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Nanoscale Supramolecular Structures in the Gels of Poly(Diallyldimethylammonium Chloride) Interacting with Sodium Dodecyl Sulfate

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Abstract: A highly ordered supramolecular structure is formed in the polyelectrolyte−surfactant complex between the anionic surfactant sodium dodecyl sulfate (SDS) and the cationic network of poly(diallyldimethylammonium chloride) (PDADMACl). From small-angle X-ray scattering (SAXS), the complexes between PDADMACl and SDS were shown to exhibit a hexagonal type of microstructure which is different from that of pure SDS. A *d* spacing of 3.7 nm corresponding to the interdistance between SDS aggregates in the gel network was obtained. The intensity of the diffraction peaks and the degree of order increased with increasing initial SDS concentration and charge content of the PDADMACl gels. The diffraction peaks were broadened when the concentration of SDS in the external solution phase was higher than its critical micelle concentration (cmc). The SAXS profiles were unexpectedly independent of the degree of cross-linking of the PDADMACl gels in the range of 0.5−2%.

Introduction

The study of polyelectrolyte gels has attracted a great deal of attention,[1] not only because of the many fundamental and interesting problems related to the charged gel state but also because of the potential applications to the pharmaceutical, environmental, and food industries. Many techniques[2−4] have been used to study the complex formation between polyelectrolytes and oppositely charged surfactants.

Polyelectrolyte gels in solution may undergo a discrete volume transition with even very small changes in the environment, such as temperature, solvent composition, and pH.[5−9] The binding of ionic surfactants with polyelectrolyte gels is a highly cooperative process.[10,11] When large amounts of ionic surfactants are absorbed, the polyelectrolyte gels collapse.[12,13] In an aqueous solution the charged surfactant chains associate inside the polyelectrolyte gel network even when the external solution concentration is significantly lower than the critical micelle concentration (cmc).[14]

The complexes of the polyelectrolyte gel and the oppositely charged surfactant could form three-dimensional supramolecular structures in aqueous solution due to a combination of hydrophobic and electrostatic interactions. It was predicted theoretically that the ions of the surfactant became more concentrated in the charged network, resulting in the formation of micelle-like aggregates.[15] 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 was found to be different from that of micelles in water.[16] Kabanov et al. reported that the complex between sodium polyacrylate and alkyltrimethylammonium bromide could form a highly ordered supramolecular structure.[17] Later, Okuzaki and Osada showed a cubic structure in the poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) gel forming complexes with *N*-alkylpyridinium chloride[18] and Khandurina et al. reported a crystalline complex between weakly cross-linked sodium polyacrylate (PANa) and cetyltrimethylammonium bromide.[19] Moreover, a complex of cationic polyelectrolyte gel and anionic−cationic mixed surfactants also produced a regular structure.[20]

In our previous paper, we showed that the complexes between a cationic polyelectrolyte gel (polydiallyldimethylammonium chloride [PDADMACl]) and an anionic surfactant (sodium dodecyl sulfate [SDS]) exhibit a highly ordered hexagonal supramolecular structure.[21] We now present a more detailed

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study on the microstructures in this polyelectrolyte gel−ionic surfactant complex by changing the parameters of the polyelectrolyte gel, i.e., the charge content and the degree of cross-linking, and by changing the concentration of the surfactant. The structural study on the alkyl chain length of the oppositely charged surfactant has been discussed elsewhere.[22]

