# Formation and Transition of Highly Ordered Structures of Polyelectrolyte−Surfactant Complexes

**Shuiqin Zhou,[†] Fengji Yeh,[†] Christian Burger,[‡] and Benjamin Chu\*,[†]**

*Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794-3400, and Max-Planck-Institut fur Kolloid- & Grenzflachenforschung, Kantstr. 55, D-14513 Teltow-Seehof, Germany*

Small-angle X-ray scattering studies on the nanostructures of water-equilibrated complexes, formed by slightly cross-linked copolymer gels of poly(sodium methacrylate/*N*-isopropylacrylamide) P(MAA/NIPAM) and fully charged sodium polystyrenesulfonate (PSS), respectively, interacting with oppositely charged surfactants of alkyltrimethylammonium bromide ($C_nTAB$, with *n* being the number of carbon atoms in the alkyl chain) at ~23 °C, are presented. In P(MAA/NIPAM)−$C_nTA$ complexes, the formation and transition of highly ordered structures were investigated in terms of the surfactant alkyl chain length and the hydrophobicity of the polyelectrolyte chain. The complexes between fully charged PMAA gel and $C_nTAB$ showed *Pm3n* cubic structures at $10 \leq n \leq 16$ but did not show highly ordered structures at $n = 8$ and 18 due to the weak hydrophobic interaction and the steric hindrance of the long alkyl chains inside the gel, respectively. In complexes formed by moderately charged P(MAA/NIPAM) gel with $C_nTAB$, the decrease in the surfactant alkyl chain length could induce the phase structure transition from *Pm3n* cubic to face-centered cubic, and then to hexagonal close packing of spheres. The longer the surfactant alkyl chain, the lower the charge density and the hydrophobicity of polyelectrolyte chains are required to form highly ordered structures inside the resulting complexes. In PSS−$C_nTA$ complexes, structures of two-dimensional (2D) hexagonal packing of cylinders were determined. The 2D hexagonal structures were different from both the layered structures in the corresponding solid-state complexes and the *Pm3n* cubic structures in PMAA−$C_nTA$ complexes, in which the PMAA chains were more flexible than the PSS chains.

## Introduction

Polyelectrolyte−surfactant complexes (PSCs) have attracted a great deal of attention, not only because of their importance in fundamental polymer physics/biophysics but also because of the potential applications to pharmaceutics, engineering, and food sciences.[1−5] Many beneficial properties of the PSCs result from the highly ordered structures formed by the self-assembly of surfactant molecules inside the PSCs. The supramolecular formation was driven by both electrostatic interactions between charged components and hydrophobic interactions between the polymer backbones and the surfactant alkyl chains. Solid-state PSCs have been explored as a new class of materials with unusual optical, electrical, and mechanical properties.[1] The study of water-equilibrated PSCs should provide us with deeper insight into the mechanism of gene transfection and biomembrane functions because many biopolymers, such as DNAs and proteins, are themselves polyelectrolytes and lipids are surfactants.

There is a significant number of publications dealing with the structures of solid-state PSCs[1,6−10] in which lamellar and modulated lamellar structures as well as face-centered cubic and hexagonal packing of cylinders have been reported. However, only a few studies were carried on the structures of water-equilibrated PSCs that have potential use in biology. Kabanov et al.[11] proposed a lamallar structure for poly(sodium acrylate) gel−$C_nTAB$ complexes. Okuzaki and Osada[12] proposed a simple cubic structure for complexes formed by poly(2-acrylamido-2-

methylpropanesulfonic acid) with alkylpyridinium chloride. However, both structures might be ill identified due to the poor resolution of the X-ray scattering curves.

