Ordered-Aggregate Formation by Surfactant-Charged Gel Interaction

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Introduction

We have recently developed a new type of electrically driven chemomechanical system which shows quick responses with wormlike motility.[1,2] The principle of this movement is based on an electrokinetic molecular assembly reaction of solvated cationic surfactants, *N*-dodecylpyridinium chloride ($C_{12}PyCl$), onto a cross-linked polymer gel made from poly[2-(acrylamido)-2-methylpropanesulfonic acid] (PAMPS). The electric field drives and controls the direction of the equilibrium to give anisotropic binding; i.e., when the dc voltage is turned on, the surfactant molecules move toward the cathode by electrophoresis and bind with the gel preferentially on the side of the PAMPS gel strip facing the anode. This causes an anisotropic contraction of the gel and bending toward the anode. On the basis of the same principle, a swinging motion of the gel was also demonstrated.[3] The gel exhibited gentle and flexible movement and is able to serve as a new class of "soft actuator" or "molecular machine" different from hydraulic engines and metallic machines.

In order to study the mechanism of this movement more in detail, we have studied[4] the shrinking process of a water-swollen PAMPS gel by immersing in a cationic surfactant solution and found that the shrinking process is essentially a stoichiometric binding reaction of the surfactant molecules with the polymer network which is characterized by two processes. One is electrostatic salt formation between the surfactant molecules and the oppositely-charged sulfonates of the gel (initiation process). The other is hydrophobic interaction between bound surfactant, which stabilizes the aggregate in such as to settle adjacent to the already occupied site along the polymer chain (propagation process).[4−6] The latter is called a "cooperative process". Thus, the aggregate process, like common micelles, is dominated by two opposing forces, a hydrophobic attractive force which prefers the aggregation of alkyl chains and an electrostatic repulsive force among the head group which prevents a growth of the aggregates. We have found that the presence of a polyelectrolyte network extremely reduces the repulsive force due to its large electrostatic potential and consequently lowers the critical concentration to give the stable aggregate.[4,5]

A number of researches regarding to the surfactant−polyelectrolyte interaction have been made.[6−10] Thomas et al.[8] have investigated the binding of an alkyltrimethylammonium bromide ($C_{10}TAB$) oppositely-charged poly(methacrylic acid) (PMAA) and found that, if the surfactant concentration is above a critical aggregation concentration (cac), they form a micellelike PMAA−C_{10}-TAB consisting of about 100 surfactant molecules for 1 coiled polymer chain. The cac was 1 or 2 orders of magnitude less than the critical micelle concentration (cmc) of the corresponding micelle. Lindman et al.[9] have studied the interaction between hyaluronan sodium salt and alkyltrimethylammonium bromide and demonstrated that the polymer−surfactant aggregate forms micellelike clusters in aqueous solution. Formation of particles with diameters ranging from 60 to 250 nm has been reported by the electrostatic interaction between polyelectrolyte and oppositely-charged surfactant.[11,12] Recently, Khokhlov et al.[13] have investigated the interaction of cetylpyridinium bromide with a cross-linked PMAA gel, and theoretical consideration of the structure of the gel−surfactant aggregate was reported. They have studied the effects of charge density and mobility, ionic strength, and network topology on complex formation.

This paper deals with the formation of higher-ordered aggregates made by the surfactant molecules and the charged polymer network. We have found that the concentration and size of an alkyl chain of the surfactant play a crucial role in the formation of crystalline aggregate in the gel. As far as we know, there have been no reports describing the formation of an ordered structure of aggregates made by oppositely-charged surfactant−network interaction.

Experimental Section

Materials. 2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS; Nitto Chemicals), *N,N'*-methylenebisacrylamide (MBAA; Tokyo Kasei), and potassium persulfate (Tokyo Kasei) were purified in the same manner in the previous paper.[3] *N*-Alkylpyridinium chlorides (CnPyCl) with $n = 4, 12, 16$ (Tokyo Kasei) were used as received, and those with $n = 8, 10, 18$ were synthesized according to the literature.[14]

Preparation of the Samples. A weakly cross-linked PAMPS gel and corresponding linear PAMPS were prepared by radical polymerization of AMPS in the same manner as described in the previous paper.[3] Samples were prepared by immersing a slightly cross-linked water-swollen PAMPS gel (13 mm diameter, 2 mm thick, dry weight 6 mg) in a 10 mL of cationic surfactant solution with various concentrations for more than 30 days until it reaches equilibrated conditions. Linear PAMPS−$C_{12}PyCl$ aggregates were obtained by mixing the same volume of a $C_{12}PyCl$ solution and a PAMPS solution (the concentration of a repeated unit is 3×10^{-3} mol L^{-1}, dry weight 6 mg) under thermostatic conditions for 1 month followed by centrifuged separation of the aggregate at 3000 rpm for 30 min. These samples are offered as specimens of X-ray measurement.