Experimental Section

Materials and Sample Preparation. The polyelectrolyte gels were prepared by free-radical copolymerization of 40 wt % monomers containing diallyldimethylammonium chloride (DADMACl; Fluka Chemika Biochemika Corp.), acrylamide (AA; Fisher Scientific), and *N*,*N*′-methylenebisacrylamide (MBAA; Fisher Scientific) in aqueous solutions. Ammonium persulfate (Fisher Scientific) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED; Fisher Scientific) (4.4 mmol/L each) were used as the initiator and the accelerator, respectively. The degree of cross-linking was determined by the amount of MBAA added to 100% total DADMACl and AA (0.5%, 1%, 2% MBAA); this value is not obligatory equal to the actual percentage of cross-linked monomer units in the gel because of different monomer reactivities. It should be noted that we are concerned with the qualitative effects of the cross-linking density (and the charge density) of the gel. Thus, the exact quantitative contents are unimportant. The molar ratio of DADMACl and AA was determined by the desired charge content (100%, 75%, 50%, 20%, 0% DADMACl). A 100% charge content means that no AA was added, whereas a 0% charge content means only AA and MBAA were added. The two monomers DADMACl and AA have very different reactivities in polymerization. When DADMACl and AA are copolymerized, the probability of inclusion of neutral AA monomer units in the chain is much higher than that of charged DADMACl units.[23] Thus, the actual charge content of the copolymer gels does not correspond to the percent DADMACl and would be lower than the values mentioned in this paper. Gelation was carried out at 22 °C for 24 h between two glass plates (65 mm × 100 mm) separated by two spacers with a thickness 0.63 ± 0.04 mm. The formed gels were then washed in a large amount of distilled water for three 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 water-washed gel of known weight was immersed in a surfactant solution of known concentration. By adjusting the volume of the surfactant solution, a charge unit ratio, γ, between the surfactant and the gel could be maintained for each complex. Each piece of gel was equilibrated in the surfactant solution for three weeks before it was measured by small-angle X-ray scattering (SAXS).

Measurement. SAXS was performed at the X3A2 State University of New York (SUNY) Beam Line, National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), using a laser-aided prealigned pinhole collimator.[24] The incident beam wavelength (λ) was tuned at 0.154 nm. An imaging plate (IP) was used as the detection system for the SAXS measurements. The sample-to-detector distance was 490 mm. The q range covered was from 0.15 to 7 nm^{-1} for the imaging plate with $q = (4\pi/\lambda)\sin(\theta/2)$, θ being the scattering angle. The experimental data were corrected for background scattering and sample transmission. The smearing effect was negligible for this setup.

Results and Discussion

A PDADMACl gel with 100% charge content and 0.5% degree of cross-linking (99.5 mol % DADMACl and 0.5 mol % MBAA) was placed in a 1.5 mmol/L SDS solution where the γ, defined as the number ratio of initial SDS molecules in the external solution to the charge units of PDADMACl, was maintained at 5:1. The swollen gel was initially transparent. It turned white and collapsed in the surfactant solution. Figure 1 shows a typical two-dimensional SAXS image of the collapsed PDADMACl−SDS complex (PSC), with sharp powder rings. For easier comparison of all the scattering data, the SAXS images were integrated radially from the center to one-dimensional profiles. The SAXS profile of the PSC (Figure 2) explicitly shows four diffraction peaks at q = 1.68, 2.94, 3.40, and 4.47 nm^{-1}, respectively. The location of these peaks has a ratio of 1:3$^{1/2}$:4$^{1/2}$:7$^{1/2}$ and indicates a hexagonal supramolecular structure. It is very different from the structure of the known anionic gel−cationic surfactant complex structures which show either a lamellar structure[17,19] or a primitive superlattice.[18] The concentrated SDS solution could form an ordered structure in a mesomorphic phase, with hexagonal cylinders being one of those liquid crystal forms. The reported *d* spacings of hexagonal SDS structures were all greater than 4 nm[25] whereas the *d* spacing in the PSC was 3.7 nm, suggesting a difference between the gel phase and the aqueous phase.

The degree of collapse of a poly(diallyldimethylammonium bromide) gel−sodium dodecyl sulfate complex (PDADMABr−SDS) has been shown to be dependent on the molar ratio

