

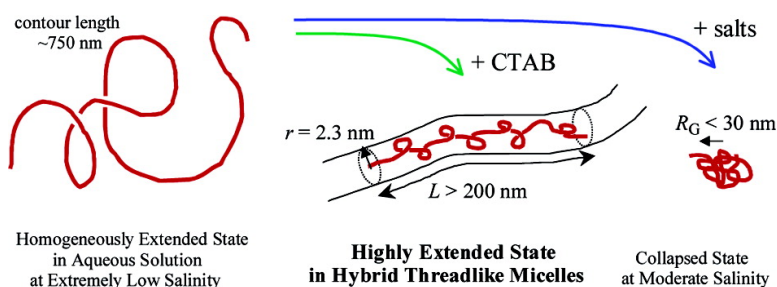
Communication

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Highly Extended Conformation of Polyelectrolytes Incorporated into Hybrid Threadlike Micelles Studied by Small Angle Neutron Scattering

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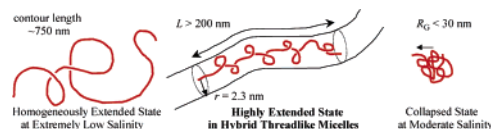
The conformation of polyelectrolytes dissolved in aqueous media is highly dependent on the concentrations of added salts, such as NaCl.¹ At moderate salt concentrations, polyelectrolytes have a collapsed conformation with a small radius of gyration, R_G , and exhibit low viscosity. In contrast, at extremely low salt concentrations, polyelectrolytes have a homogeneously extended conformation due to strong electrostatic repulsion (cf. Scheme 1). In aqueous systems containing sheathlike substances that can insulate incorporated polyelectrolytes from the bulk aqueous phase, the conformation of the polyelectrolyte is governed by the shape of the sheath interior, irrespective of the characteristics of the bulk aqueous phase. Recently, we have established *supramolecular* systems involving long threadlike micelles consisting of polyelectrolytes and surfactants. We have named these micelles *hybrid threadlike micelles*² to distinguish them from ordinary threadlike micelles³ consisting of surfactants and low molar mass additives.

Our hybrid threadlike micelles consist of a surfactant, cetyltrimethylammonium bromide (CTAB), and a sodium salt of partially sulfonated polystyrenes (NaPSS). Measurements from transmission electron micrographs (TEM) indicate that the radius of these micelles is ca. 2 nm, and that the length is sufficient to allow entanglements.² Phenyl rings of NaPSS containing both styrene and sulfonated styrene components interact with cationic headgroups of CTAB due to cation- π interaction,^{2,4} whereas the backbone of the polyelectrolyte possibly prefers a deeper interior of the micelles due to its high hydrophobicity. Addition of a small amount of simple salts to the hybrid threadlike micellar system does not influence the threadlike micellar shape.² These indicate that locations of NaPSS associated with hybrid threadlike micelles are tightly restricted to the interior of the micelles. Consequently, the conformation of polyelectrolytes incorporated into hybrid threadlike micelles should be highly extended along the micelles (cf. Scheme 1). However, in practice, is it possible for the polyelectrolyte to assume such an extended conformation with lower entropy than that of the spherically collapsed conformation usually observed in aqueous solution at moderate salt concentrations?

The objective of this study was to confirm that the polyelectrolyte in hybrid threadlike micelles, sheathlike substances, has a highly extended conformation, using small angle neutron scattering (SANS) techniques. SANS (and small angle X-ray scattering) techniques have been widely used for structural studies of polymer-surfactant complexes and have provided decisive information to discuss solution structures.⁵

Deuterated and normal polystyrene⁶ with the same number average molar mass (ca. 340×10^3) were sulfonated at ca. 50%⁷ and were obtained in the form of sodium salt. These polyelectrolytes, NadPSS and NaPSS, were combined with CTAB to form hybrid threadlike micelles in D₂O solution.

Scheme 1. Schematic Depiction of Conformation Changes in a Polyelectrolyte Molecules with the Same Average Molar Mass as that of the Polyelectrolytes Examined in This Study, Depending on Conditions



In this system, the concentrations of CTAB and the total polyelectrolytes, c_D and c_P , in monomer units, were maintained at 25 mM, while the fraction of NadPSS, x_D , relative to NaPSS was maintained at 0, 0.05, or 0.2. Each prepared solution was transparent and viscoelastic due to entanglements between the hybrid threadlike micelles, as has also been observed in aqueous hybrid threadlike micellar systems² containing only NaPSS.

