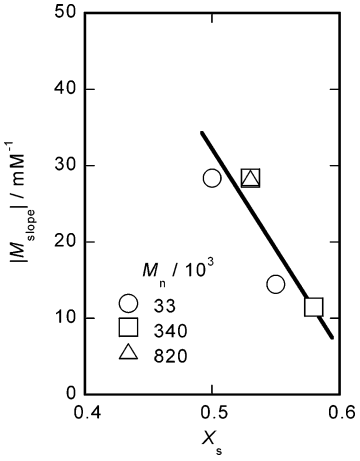
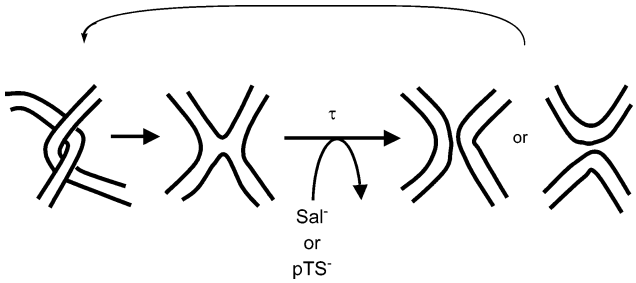


Figure 10. Dependence of $|M_{slope}|$ on X_S for the systems of CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W under the condition of $c_P = c_D$.

Scheme 2



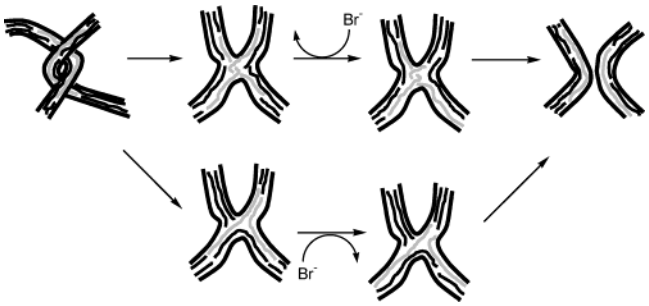
with the $X_S < 0.41$. According to the classical theory of rubber elasticity,[29] the magnitude of G_N is proportional to the number density of entanglements in the system. In the CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W systems, the value of G_N is markedly altered by increases in $[Br^-]^*$, even with constant c_P ($=c_D$), as described above. This suggests that the flexibility of hybrid threadlike micelles depends on the value of $[Br^-]^*$ to such a degree that $[Br^-]^*$ influences the number density of entanglements.

Discussion

Entanglement Release Mechanism in Hybrid Threadlike Micellar Systems. In ordinary threadlike micellar systems such as CTAB:NaSal/W or CTAB:Na*p*TS/W, the entanglement release mechanism, which exhibits simple Maxwell element type viscoelasticity, is well explained by a phantom crossing model[4−7] in which entanglement between two distinctive ordinary threadlike micelles is assumed to occur via a crossing-through reaction after a lifetime equal to the (mechanical) relaxation time, and the entanglement point generates individual threadlike micelles just like the crossing-through behavior of phantoms. Moreover, the relaxation time is highly dependent on the concentration of freely dissociated Sal^- or pTS^- ions in the bulk aqueous phase.[4−7] Hence, the anions Sal^- and pTS^- act as catalytic agents for the crossing-through reaction in the ordinary threadlike micellar system. The relaxation process of the phantom crossing model for the ordinary threadlike micellar system described above is schematically depicted in Scheme 2.

In hybrid threadlike micellar systems such as CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W, which also exhibit Maxwell element type viscoelasticity, there