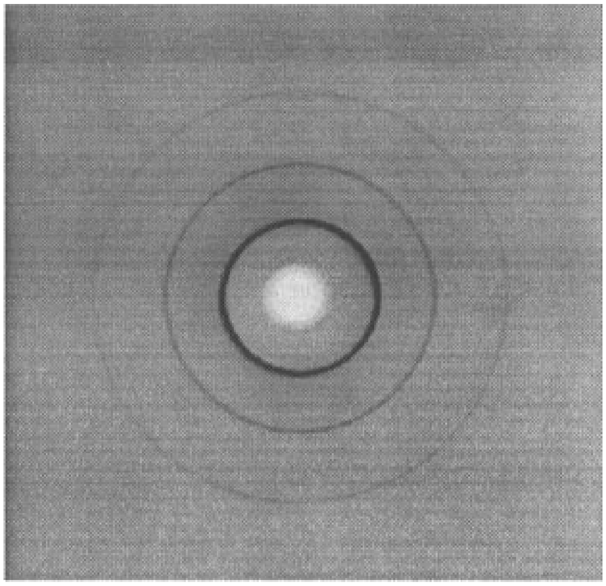

Figure 1. 2-D SAXS image of the PDADMACl−SDS complex.

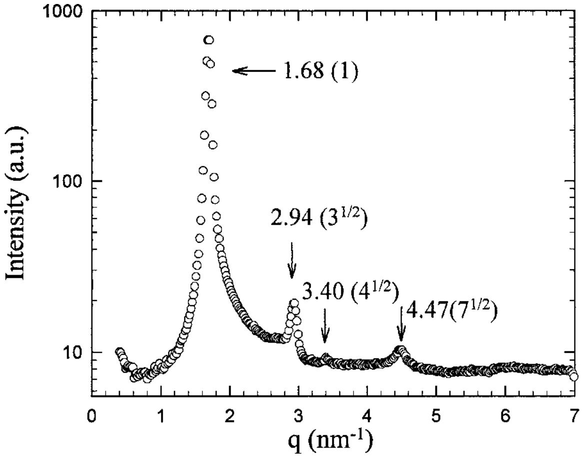

Figure 2. SAXS profile of the PDADMACl−SDS complex. The gel charge content is 100%, and the degree of cross-linking is 0.5%.

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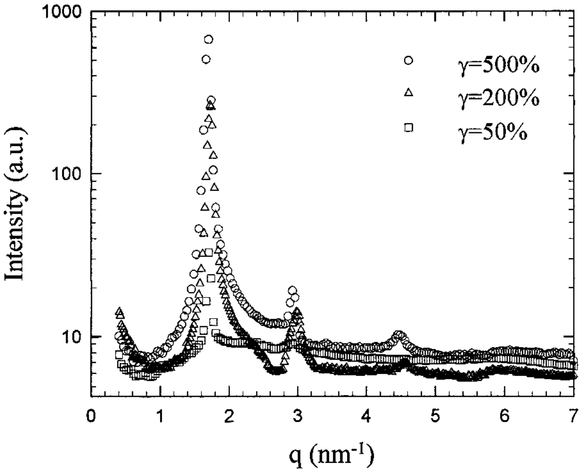

Figure 3. PDADMACl−SDS complexes with various γ ratios. The gel charge content is 100%, and the degree of cross-linking is 0.5%. The initial SDS concentration in the external solution phase is 1.5 mmol/L. Hollow circles (γ = 500%, charge content 100%) in Figures 3 and 4 denote the same data.

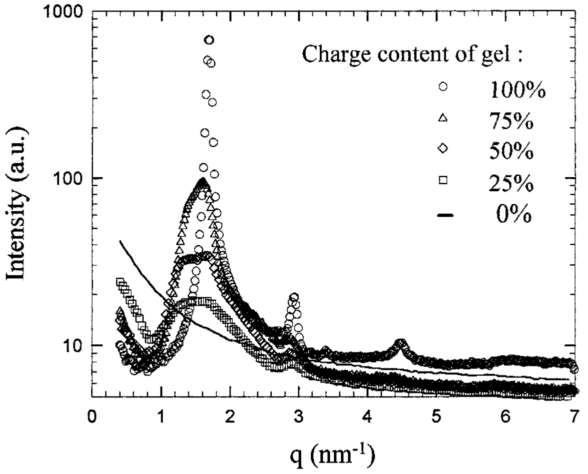

Figure 4. PDADMACl gel with various charge contents in SDS solution. The degree of cross-linking is 0.5%, and γ is 500%. The initial SDS concentration in the external solution phase is 1.5 mmol/L. Hollow circles (γ = 500%, charge content 100%) in Figures 3 and 4 denote the same data.