In our laboratory in the past few years, synchrotron small-angle X-ray scattering (SAXS) has been used to investigate the structures of the complexes formed by cationic gels of poly-(diallyldimethylammonium chloride) (PDADMACl) interacting with anionc surfactants of sodium alkyl sulfate ($SC_nS$).[13−15] Complexes of PDADMA−$C_nS$ showed structures of hexagonal packing of cylinders at $n \geq 12$ and of cubic at $n \leq 10$, respectively. Very recently, we have explored another series of complexes formed by copolymer gels of poly(sodium methacrylate/*N*-isopropylacrylamide) P(MAA/NIPAM) interacting with alkyltrimethylammonium bromide ($C_nTAB$), where the desired charge density of polyelectrolyte chains could be controlled more quantitatively due to the similar reactivity ratio of component *i* ($r_i$) for the two comonomers, namely, $r_1 = 0.89$ for NIPAM and $r_2 = 1.13$ for MAA, respectively.[16] In our previous paper,[17] we investigated the charge density effects of polyelectrolyte chains on the nanostructures of P(MAA/NIPAM) gel complexes with $C_{14}TA$ and $C_{12}TA$. The observed structures of *Pm3n* cubic, face-centered cubic (FCC), and hexagonal close packing of spheres (HCP) were analyzed in detail. The structural elements of spheres and rods were shown to be the micelles formed by the self-assembly of surfactant molecules inside the gels. In this paper, we present the effects of hydrophobic character (due to the surfactant alkyl chain length and the polyelectrolyte chains) on the formation and transition of highly ordered PSC structures. The structures of P(MAA/NIPAM) gel−

[†] State University of New York.
[‡] Max-Planck Institute.

$C_nTA$ complexes with $8 \leq n \leq 18$ were studied. The complexes formed by interactions of $C_{10}TAB$ with sodium polymethacrylate (PMAA) and sodium polyacrylate (PAA) gels were compared, as PMAA and PAA have different degrees of hydrophobicity in the backbone chains. The flexibility effects of polyelectrolyte chains on the nanostructures of PSCs were also examined.

### Experimental Section

**Materials.** Methacrylic acid (MAA) monomer (Aldrich, 98.5%) was vacuum distilled. NIPAM monomer (ARCOS, 99%) was purified by recrystalization in a toluene/hexane mixture. *N,N′*-Methylenebisacrylamide (BIS) (Ultragrade, Pharmacia LKB) as a cross-linker and ammonium persulfate (APS) (Aldrich, 98+%) as an initiator were used as received. The dialyzed sodium polystyrenesulfonate (PSS) ($M_w$ = 18000 g/mol, $M_w/M_n \leq 1.1$) was purchased from Pressure Chemical Co. The surfactants $C_8TAB$, $C_{10}TAB$, and $C_{14}TAB$, from Lancaster (98%), and $C_{12}TAB$ ($\geq$98%), $C_{16}TAB$ ($\geq$99%), and $C_{18}TAB$ (>97%), from Fluka, were used without further purification. Deionized water was distilled before use.

**Gel Preparation.** Gels were prepared by free radical copolymerization. A 15 wt % aqueous solution (5−8 mL) of the reaction mixture with a desired comonomer molar ratio and a cross-linker density of 1 mol % (of total monomers) was bubbled with nitrogen for 15 min to remove oxygen in the reaction mixture. A 35 $\mu$L amount of 10 wt % APS solution was added to the mixture. The final solutions were filtered through a 0.22 $\mu$m Millipore filter and injected into the space between two glass plates which were separated by two spacers with a thickness of $0.63 \pm 0.04$ mm. Gelation was carried out at 65 °C for 24 h. One portion of the resulting gel was washed in distilled deionized water to remove the unreacted monomers and was titrated with aqueous sodium hydroxide solution to determine the composition of the copolymer. Another portion of the gel was washed in a large amount of dilute sodium hydroxide solution ($\sim$5 × $10^{-5}$ M) for 3 weeks in order to neutralize the poly(methacrylic acid) or poly(acrylic acid) and to remove the unreacted monomers. The dilute sodium hydroxide solution was changed every 1−2 days, and the final pH value was kept at $\sim$8.2.

**Gel−Surfactant Complexation.** Complexes were prepared by immersing known amounts of neutralized and water swollen gel disks (10 mm diameter, 2−3 mm thick) in a very dilute aqueous sodium hydroxide solution of surfactants (pH $\approx$ 8−9). The surfactant concentration was approximately one-third of the critical micelle concentration (CMC) for the corresponding surfactant in the external solution phase. The total volume of the surfactant solution was controlled at such a level that the number of surfactant molecules was always in excess of the number of charged groups in the copolymer chains for complexation. The gel disks were equilibrated in the surfactant solution for about 4−8 weeks, depending on the solution concentration, before being taken out for SAXS measurements. In addition, the equilibrated P(MAA/NIPAM) gel−$C_nTA$ ($n$ = 12−16) complexes were also washed on the surface by water and vacuum-dried to determine the compositions of the dried PSCs by elemental analysis (M-H-W Lab, AZ). No bromine was detectable inside these PSCs.