Because each phenyl ring of the polyelectrolytes has a specific cation- π interaction with the CTA⁺ in hybrid threadlike micelles, NadPSS and NaPSS interacting with CTAB behave as distinct polymers with the same degree of polymerization, degree of sulfonation, and conformation, but with different scattering length densities, β_D and β_H . In such a system, the differential cross-section of coherent scattering, $I_{\text{coh}}(x_D)$, is given by eq 1 with the following parameters: N , number density of the polymers; Z , degree of polymerization; v_p , molar volume of the polymers interacting with CTAB; N_A , Avogadro's number; β_m , scattering length density of medium D₂O; $P_1(q)$, particle scattering factor; $P_2(q)$, interparticle structure factor.⁸

$$I_{\text{coh}}(x_D) = N^2 Z^2 v_p^2 N_A^{-2} \{(\beta_D - \beta_m)^2 x_D + (\beta_H - \beta_m)^2 (1 - x_D)\} P_1(q) + N^2 Z^2 v_p^2 N_A^{-2} \{\beta_D x_D + \beta_H (1 - x_D) - \beta_m\}^2 P_2(q) \quad (1)$$

SANS experiments⁹ were performed on the hybrid threadlike micellar system in D₂O at 25 °C, over a range of scattering vector,

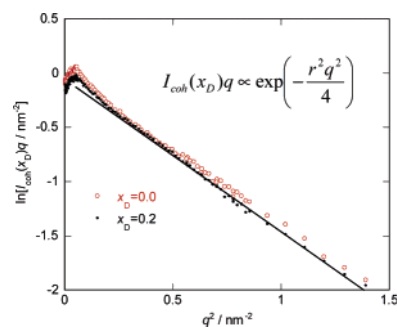


Figure 1. Cross-section plots, $\ln[I_{\text{coh}}(x_D)q]$ versus q^2 , for hybrid threadlike micellar solutions at $x_D = 0$ and 0.2. The linearly decreasing region with a slope of -1.35 nm^2 suggests that the approximate local shape of particles in the system is a rod with a radius of 2.3 nm on the basis of an equation¹⁰ shown in the figure. The proportional difference between $I_{\text{coh}}(0)$ and $I_{\text{coh}}(0.2)$ for values of $q > 0.5 \text{ nm}^{-1}$ ($q^2 > 0.3 \text{ nm}^{-2}$) is clearly visible.

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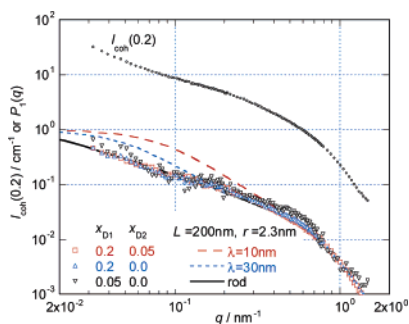


Figure 2. Dependence of differential cross-section of coherent scattering, $I_{\text{coh}}(x_D)$, on the value of scattering vector, q , for hybrid threadlike micellar solutions with $c_D = c_P = 25$ mM at a deuterated polymer fraction of $x_D = 0.2$. This figure shows the q -dependence of $P_1(q)$ obtained for each combination of $I_{\text{coh}}(x_D)$ at $x_D = 0, 0.05$, and 0.2 , using eq 2 assuming $\kappa = 0$. Also shown are theoretical scattering factors calculated for a rigid rod¹⁰ and wormlike cylindrical particles¹² with the parameters shown.

q , from 3×10^{-2} to 2 nm^{-1} . Figure 1 shows the cross-section plots, $\ln[I_{\text{coh}}(x_D)q]$ versus q^2 , for the system at $x_D = 0$ and 0.2 , which provide information about the local structure of hybrid threadlike micelles in the system, which is useful in detailed examination of the polyelectrolyte conformation. For hybrid threadlike micelles in a rodlike shape with a radius, r , the $I_{\text{coh}}(x_D)q$ curve is a good approximation of an exponential function of q^2 for values of q greater than the reciprocal of r .¹⁰ The linear relationship shown in Figure 1 indicates that the local shape of the hybrid threadlike micelle is a rod with $r = 2.3$ nm, as schematically shown in Scheme 1. This r is close to the value obtained from TEM measurements.²

The q -dependence of $I_{\text{coh}}(x_D)$ for samples at $x_D = 0.2$ is shown in Figure 2 as an example. Although $I_{\text{coh}}(x_D)$ curves other than the one at $x_D = 0.2$ are not shown in Figure 2, because the x_D -dependence of the curves is small, $I_{\text{coh}}(x_D)$ clearly decreases with increasing x_D at the same q value as that shown in Figure 1.

