Interaction of Slightly Cross-Linked Gels of Poly(diallyldimethylammonium chloride) with Surfactants

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Introduction. Polyelectrolyte gels in solution may undergo a discrete volume transition with even very small changes in the environment, such as temperature, solvent composition, pH value, etc.[1–5] A low molecular weight surfactant with opposite charges can also interact with polyelectrolyte gels and induce a sharp conformational transition.[6]

The interactions of polyelectrolyte gels with oppositely charged surfactants could produce interesting three-dimensional structures in aqueous solution. The structure formation is due to a combination of hydrophobic interactions and electrostatic interactions between the polymeric gel and the surfactants. Polyelectrolyte–surfactant complexes could be formed even at extremely small surfactant concentrations in the external phase, much smaller than the critical micelle concentration (cmc) of the surfactants in aqueous solution. It was predicted theoretically that the ions of the surfactant become more concentrated in the charged network, resulting in the formation of micelle-like aggregates.[7,8] From the excimer formation of SDS and pyrene in both the gel phase and the external aqueous phase, the structure of surfactant aggregates in a polyelectrolyte network is different from that of micelles in water.[9] Starodoubtzev and Philippova found that the cmc of SDS in a poly(diallyldimethylammonium bromide) (PDADMABr) gel was about tenfold lower than that in aqueous solutions.[10]

In the present work, small-angle X-ray scattering (SAXS) was used to investigate the structure of polyelectrolyte–surfactant complexes between the ionic surfactants, sodium sulfate, and the cationic network of poly(diallyldimethylammonium chloride) (PDADMACl).

Experimental Section. The polyelectrolyte gels were prepared by free-radical copolymerization of diallyldimethylammonium chloride (DADMACl; 99.5 mol %) and *N,N'*-methylenebisacrylamide (0.5 mol %) in 40% aqueous solutions. Ammonium persulfate (4.4×10^{-3} mol/L) and *N,N,N',N'*-tetramethylethylenediamine (4.4×10^{-3} mol/L) were the initiator and accelerator, respectively. Gelation was carried out at 22 °C for 22 h between two glass plates (65 mm × 100 mm) separated by two spacers with a thickness 0.63 ± 0.043 mm. The formed gels were then washed in a large amount of distilled water for 3 weeks. The distilled water was changed every 1–2 days. The surfactants were bought from Lancaster Synthesis Inc. (99%) and used without further purification.

For complexation, a piece of gel of known weight was immersed in a surfactant solution of known concentration. By adjusting the volume of the surfactant solution, a certain charge unit ratio, γ, between the surfactant and the gels could be maintained for each complex. Each piece of gel was equilibrated in the surfactant solution for 3 weeks before it was sealed in a thin-walled (0.01 mm thick) capillary tube for SAXS experiments.

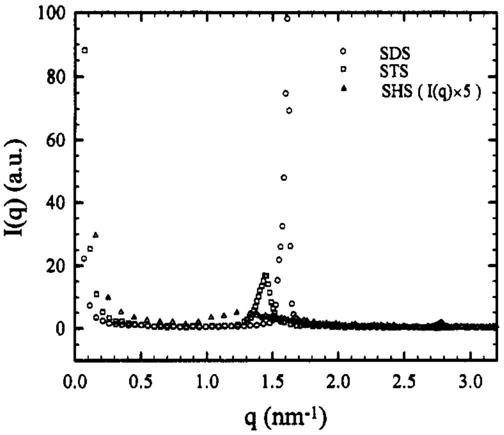

Figure 1. SAXS profile of collapsed PDADMACl gel in different surfactants. γ, defined as the total number of chargeable groups in the surfactant to that of chargeable monomer unit (DADMACl) in the gel, is 500%. The X-ray intensity of SHS–gel complex is multiplied by a factor of 5.

SAXS was performed at the X3A2 State University of New York (SUNY) Beam Line, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), using a laser-aided prealigned pinhole collimator.[11] The incident beam wavelength was tuned at 0.154 nm, but the higher order harmonics were also present. Two different kinds of detectors, a linear position-sensitive detector (manufactured by Braun) and an imaging plate (IP), were used for the SAXS measurements. The sample-to-detector distances were 465 mm for the Braun detector and 750 mm for the IP, respectively. The q range covered was from 0.1 to 3.2 nm^{-1} for the Braun detector and from 0.08 to 4 nm^{-1} for the imaging plate. The scattering vector $\mathbf{q}$ is defined as $\mathbf{q} = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle between the incident and the scattered light. The experimental data were corrected for background scattering and sample transmission. The smearing effect is negligible for this setup.