**PSS−Surfactant Complexation.** Surfactant solutions of $C_n$-TAB ($n$ = 12−18) were prepared at concentrations of about 1−3 times that of CMC. A stoichiometric amount of PSS solution (0.01 g/mL) was slowly added to the stirred surfactant solutions. The turbid products were allowed to settle for 1 week. The precipitated complexes in the bottom layer were used for SAXS measurements.
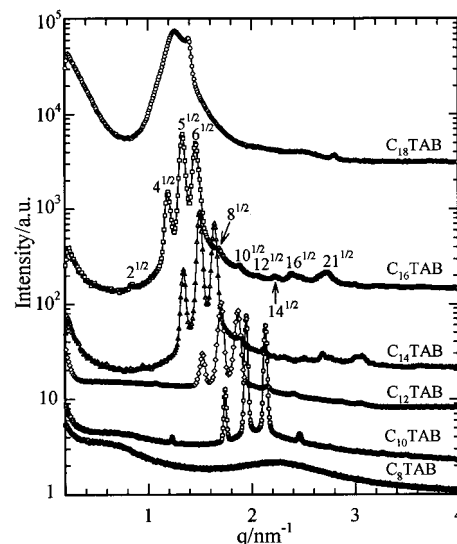


**Figure 1.** Typical SAXS profiles of PMAA gel−$C_nTA$ complexes at different surfactant alkyl chain length.

**X-ray Scattering Measurements.** SAXS measurements were performed at the X3A2 State University of New York Beam Line, National Synchrotron Light Source at Brookhaven National Laboratory, using a laser-aided prealigned pinhole collimator.[18] The incident beam wavelength ($\lambda$) was tuned at 0.154 nm. A 2D detector imaging plate was used in conjunction with an image scanner manufactured by Fujitsu Co. as the detection system. The sample to detector distance was 787 mm, corresponding to a $q$ range of $0.2 \leq q \leq 4.8$ nm$^{-1}$, with $q = (4\pi/\lambda) \sin(\theta/2)$ and $\theta$ being the scattering angle between the incident and the scattered X-rays. The experimental data were corrected for background scattering and sample transmission. The smearing effect was negligible for this setup. Experiments were also performed at the X27C Advanced Polymers Beam Line with $\lambda = 0.1307$ nm and a sample to detector distance of 1005 mm.

### Results and Discussion

**P(MAA/NIPAM) Gel−$C_nTA$ Complexes.** The complexation of P(MAA/NIPAM) gels with $C_nTAB$ solutions was formed by a slow diffusion of $C_nTAB$ molecules into the swollen hydrogels. The binding of $C_nTA$ cations to the anionic P(MAA/NIPAM) chains induced the collapse of the hydrogels. Depending on the charge content of the polyelectrolyte chain, the surfactant solution concentration, and the surfactant alkyl chain properties, the gels showed different collapse kinetics and degrees of collapse. The elemental analysis results showed that the complex formation was essentially a stoichiometric binding reaction of the surfactant molecules with the copolymer network chains in terms of charges. No bromine was detectable inside the complexes. Accordingly, there could only be slightly cross-linked negatively charged PMAA or P(MAA/NIPAM) chains, $C_nTA$ cations, and water inside the complexes after the gels reached the equilibrium of collapse.