Scheme 3

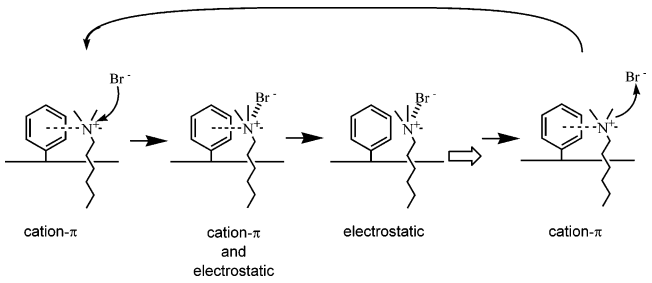


are no dissociated Sal^- or pTS^- ions acting as catalytic agents, unlike the case with the ordinary threadlike micellar system. However, the present finding that τ is considerably influenced by $[Br^-]^*$ indicates that Br^- acts as a catalytic agent in place of Sal^- or pTS^- in the hybrid threadlike micellar systems (Figure 6). The findings suggest that the mechanism by which Br^- accelerates the entanglement release process in the hybrid threadlike micellar system is possibly rather different from that by Sal^- or pTS^- in the ordinary threadlike micellar system. From the phenomenological sense, the relationship between τ and $[Br^-]^*$ observed in the hybrid threadlike micellar systems is essentially identical with that between τ and $[Sal^-]^*$ or $[pTS^-]^*$ for the ordinary threadlike micellar systems,[4−7] except for detailed exponent values.

Another possible theoretical model for the explanation of the unique viscoelastic behavior of the ordinary threadlike micellear system has been proposed by Cates et al.[30−32] In the Cates model, the value of τ is expressed in the form of power law of c_D or the volume fraction (ϕ) of micelles, and the model appears to work successfully in some ordinary threadlike micellar systems.[3] However, the value of τ in the hybrid threadlike micellar system is governed by neither c_D nor ϕ, but only by $[Br^-*]$ as recognized in Figure 6. Consequently, it does not make sense to apply the Cates model for the explanation of unique viscoelastic behavior of the hybrid threadlike micellar systems obtained in this study.

When considering the entanglement release mechanism of hybrid threadlike micellar systems based on the essence of the phantom crossing model, one should take into account the effects of the polymers, P(St/NaSS), contained in the micellar interior, as schematically depicted by Scheme 3. In the cross section of hybrid threadlike micelles shown in Scheme 3, only two polymer molecules are shown for simplicity, although it is likely that several polymer molecules are present at any cross section. When two hybrid threadlike micelles approach to form an entanglement, they merge at a tentative entanglement point. Then, several other pairs of polymers form additional entanglements at the tentative entanglement point and/or some polymers pass through the entanglement point. The passing of a polymer through the tentative entanglement point over two distinct hybrid threadlike micelles generates a new crossing-through reaction and lengthens the relaxation time, τ; this process is necessary for entanglement release in the hybrid threadlike micellar system. The diffusivity of polymer molecules contained in hybrid threadlike micelles due to Brownian motion essentially determines polymer migration in hybrid threadlike micelles. Under certain conditions, polymer migration at the tentative entanglement point is the rate-determining process for the entire relaxation. It is likely that

Scheme 4



the time necessary for a polymer positioned across a tentative entanglement point to escape from the region of the entanglement point is related to the entire relaxation time, τ.

Unfortunately, there is no realistic model that can explain the present proportionality in the relationship between τ and M_n. On the other hand, when a lower molecular weight polymer with a contour length not sufficiently long for it to be positioned across a tentative entanglement point is contained in hybrid threadlike micelles, the presence of the polymer at the tentative entanglement point is not a particularly important factor in the entire relaxation process. In that case, the relaxation time, τ, becomes a constant value irrespective of M_n, just as in the ordinary threadlike micellar systems.

Contribution of Cation−π Interaction in Viscoelastic Behavior. In the present hybrid threadlike micellar systems, CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W, electrostatic interaction between CTA^+ and the electrolyte, SS^-, is sufficiently low for the formation of hybrid threadlike micelles. However, the system contains weak intermolecular interaction between CTA^+ and both neutral and electrolyte regions, St and SS^-, known as the cation−π interaction. The importance of the cation−π interaction for the hybrid threadlike micelle formation cannot be ignored since the two polymers[20,21] forming hybrid threadlike micelles with CTAB contain both electrically neutral and anionic phenyl rings such as St, SS^-, *p*-vinylbenzoic acid, or *p*-vinylbenzoate and the molar ratio between CTAB and the total of phenyl ring regions is always close to unity when hybrid threadlike micelles form at the greatest viscoelasticity. Recently, the cation−π interaction has been recognized as important intermolecular interaction widely and has been considered to be the fourth interaction for the construction of second and third protein structure.[26−28] We show speculative interpretation based on the idea concerned in the cation−π interaction for the dependence of T_{slope} on X_S (Figure 8) for the present hybrid threadlike micellar systems below.