Results and Discussion. Three ionic surfactants, sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS), and sodium hexadecyl sulfate (SHS), with a hydrophobic chain length of 12, 14, and 16, respectively, were used to study the polyelectrolyte–surfactant complexes. The SAXS profile for the three different polyelectrolyte-surfactant complexes (PSC) is shown in Figure 1. Two sharp and intense diffraction peaks show up at 1.46 and 1.64 nm^{-1} for the PSC with STS (squares) and SDS (circles), respectively. A SAXS peak for SHS (triangles) is located at 1.19 nm^{-1} but is much weaker and broader. For the polyelectrolyte–SDS complex, a small blip found at q equal to about 2.8 nm^{-1} could be considered as a second-order peak. The distance ratio of the first to the second order is 1/1.74. An IP which could cover a higher q range was used to examine the structure. The X-ray images showed isotropic powder ring(s) for all the samples (C_{12}, C_{14}, and C_{16}) investigated. Figure 2 shows the integrated SAXS profile of a SDS–gel complex from the IP. The first three peaks, as indicated by arrows in Figure 2, show up clearly at 1.64, 2.85, and 3.30 nm^{-1}, respectively. The location of the three peaks has a ratio of 1:1.74:2.01. These sharp diffraction peaks indicate that the structure in the gel

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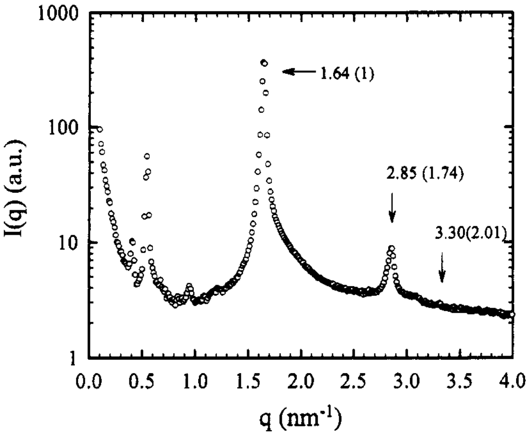

Figure 2. Integrated SAXS profile of PDADMACl–SDS complex from an IP. The peaks at $q < 1$ nm^{-1} are due to the higher order harmonics of the incident beam and can be taken into account by considering the peaks (with arrows indicated) based on $\lambda = 0.154$ nm.

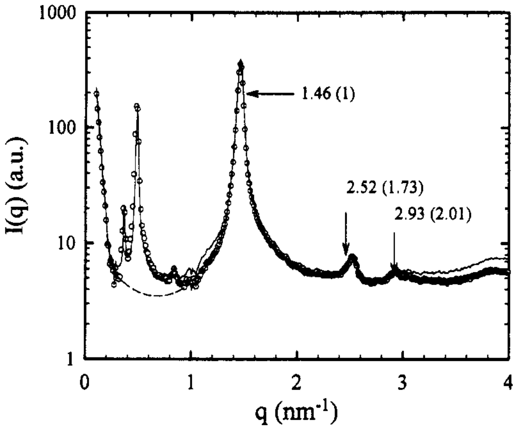

Figure 3. Integrated SAXS profile of PDADMACl–STS complex from an IP. The dashed line shows the best fitting curve of experimental data with the assumption that there is no excess scattering for q between 0.2 and 1.1 nm^{-1}. The solid line represents a hypothetical scattering curve from a combination of multiple wavelengths, λ, $\lambda/3$, and $\lambda/4$, based on the dashed-line curve coming from monochromatic X-rays at wavelength λ. The exercise demonstrates that all the peaks can be accounted for by invoking the presence of higher order harmonics. The structure reveals three main peaks as illustrated by the arrows.

must be in a highly ordered state, in agreement with the results of Osada and Okuzaki,[14] who have recently reported a polycrystalline structure formed in a cationic surfactant–anionic polymer network complex. The relationship between peak positions could be attributed to an X-ray diffraction pattern from a two-dimensional hexagonal array. In Figure 2, it is noted that there were many additional peaks at $q < 1.5$ nm^{-1}. These peaks were also present in the STS–gel complex, as shown in Figure 3.