*Effects of Surfactant Alkyl Chain Length.* Figure 1 shows SAXS profiles of the complexes formed by fully charged PMAA gel with $C_nTAB$ surfactants having different alkyl chain length. Obviously, the length of the hydrophobic alkyl chains of the surfactants plays a significant role in the structure formation in gel−surfactant complexes. The PMAA gel−$C_8TAB$ complex showed a weak broad peak, indicating that no well-defined ordered structure was formed. When $n$ was increased to 10, very

Polyelectrolyte−Surfactant Complexes

*J. Phys. Chem. B, Vol. 103, No. 12, 1999* **2109**

sharp scattering peaks were exhibited, indicating the formation of highly ordered supramolecular structures. By further increasing $n$ to 12, 14, and 16, similar sharp scattering peaks were observed in the SAXS curves. The peak location in all of the four curves ($n = 10-16$) had a ratio of $2^{1/2}:4^{1/2}:5^{1/2}:6^{1/2}:8^{1/2}:10^{1/2}:12^{1/2}:14^{1/2}:16^{1/2}:21^{1/2}$, suggesting a cubic structure of $Pm3n$ space group having been formed inside the PSCs. The proposed Miller indices of the corresponding diffraction planes are 110, 200, 210, 211, 220, 310, 222, 321, 400, 420, 421. The detailed analysis of the $Pm3n$ cubic structure has been presented elsewhere.[17,19−21] Briefly, the $Pm3n$ cubic structure consisted of spheres located at body-centered cubic (BCC) positions and a 3D cagelike network of rods which might be connected or disconnected. As expected, the structures in PSCs formed by surfactants with longer alkyl chains showed larger interplanar distances. In addition, the longer the alkyl chains in a surfactant, the stronger and sharper the high-order scattering peaks at large $q$ values would appear. The above results indicated that the strong hydrophobic interactions of surfactant/surfactant and surfactant/polymer chains were necessary in driving the self-assembled surfactant molecules, i.e., micelles, to form highly ordered supramolecular structures. However, when $n$ was increased to 18, the sharp scattering peaks disappeared again in the SAXS profiles. In principle, the very strong hydrophobic interactions between the long alkyl chains and the polymer backbone chains should lead to the formation of highly ordered structures with sharp scattering peaks and high-resolution SAXS profiles. The less ordered structure in the PMAA gel−$C_{18}$TA complex could be attributed to the steric hindrance from the relatively small mesh size of the polymer gel for the long $C_{18}$-TA ions to arrange an orderly structure of micelles inside the PMAA gel, as evidenced by experiments that higher cross-linker density (corresponding to smaller mesh size) of the polymer gel would hinder the surfactant molecules from forming highly ordered supramolecular structures.[17] The highly ordered supramolecular structure in PSCs was formed by a self-assembly of surfactant molecules inside the three-dimensional (3D) gel network. An increase in the surfactant alkyl chain length for a gel with a fixed mesh size or in the cross-linking density of the gel for a surfactant with a fixed alkyl chain length could prevent the surfactant molecules from forming ordered supramolecular structures inside the 3D gel network.

Figure 2 shows a series of SAXS curves obtained from P(MAA/NIPAM) gel−$C_n$TA ($n = 12-18$) complexes with 67 mol % charge content in the P(MAA/NIPAM) chains. Two features should be noted. First, the PSC formed by $C_{18}$TA ions interacting with 67 mol % charge content in the P(MAA/NIPAM) chains also showed a highly ordered $Pm3n$ cubic structure. The elemental analysis results for P(MAA/NIPAM) gel−$C_n$TA ($n = 12-16$) complexes showed that the complex formation follows a stringent 1:1 stoichiometric reaction between the charged copolymer chains and the surfactant molecules in terms of charges; thus, the decrease in charge density of the P(MAA/NIPAM) chains led to a decrease in the number density of $C_n$TA chains inside PSCs. Relatively, there would be more free space available (or less steric hindrance) for each $C_n$TA chain inside the complex even though the mesh size of the gel was kept unchanged. Accordingly, the strong hydrophobic interactions of long $C_{18}$TA chains could still drive themselves to self-assemble to form micelles and subsequently ordered supramolecular structures. Second, a decrease in the surfactant alkyl chain length could induce a structural phase transition of the resulting PSC. When $n$ decreased from 18 to 16 (or 14), the P(MAA/NIPAM) gel complexes with $C_{16}$TA or $C_{14}$TA
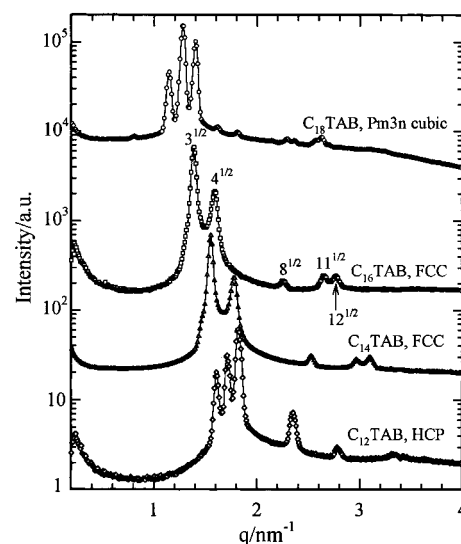