between the SDS and the network repeating unit[20] which is equivalent to the γ ratio here. By varying the γ ratio, the diffraction intensity of the PSC decreased with decreasing γ values. The small shifts in its peak positions were within the experimental error limit. The degree of supramolecular order in the PSC increased with increasing amount of SDS as shown in Figure 3. The interaction between the polyelectrolyte network and the oppositely charged surfactant molecules was initially driven by ion exchange which caused the surfactant molecules to be absorbed at very low surfactant concentrations by the polymer network. Once the surfactants are inside the network, the hydrophobic interaction between the long alkyl tails of the surfactant molecules and the hydrophobic polymer backbone could result in the formation of ordered structures in the PSC. Thus, the more surfactants were absorbed inside the gels the higher the degree of supramolecular order of the PSC would become. The lower scattered intensity and less prominent higher order peaks for $\gamma = 50\%$ in Figure 3 could be accounted for by the presence of less surfactants per unit cationic charge inside the PSC.

Polyelectrolyte gels do not interact with the surfactants containing charged groups with the same sign of charge, except for the polyelectrolyte network having long hydrophobic tails.[26] It is clear that the charge content of the PDADMACl gel should play a major factor in the complex formation. To change the charge content of the gel, a neutral monomer, acrylamide (AA), was copolymerized with DADMACl. By varying the mole fraction of AA, a set of polyelectrolyte gels with different amounts of charge content at 100%, 75%, 50%, 25%, and 0% (pure polyacrylamide gel) were prepared. Figure 4 shows the SAXS profiles at different charge contents of the PDADMACl.

It can be seen that the degree of supramolecular order of the PSC decreased with decreasing charge content of the gel. The diffraction peaks become broader and shift to lower *q* values. Although the diffraction peaks are broader for copolymer gels, the second-order peak could still be resolved unambiguously even down to the 25% charge content. The SAXS profiles in Figure 4 are very different from those in Figure 3. In Figure 3, the positions of the diffraction peaks remained the same for γ = 50%, 200%, and 500%, whereas in Figure 4, the diffraction peaks became broadened and shifted slightly to lower *q* values with decreasing charge content. It seems that the higher charged polyelectrolyte gels not only provide a strong driving force for the surfactant molecules to move into the gel phase but also ensure that the micelles formed are more ordered. One thing is very clear: the crystalline structure could not be formed without the charges in the polymer network. Figure 4 shows that, for a neutral (0% charge) polyacrylamide gel, no ordered structure was observed.

The scale over which the supramolecular order in the PDADMACl−SDS complex is practically perfect was estimated to be greater than 80 nm (γ = 500%) by using the Scherrer formula.[21] Since a supramolecular structure is formed in the three-dimensional network, an effect from the mesh size of the network should be expected. In order to alter the mesh size of the network, the gels were synthesized at different degrees of cross-linking, 0.5%, 1%, and 2%, respectively. The degree of swelling of the gels in water, defined as $D = (W_{\mathrm{swollen}} - W_{\mathrm{dry}})/W_{\mathrm{dry}}$, shows a remarkable drop from $D = 944$ to $D = 143$ for 0.5% to 2% degree of cross-linking, respectively, with W and the subscript defining the weight and the state of the gel. The D values indicate that the mesh size is smaller as the degree of cross-linking is higher. The results from SAXS surprisingly show that the scattering profiles of the three different degrees of cross-linking can be superimposed on one another, as shown in Figure 5. The mesh size dependence is characteristic for the fully swollen state. For the collapsed gel−surfactant complex it has been observed that the degree of swelling is practically the same.[22] The collapsed gels are stabilized by attractive interactions which would compensate the initial mesh size difference. However, the degree of supramolecular order is so pronounced that the above observation cannot be used to explain why the SAXS profiles are independent of the degree of cross-linking in the range of 0.5−2%. Normally, we would expect that a higher concentration of the cross-links would disturb the ordering.