Cation−π interaction between a dissociated CTA^+ cation and a St region on the surface of hybrid threadlike micelles may change the interaction partner of CTA^+ from St to a Br^- anion, which approaches from the bulk aqueous phase to the micellar surface and remains there because the electrostatic interaction is much stronger than the cation−π interaction. This kind of interaction exchange between electrostatic and cation−π interaction would allow the polymer contained in the hybrid threadlike micelle to migrate at a higher diffusion constant because it easily unfastens *snap hooks* generated between CTA^+ and St. During the time that Br^- is involved in the interaction exchange, a St region becomes free and obtains higher mobility or diffusivity, as schematically depicted in Scheme 4. This effect of increasing the diffusivity of polymers contained in hybrid threadlike micelles due to the interaction exchange resulting from the collision of Br^- with the surface of micelles should be stronger at higher values of $[Br^-]^*$ and the fraction of neutral St parts, $1 - X_S$. Hence, the X_S dependence of the efficiency, T_{slope}, for τ of $[Br^-]^*$, in which T_{slope} decreases with increasing value of X_S, is qualitatively explained by the interaction exchange process described above (Figure 8).

The results of $[Br^-]^*$ measurements indicate that the surface of hybrid threadlike micelles is always slightly positively charged; ca. 20% of Br^- ions are dissociated from CTAB interacting with electrically neutral St regions in the hybrid threadlike micelle irrespective of both M_n and X_S of polymers. If the electrostatic shielding effect caused by the presence of Br^- is the main reason for the enhancement of G_N, the value of G_N should decrease with increasing $[Br^-]^*$, which is not the case in the present hybrid threadlike micellar system. General polyelectrolyte studies[33] indicate that the rigidity of threadlike substances due to repulsive interaction among electric charges on their surface is effectively reduced by the electric shielding effect caused by the presence of additive salts. Thus, the entanglement density decreases with decreasing rigidity of threadlike substances in general. In the present study, the value of G_N always increased with increasing $[Br^-]^*$ (Figure 9a), indicating that the electrostatic shielding effect is less important for enhancement of G_N in the present hybrid threadlike micellar system.

Concluding Remarks

In the present study, hybrid threadlike micelles formed in an aqueous solution of a cationic surfactant, CTAB, and random copolymers of styrene and sodium styrenesulfonate, P(St/NaSS)s. The CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W systems exhibited marked viscoelasticity due to entanglement between these hybrid threadlike micelles, the viscoelasticity of which is well described by the simple behavior of a Maxwell element with one set of relaxation time, τ, and strength, G_N.

The viscoelastic variables, τ and G_N, of the hybrid threadlike micellar systems CTAB:P(St/NaSS)/W and CTAB:P(St/NaSS):NaBr/W are affected in a complex fashion by the degree of sulfonation of polymers, X_S, the concentration of freely dissociated Br^- ions, $[Br^-]^*$, and the molecular weight of the incorporated polymer, M_n, even with constant polymer concentration, c_P. When X_S is maintained at a constant value, the τ value is a steeply decreasing function of $[Br^-]^*$, depending on the value of M_n. At a fixed $[Br^-]^*$ value, τ is approximately proportional to M_n irrespective of c_P. This proportionality is a characteristic relationship of this hybrid threadlike micelllar system. At a constant value of X_S, the value of G_N is an increasing function of $[Br^-]^*$, depending on the value of c_P. At a fixed $[Br^-]^*$ value, G_N is proportional to the square of c_P irrespective of M_n, which is also the case for ordinary entangled polymer systems. Thus, the presence of Br^- ions has a strong effect on the entanglement release mechanism and stiffness of the present hybrid threadlike micelles.

The present evidence indicates that the behavior of hybrid threadlike micellar systems is basically described by the phantom crossing model. However, the present finding that the presence of incorporated polymers lengthens the relaxation time, τ, suggests the need for modification of this model.

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