We attribute the peaks below 1 nm^{-1} in Figures 2 and 3 as due mainly to the diffraction by higher order harmonics from the incident beam at $\lambda = 0.0513$ and $\lambda = 0.0385$ nm^{-1}. The dashed line in Figure 3 presents the best fitting curve of the SAXS profile without X-ray diffraction from higher order harmonics. With the higher order harmonics, the SAXS curve at q nm^{-1} was rescaled to 1/3 and 1/4 in q space and to the intensity ratio of the peaks at 0.48 and 1.46 nm^{-1}. The solid line in Figure 3 represents a combination of the dashed line and the simulated SAXS pattern from higher order harmonics. It matches exactly the experimental curve.

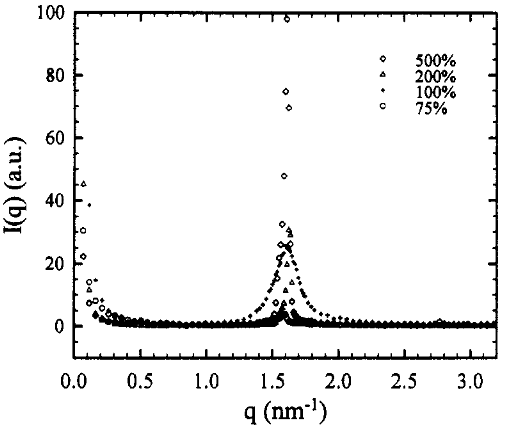

Figure 4. SAXS profile of PDADMACl–SDS complex at various γ ratios.

For an equilibrium swollen gel interacting with an aqueous surfactant solution, the gel volume depends on the amount of the embedded surfactant when the content of the surfactant is relatively small. Further increase in the surfactant content leads to a gel collapse. However, the surfactant concentration could keep on increasing in the gel phase even when the gel has been collapsed. This phenomenon holds true for both anionic gel–cationic surfactant and cationic gel–anionic surfactant systems.[6,9] Figure 4 shows the SAXS profile of the PSC with different charge unit ratios, γ, between the surfactant and the gel. The intensity is proportional to γ, but the diffraction peaks remain at the same (q) position. The results demonstrate again that the structure is induced by the surfactants.

The mean paracrystallite size in a given sample may be estimated from the Bragg peaks in a powder pattern by the Scherrer formula.[12] With spherical symmetry, the paracrystallite radius is given by[13]

$$R = 0.277\lambda/(\mathrm{B} \cos \theta) \qquad (1)$$

where B is the full width at half-maximum intensity (in radians) of the Bragg peak observed at a mean scattering angle of 2θ. Then the long-range order dimension is about 40 nm in the SDS gel with a $\gamma = 100\%$. The dimension increases with increasing γ values.

Both theoretical and experimental results have shown that the cmc for a surfactant in the gel phase is much lower than that in the external aqueous phase.[6–10] The micelles in the gel phase should also be different from those in the aqueous phase. This is accounted for by the immobilized charges which are attached to the polymer backbone, forming a higher local charge concentration. The surfactants formed a crystal-like structure in the present polyelectrolyte gel. From the SAXS results, a hexagonal array would be the most probable arrangement for the surfactants which are different from the cubic lattice structure as reported by Osada and Okuzaki.[14]

The observation we have reported in this Communication is certainly counterintuitive. How could randomly cross-linked (cationic) gels form highly ordered structures when complexed with (anionic) surfactants? There are many intriguing questions which need to be answered. For example, why is the well-ordered structure formed only with C_{12} and C_{14} hydrophobes, but not with C_{16}, as shown in Figure 1? What controls the lattice spacing? What is the effect on the gel cross-link density? The most interesting problem is to try to learn more about the structure of the PSCs. Obviously, we need to have a quantitative determination on the amount of surfactant entering the gel phase, a better SAXS image to higher *q* values, and, most importantly, larger crystals, which cannot be grown in the usual fashion. Further study on the details is in progress.

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