**Figure 2.** Structure transition of P(MAA/NIPAM) gel−$C_n$TA complexes with 67 mol % charge content in the copolymer chains, as induced by decreasing the surfactant alkyl chain length.
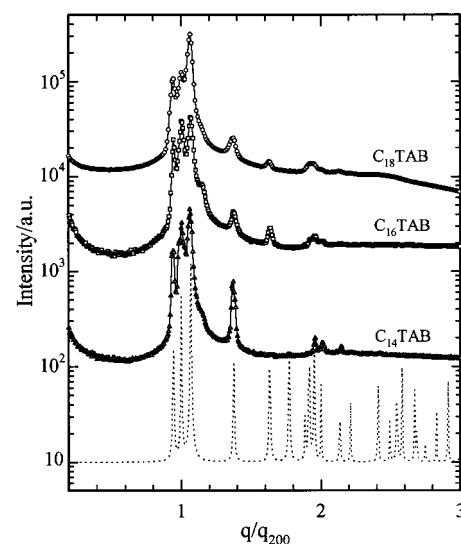


**Figure 3.** SAXS profiles of P(MAA/NIPAM) gel−CnTA complexes with 50 mol % charge content in the copolymer chains, where the $q$ scale has been normalized to $q/q_{200}$ with $q_{200} = 1.27$, 1.40, and 1.58 nm$^{-1}$ for $n = 18$, 16, and 14, respectively. The dotted line represents the calculated scattering curve based on an orthorhombic unit cell model for HCP structure.

showed another type of nanostructure. Five sharp scattering peaks with a spacing ratio of $3^{1/2}:4^{1/2}:8^{1/2}:11^{1/2}:12^{1/2}$ were observed, indicating a structure of face-centered cubic close packing of spheres (FCC). The corresponding diffraction planes could be indexed as 111, 200, 220, 311, 222. By further decreasing $n$ to 12, the structure of the P(MAA/NIPAM) gel−$C_n$TA complex changed again. The sharp scattering peaks could be indexed according to a structure of hexagonal close packing of spheres (HCP) (see Figure 3). Again, when the strength of electrostatic interactions between polyelectrolyte chains and polar heads of the surfactant was kept unchanged, variation in the surfactant alkyl chain length could determine the structure formation inside the PSCs. The decrease in the surfactant alkyl chain length could reduce the hydrophobic interactions between surfactant/surfactant and surfactant/polymer chains but increase the interfacial area ratio of polar-to-apolar moieties of the surfactant molecules. The former effect should reduce the driving force for $C_n$TA ions to self-assemble, while the later

**2110** *J. Phys. Chem. B, Vol. 103, No. 12, 1999*

Zhou et al.

effect could increase the interfacial curvature for $C_nTA$ ions favorably to easily form spherical micelles. Eventually, the decrease in the alkyl chain length of $C_nTA$ cations led to the structural transition from $Pm3n$ cubic, containing both rods and spheres, to FCC and HCP, in which the structural elements were only spheres. As analyzed above, there were only anionic PMAA or P(MAA/NIPAM) chains, $C_nTA$ ions, and water inside the gel−surfactant complexes. Thus, the structural elements of rods and spheres could only be formed by the self-assembly of $C_nTA$ ions inside the complexes. There was still a large amount of water (e.g., $\phi_w > 0.36$) inside the complexes even though the anionic gel had reached the collapsed limit. The distribution of the polyelectrolyte chains, $C_nTA$ ions, and water should be of type I;[19] namely, the apolar alkyl chains of $C_nTA$ ions were inside the rods or spheres, while water and copolymer chains stayed outside. The copolymer network chains might also be partially distributed at the polar/apolar interface of the spherical or cylindrical micelles, stabilized by both electrostatic and hydrophobic interactions of surfactant/copolymer chains.