$$P_1(q) = \frac{N_A^2}{NZ^2 v_p^2 (\beta_H - \beta_m)^2} \frac{I_{\text{coh}}(x_{D1}) - I_{\text{coh}}(x_{D2}) \left\{ \frac{x_{D1}(\kappa - 1) + 1}{x_{D2}(\kappa - 1) + 1} \right\}^2}{x_{D1}(\kappa^2 - 1) + 1 - \left\{ x_{D2}(\kappa^2 - 1) + 1 \right\} \left\{ \frac{x_{D1}(\kappa - 1) + 1}{x_{D2}(\kappa - 1) + 1} \right\}^2} \quad (2)$$

The reason for the decrease with increasing x_D is that the difference between β_D and β_m is smaller than the difference between β_H and β_m .¹¹ Using eq 1, $P_1(q)$ can be determined from the $I_{\text{coh}}(x_D)$ curves obtained at different x_D values using eq 2, with a ratio of $\kappa = (\beta_D - \beta_m)(\beta_H - \beta_m)^{-1}$.

Because the front factor of eq 2, $N_A^2 N^{-1} Z^{-2} v_p^{-2} (\beta_H - \beta_m)^{-2}$, for this system was calculated as ca. 8.6×10^{-3} , $P_1(q)$ was obtained for each $I_{\text{coh}}(x_D)$ combination assuming $\kappa = 0$, as seen in Figure 2.¹¹ The agreement among the values obtained for different combinations strongly indicates that the present analytical method is valid. Consequently, the obtained $P_1(q)$ curve shows the conformation of polyelectrolytes incorporated in hybrid micelles in the system.

The solid line in Figure 2 represents the particle scattering factor of a rigid rod¹⁰ with length L and an r value of 200 and 2.3 nm, respectively. The broken and dotted lines represent scattering factors of wormlike cylindrical particles¹² with the same L and r values, but with persistence lengths, λ , of 10 and 30 nm, respectively. Because the agreement between the solid line and the obtained $P_1(q)$

appears reasonable across the entire q range, we conclude that the polyelectrolytes are crowded into the hybrid threadlike micellar interior with high confinement of $r = 2.3$ nm, and that the conformation of the polyelectrolytes in the micelle is extended, with a length greater than 200 nm, as schematically depicted in Scheme 1. Because the fully extended (contour) length of the polyelectrolytes is ca. 750 nm, the polyelectrolytes preferentially assume the highly extended conformation with extremely low entropy, when they are incorporated into hybrid threadlike micelles. Moreover, because the polyelectrolytes behave as rigid rods in hybrid threadlike micelles, the micelle maintains greater rigidity than that of ordinary threadlike micelles between surfactants and low molar mass additives.²

Acknowledgment. The authors thank Prof. M. Shibayama, the University of Tokyo, and Prof. Y. Takahashi, Kyushu University, for their technical support in SANS experiments and valuable comments to complete this study. T.S. thanks Kao Co. Ltd. for their financial support. K.N. expresses special thanks to the Center of Excellence (21COE) program "Creation of Integrated EcoChemistry of Osaka University".

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- (6) Deuterated polystyrene ($M_n = 340 \times 10^3$ and $M_w/M_n = 1.08$) was purchased from Polymer Source Inc. (Montreal), and normal polystyrene with the same M_n and M_w/M_n was donated by TOSOH Ltd. (Tokyo).
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- (11) The value of β_m for D₂O is $6.38 \times 10^{10} \text{ cm}^{-2}$. Because the molar volume of the NaPSS in aqueous solution was calculated to be $105 \text{ cm}^3 \text{ mol}^{-1}$ in monomer units, using density measurements, and the molar volume of CTAB was $365 \text{ cm}^3 \text{ mol}^{-1}$ (Dearden, L. V.; Woolley, E. M. *J. Phys. Chem.* **1987**, *91*, 4123–4127); v_p for the polymer interacting with CTAB was calculated to be $470 \text{ cm}^3 \text{ mol}^{-1}$. Moreover, the molar scattering length of the NaPSS interacting with CTAB was $2.22 \times 10^{-12} \text{ cm}$ in average monomer units; consequently, β_H was calculated to be $0.28 \times 10^{10} \text{ cm}^{-2}$. Using these values, the front factor of eq 2, $N_A^2 N^{-1} Z^{-2} v_p^{-2} (\beta_H - \beta_m)^{-2}$, was calculated to be 8.6×10^{-3} . Because the obtained x_D value was low, the NaPSS can be considered as guest molecules in hybrid threadlike micelles consisting of NaPSS and CTAB. In such a system, β_D is calculated to be $6.60 \times 10^{10} \text{ cm}^{-2}$, using a scattering length and molar volume of $11.5 \times 10^{-12} \text{ cm}$ and $10^5 \text{ cm}^3 \text{ mol}^{-1}$, respectively, and the κ value consequently decreases nearly to zero. In practice, for values of κ from -0.1 to 0.4 , the calculated $P_1(q)$ value does not noticeably vary with changes in the value of κ .
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