A distinct final collapsed state has been observed for PDADMACl gels in SDS solution for the initial SDS concentration above and below the cmc.[27] It is also noted that the PSC did not collapse completely in the SDS solution with initial SDS concentration above the cmc. Figure 6 shows the SAXS measurements for a PDADMACl−SDS complex with the initial SDS concentration above its cmc in the external solution phase.

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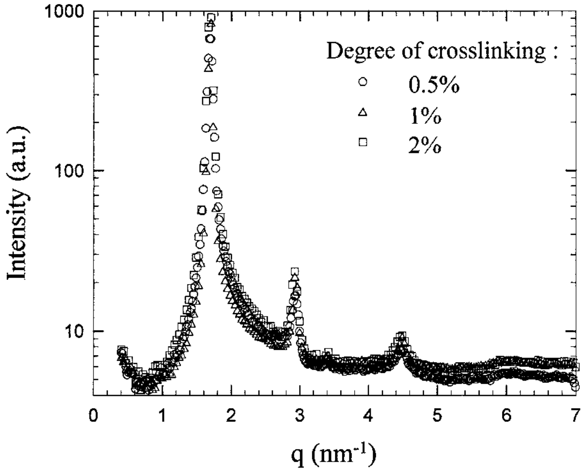

Figure 5. PDADMACl−SDS complexes with various degrees of cross-linking. The gel charge content is 100%, and γ is 500%. The initial SDS concentration in the external solution phase is 1.5 mmol/L.

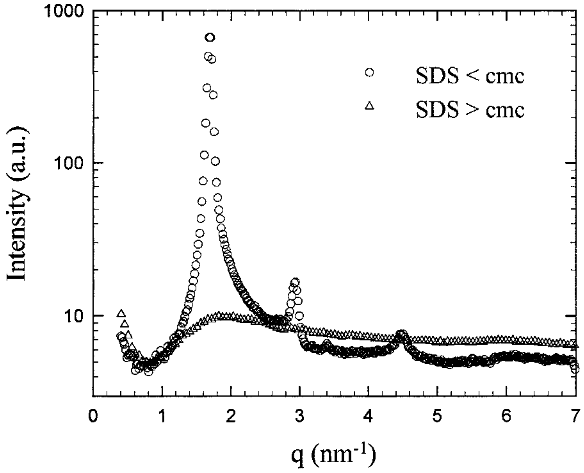

Figure 6. PDADMACl gel in various external SDS concentrations: (△) 15 mmol/L, (○) 1.5 mmol/L.

The diffraction peaks were broadened and the perfect order in the supramolecular structure of PSC essentially disappeared when the initial external SDS concentration was greater than its critical micelle concentration (~8 mmol/L). No adequate reason could account for this result, although our studies (to be published) have shown that this disappearance is not a kinetic effect. Further study is in progress.

Conclusion

The structures of the PDADMACl−SDS complex were examined by using SAXS under different experimental conditions, such as variations of the charge content and of the degree of cross-linking of PDADMACl, of the molar ratio between the surfactants and the network repeating units, and of the initial surfactant concentration. The SAXS results of the SDS−PDADMACl complex suggest the existence of a hexagonal supramolecular structure in the gel phase. The structure of the PSC is different from that of pure SDS. The characteristic distance *d* of the superstructure in the gel phase could be estimated from the primary diffraction peak: $d = 3.7$ nm. The scattered X-ray intensity and the degree of order in the SDS−gel complex increased with increasing amount of SDS embedded in the gel phase. This observation is in agreement with the result reported by Okuzaki and Osada for PAMPS gel−*N*−alkylpyridinium chloride complexes.[18] The SAXS results show that the degree of order of the SDS−gel complex also increases with increasing charge content of the polyelectrolyte gels, demonstrating that the charged monomer units not only are responsible for the initial ion exchange but also stabilize the aggregates. It is surprising that the degree of cross-linking of the PDADMACl gels below 2% has no effect on the PSC structure, probably due partially to the compensating effects on the mesh size of the collapsed gel with different degrees of cross-linking.

PSC does not form a highly ordered supramolecular structure in the gel phase when the initial external SDS concentration is above its cmc. The scattering profile becomes similar to that from SDS micelles in an aqueous solution.

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