Figure 3 shows SAXS profiles of P(MAA/NIPAM) gel−$C_n$-TA ($n = 14−18$) complexes with 50 mol % charge content in the copolymer gel network, where the $q$ scale has been normalized to $q/q_{002}$ with $q_{002} = 1.27$, 1.40, and 1.58 nm$^{-1}$ for $n = 18$, 16, and 14, respectively. When the charge density of the polyelectrolyte chain was reduced to 50 mol %, all three of the complexes showed a HCP structure. In our previous paper,[17] we have chosen an orthorhombic unit cell containing four spheres inside to describe the HCP structure. The dotted line in Figure 3 shows the simulation scattering curve calculated from the orthorhombic unit cell model, which matched the experimental curves satisfactorily. However, the relative intensities of the scattering peaks of the SAXS curve from P(MAA/NIPAM) gel−$C_{18}TA$ complex were different from those of the calculated scattering curve; namely, the intensity of the second peak was much lower than that of the corresponding peak in the calculated scattering curve. The low intensity of the second scattering peak might be attributed to the coincidence of the peak position with the first minimum of the form factor function of a sphere, $|F(q,R)|^2 = \{3/(qR)^3[\sin(qR) − qR\cos(qR)]\}^2$ with $R$ being the radius of the sphere. This coincidence requires that the diameter of the spheres must be about 14% larger than the sphere-to-sphere center distance. It means that the spheres inside the HCP structure touched each other and were deformed slightly. The compositions and HCP structure parameters of the P(MAA/NIPAM) gel−$C_nTA$ ($n = 14−18$) complexes with 50 mol % charge content in the copolymer chains were summarized in Table 1. By knowing the volume fraction ($\phi_{CnTA}$) and the concentration ($C_{CnTA}$, w/v) of $C_nTA$ cations inside PSCs and the dimension of the orthorhombic unit cell ($a$, $b$, $c$) with four spheres for the HCP structure, we can calculate the radius ($R_{sph}$) and the aggregation number ($N_{agg}$) of spherical micelles inside the complexes as follows

$$\phi_{CnTA} = [4(4\pi/3)(R_{sph})^3]/abc \qquad (1)$$

$$N_{agg} = C_{CnTA}N_A(abc)/(4M_{CnTA}) \qquad (2)$$

where the $M_{CnTA}$ is the molar mass of $C_nTA$ ions. The obtained $R_{sph}$ and $N_{agg}$ values were also listed in Table 1. The shortening of the hydrophobic alkyl chains of the surfactant led to the decrease in both the radius and the aggregation number of spherical micelles formed inside polyelectrolyte gels. The longer alkyl chains of $C_nTA$ could lead to a less compact structure and stronger hydrophobic interactions, allowing incorporation of more monomers. It should be noted that only the monodis-

**TABLE 1: Compositions and HCP Structure Parameters of P(MAA/NIPAM) gel−$C_nTA$ Complexes with 50 mol % Charge Content in the P(MAA/NIPAM) Chains**[a]

| alkyl chain length | composition | dimension of unit cell/nm | $R_{sph}$/ nm | $N_{agg}$ | $N_{agg}$ (in water)[22] |
|---|---|---|---|---|---|
| $n = 18$ | $\phi_{C18TA} = 0.43$ $\phi_p = 0.21$ $\phi_w = 0.36$ | $a = 6.04$ $b = 10.5$ $c = 9.87$ | 2.52 | 105 | 112 |
| $n = 16$ | $\phi_{C16TA} = 0.40$ $\phi_p = 0.22$ $\phi_w = 0.38$ | $a = 5.50$ $b = 9.52$ $c = 8.98$ | 2.25 | 87 | 81 |
| $n = 14$ | $\phi_{C14TA} = 0.35$ $\phi_p = 0.22$ $\phi_w = 0.43$ | $a = 4.84$ $b = 8.39$ $c = 7.91$ | 1.89 | 53 | 64 |