Measurement. The binding process of surfactant molecules with the gel was followed spectrophotometrically, i.e., by observing the change in UV absorption of an aqueous solution of surfactant molecules at 259 nm (molar extinction coefficient: $\epsilon = 4070$) containing a piece of a cylindrical PAMPS gel. The electromotive force was potentiometrically measured by a surfactant-selective membrane electrode[6] for the determination of free surfactant concentration for a polymer solution system. All measurements were carried out at 25 °C after 1 month under equilibrium and wet conditions. The degree of binding (β) of the sample, defined as a molar ratio of bound surfactant to the total sulfonic acid group, was adjusted by changing the concentration of the surfactant solution. Ni-filtered Cu Kα radiation (40 kV, 30 mA) was used for wide- and small-angle X-ray measurements by a X-ray diffractometer (Shimazu XD-610, SAG-6A). X-ray diffraction photographs were taken with a Polaroid Laue camera (Shimazu universal camera; camera distance, 154 mm; exposure time, 4 h; sample thickness, ca. 1 mm).

Results and Discussion

When a weakly cross-linked water-swollen PAMPS gel is immersed in a cationic surfactant solution, the surfactant molecules bind with the polymer network and the gel undergoes contraction with time. The

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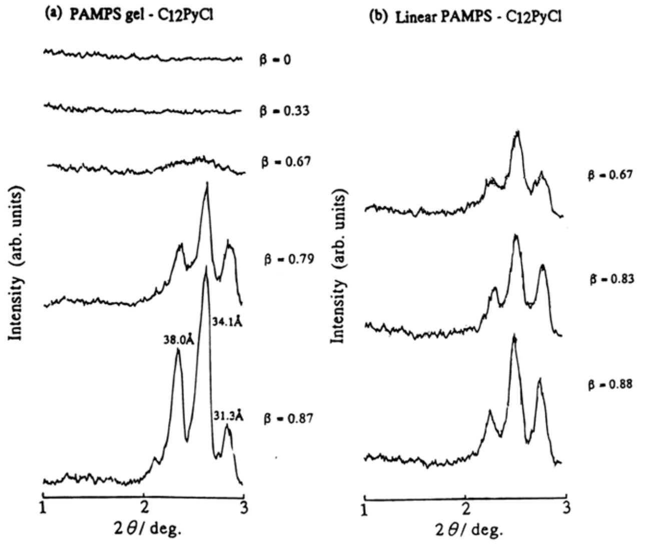


Figure 1. Small-angle X-ray diffraction (SAXD) diagrams of PAMPS gel–$C_{12}PyCl$ (a) and linear PAMPS–$C_{12}PyCl$ (b) aggregates as a function of the degree of binding (β). $T = 25$ °C. The water content of PAMPS gel–$C_{12}PyCl$ aggregates is 76–78% in all specimens.

process is strongly dependent on the size of the alkyl chain of the surfactant, and when the alkyl chain size was C_{10} or larger, the gel contracted quickly and became 10% of its initial volume, while C_4PyCl and C_8PyCl could induce no more than 80%.[4] This contractile behavior is associated with the neutralization of negative charges in the gel by forming a complex with surfactant cations which consequently decreases the osmotic pressure difference between the inside of the gel and the surrounding solution.

In order to investigate the structure of a PAMPS gel–CnPyCl aggregate, wide- and small-angle X-ray diffraction analyses were made. $C_{12}PyCl$ powder showed clear diffraction peaks at 19.3 and 15.28° in 2θ which correspond to 5.8 and 4.6 Å d-spacings. However, no appreciable diffraction pattern appeared for the dry and wet PAMPS gel–$C_{12}PyCl$ aggregate in wide-angle X-ray diffraction (WAXD). DSC measurement of the gel aggregate exhibited no endothermic peak or glass transition step up to 200 °C. In agreement with WAXD and DSC measurements, the dry and wet aggregates exhibited no birefringence in a temperature range between 25 and 200 °C by optical microscopic observation under crossed polarizers. These results indicate that the $C_{12}PyCl$ cannot make an arrangement in the PAMPS network to give crystalline structure in a molecular order. In other words, $C_{12}PyCl$ molecules have no short-range periodicity in the gel.