[a] $\phi_{CnTA}$, $\phi_p$, and $\phi_w$ are volume fraction of $C_nTA$ ions, P(MAA/NIPAM) chains, and water inside PSCs, respectively. $R_{sph}$: radius of spherical micelles of $C_nTA$ ions inside PSCs. $N_{agg}$: aggregation number of micelles packed inside PSCs.
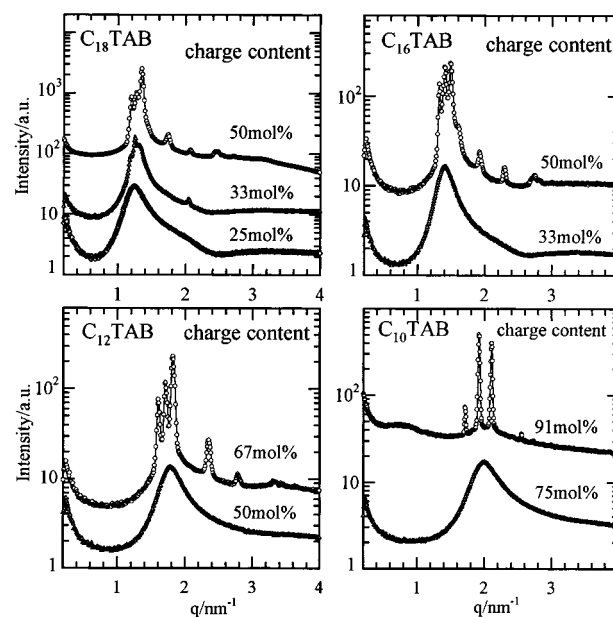


**Figure 4.** Alkyl chain length effects of surfactant on the order−disorder structure transition of P(MAA/NIPAM) gel−$C_nTA$ complexes occurring at various charge density of P(MAA/NIPAM) chains.

perse spherical micelles formed by $C_nTA$ cations were taken into account when calculating the $R_{sph}$ values. If we considered the thickness of the hydrated counterions of P(MAA/NIPAM) chains and the polydispersity of spherical micelles, it would be possible that the diameter of micelles could be very close to (or even larger than) the sphere-to-sphere center distance ($a$) inside the HCP structures under certain experimental conditions. Furthermore, the $N_{agg}$ values of $C_nTA$ micelles formed inside the polyelectrolyte gels with 50 mol % charge in the copolymer chains were close to those of $C_nTA$ micelles formed in water (outside the P(MAA/NIPAM) gel).[22] Usually, the addition of electrolyte to a surfactant aqueous solution can lead to a decrease in the CMC and an increase in the $N_{agg}$ of surfactants. However, the complexation between polyelectrolyte gels and surfactant molecules follows a stringent 1:1 stoichiometry in terms of charges. Thus, in addition to the alkyl chain length of surfactant, the charge density and the flexibility of polyelectrolyte chains will also strongly affect the $N_{agg}$ of micelles formed inside PSCs.

Figure 4 shows the effects of surfactant alkyl chain length on the order−disorder structure transitions of the resulting PSCs. With decreasing $n$ from 18 to 10, the charge density of polyelectrolyte chains must be increased dramatically to induce
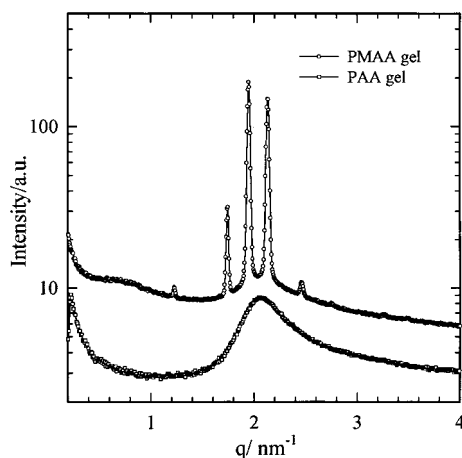
Polyelectrolyte−Surfactant Complexes

*J. Phys. Chem. B, Vol. 103, No. 12, 1999* **2111**



**Figure 5.** SAXS profiles of PMAA gel−$C_{10}$TA and PAA gel−$C_{10}$TA complexes in which the hydrophobicity of polyelectrolyte chains determined the formation of highly ordered structures.