In order to investigate the higher-ordered structure, a structure analysis of the wet aggregate was made using the data of SAXD and the results are shown in Figure 1 (sample thickness, ca. 1 mm). PAMPS gel (a) containing no surfactant molecule ($\beta = 0$) showed no diffraction peak through a whole 2θ range, indicating that the gel is essentially amorphous. With increasing β up to 0.67 no clear peak has been observed, while the aggregate of $\beta = 0.79$ suddenly showed three sharp peaks at $2\theta = 2.33$, 2.59, and 2.83 corresponding to d-spacings of 37.9, 34.1, and 31.2 Å, respectively. This fact indicates that the surfactant molecules are rather randomly dispersed without making any structure on the polymer network, but sufficiently long sequence, continuously adjacent bindings side by side are formed when β becomes 0.8 or higher. On the other hand, a linear PAMPS–$C_{12}PyCl$ wet aggregate (b) showed diffraction peaks at $\beta = 0.67$ and a further increase in β caused only a slight increase in the diffraction intensity of the SAXD diagram (samples with β less than 0.67 did not form an aggregate large enough to be separated by the centrifuge). This suggests that there exists an extensive cooperative binding process of the surfactant binding in the linear anionic polymer and a much less cooperative process in the network. This result well coincides with our previous experimental results in which was demonstrated the enhanced cooperativity of linear PAMPS than its network.[4] It should be mentioned here the structure of the dried surfactant–gel aggregates. When the aggregate was dried *in vacuo*, the SAXD peaks shifted to higher 2θ values and appeared at 2.74 and 3.00 corresponding to d-spacings of 32.3 and 29.4 Å, respectively. This result indicates that the surfactant molecules in the wet gel are loosened for a few angstroms by the presence of water; nevertheless, they can organize the molecular structure in the wet state.

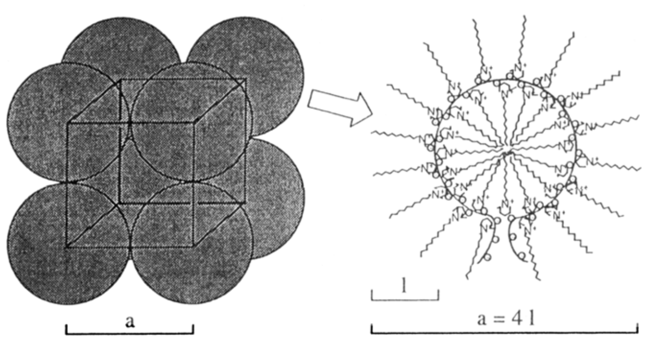
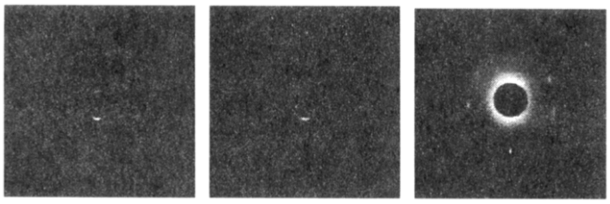


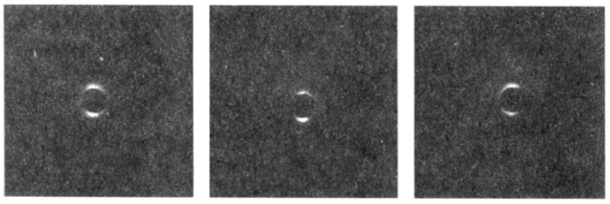
Figure 2. Schematic illustration of the structure of a PAMPS gel–surfactant aggregate.

The values of $\sin^2\theta$ for each diffraction peak have been calculated as a ratio of 4:5:6, which indicates that the three peaks can be attributed to the diffraction from (200), (210), and (211) layer lines of the primitive lattice. A lattice constant of the PAMPS gel–$C_{12}PyCl$ aggregate was calculated as $a = 76.2$ Å, which was somewhat smaller than that of the linear PAMPS–$C_{12}PyCl$ aggregate of $a = 77.1$ Å. The value of the lattice constant is almost twice the diameter of the micelle formed in the absence of PAMPS, suggesting the formation of a large cluster in the polymer network. This well coincides with the results of Thomas et al.[8] who investigated the structure of the micelles formed by anionic polyelectrolyte–cationic surfactant molecules. They have also observed that the presence of polyelectrolyte brings about a larger micellelike aggregate. Figure 2 shows the schematic illustration of the PAMPS gel-$C_{12}PyCl$ aggregate. The figure also shows that the surfactant molecules form a liquid-crystalline-like micellar aggregate in the network, thus constructing a higher ordered crystalline structure of the primitive lattice.

Effect of the alkyl chain size on the structure formation has been studied using various CnPyCl, and the results of SAXD of the wet aggregates are shown in Figure 3. Degree of binding (β) of all samples has been controlled in a range of 0.68–0.88. One can easily see that C_4PyCl and C_8PyCl showed no appreciable diffraction other than extremely weak halos. On the other hand, a clear Debye–Scherrer ring of the polycrystalline structure was observed when the alkyl chain size of the



C_4PyCl - PAMPS gel ($\beta = 0.68$) C_8PyCl - PAMPS gel ($\beta = 0.88$) C_{10}PyCl - PAMPS gel ($\beta = 0.74$)



C_{12}PyCl - PAMPS gel ($\beta = 0.87$) C_{16}PyCl - PAMPS gel ($\beta = 0.72$) C_{18}PyCl - PAMPS gel ($\beta = 0.76$)

Figure 3. Small-angle X-ray diffraction patterns for PAMPS gel–CnPyCl aggregates with various alkyl chain sizes. Samples were prepared in the same manner described in Figure 6. $T = 25$ °C. Water content of PAMPS gel–CnPyCl aggregates: C_4PyCl, 97%; C_8PyCl, 96%; C_{10}PyCl, 65%; C_{12}PyCl, 76%; C_{16}PyCl, 76%; C_{18}PyCl, 76%.

surfactant becomes C_{10} or larger, despite the fact that no diffraction has appeared in the wide-angle X-ray diffraction. Thus, an increase in two carbon atoms of the surfactant exclusively favors the formation of an ordered structure of the aggregate even in the swollen polymer network.

Using the data obtained from SAXD measurements, we have determined lattice constants of the wet aggregates by the least-squares method, and the results are listed in Table 1. The lattice constant of the primitive unit cell increased with an increase in the alkyl chain length of the surfactant, and an increase in the lattice constant for each CH_2 group was calculated as 5.91 Å/CH_2 group, which well coincides with the theoretical assumption derived from the molecular model.

Table 1. Primitive Unit Cell Parameter for a PAMPS Gel–CnPyCl System with Various Alkyl Chains[a]

	lattice constant (Å)
C_{10}PyCl–PAMPS gel	64.7
C_{12}PyCl–PAMPS gel	76.2
C_{16}PyCl–PAMPS gel	100.5
C_{18}PyCl–PAMPS gel	111.6

[a] Water content of PAMP gel–CnPyCl aggregates: C_4PyCl, 97%; C_8PyCl, 96%; C_{10}PyCl, 65%; C_{12}PyCl, 76%; C_{16}PyCl, 76%; C_{18}PyCl, 76%.

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References and Notes

(1) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242.
(2) Osada, Y.; Ross-Murphy, S. B. *Sci. Am.* **1993**, *268* (5), 82.
(3) Okuzaki, H.; Osada, Y. *J. Biomater. Sci.* **1994**, *5* (5), 485.
(4) Okuzaki, H.; Osada, Y. *Macromolecules* **1994**, *27*, 502.
(5) Okuzaki, H.; Eguchi, Y.; Osada, Y. *Chem. Mater.* **1994**, *6* (10), 1651.
(6) Hayakawa, K.; Santerre, J. P.; Kwak, J. C. T. *Macromolecules* **1983**, *16*, 1642.
(7) Shirahama, K.; Tashiro, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 377.
(8) Chu, D. Y.; Thomas, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 6270.
(9) Thalberg, K.; Lindman, B. *J. Phys. Chem.* **1989**, *93*, 1478.
(10) Canane, B. *J. Phys. Chem.* **1977**, *81* (17), 1639.
(11) Dubin, P. L.; Rigsbee, D. R.; Mcquigg, D. W. *J. Colloid Interface Sci.* **1985**, *105* (2), 509.
(12) Seki, M.; Morishima, Y.; Kamachi, M. *Macromolecules* **1992**, *25*, 6540.
(13) Khokhlov, A. R.; Kramarenko, E. Yu.; Makhaeva, E. E.; Starodubtzev, S. G. *Macromolecules* **1992**, *25*, 4779.
(14) Malovikova, A.; Hayakawa, K.; Kwak, J. C. T. *J. Phys. Chem.* **1984**, *88*, 1930.

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