the formation of a highly ordered structure. For P(MAA/ NIPAM) gel−$C_{18}$TA complexes, one broad SAXS peak at a charge content of 25 mol % in P(MAA/NIPAM) chains was changed to a few sharp scattering peaks at a charge content of 33 mol %, and further to a well-defined HCP structure at a charge content of 50 mol %, respectively. In contrast, the transition from one broad peak with less ordered structure to a series of sharp SAXS peaks with well-defined ordered structures occurred at charge contents of 50, 67, and 91 mol % for $n = 16$, 12, and 10, respectively. The results indicated that the longer the hydrophobic alkyl chains of surfactant, the lower the charge content of polyelectrolyte network chains required to form a highly ordered structure inside PSCs. In other words, the coupling of hydrophobic interactions and electrostatic interactions was very important to drive the surfactant molecules and polymer chains to form ordered supramolecular structures made up of micelles inside the PSCs. Once the hydrophobic interactions were reduced, the electrostatic interactions had to be strengthened to drive a well ordered molecular packing of surfactants inside the PSCs.

*Hydrophobicity Effect of Polyelectrolyte Chains.* Figure 5 shows the SAXS curves of complexes formed by fully charged 1.0 mol % cross-linked PMAA gel and PAA gel interacting with the $C_{10}$TAB surfactant, respectively. The only difference between the two complexes was the composition of the polyelectrolyte network chains; namely, PMAA chains were more hydrophobic than PAA chains due to the presence of a methyl group (instead of a hydrogen atom) per repeating unit in PMAA. The PAA gel−$C_{10}$TA complex showed only a broad SAXS peak, indicating no well-defined ordered structure formed, while the PMAA gel−$C_{10}$TA complex showed a SAXS curve with a number of sharp scattering peaks that could be indexed as the *Pm3n* cubic structure. This big difference in the structural order of the two complexes indicated that the hydrophobicity of polyelectrolyte chains also took an important role in driving the ordered molecular packing inside the PSCs. The hydrophobic interactions existed not only among the surfactant alkyl chains but also between the surfactant alkyl chains and the hydrophobic backbone chains or side groups of the polymer. The strong hydrophobicity of polyelectrolyte chains will improve the surfactant/polymer hydrophobic interactions, especially for those copolymer chains distributed at the polar/apolar interface of the surfactant, and thereby stabilizes the formed micelles inside the PSCs. Meanwhile, the charged groups of the polymer chains could also stabilize the arrangement of polar heads of the surfactant in the micelles via electrostatic interactions.
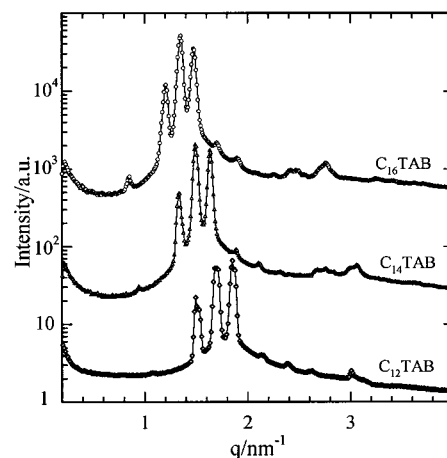


**Figure 6.** SAXS profiles of PAA gel−$C_n$TA complexes with $n \geq 12$.
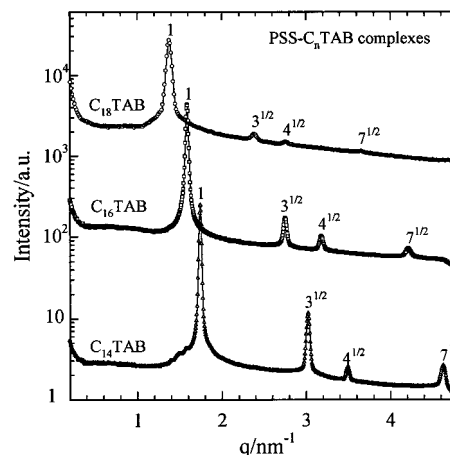


**Figure 7.** SAXS profiles of PSS−$C_n$TA complexes in which 2D hexagonal supramolecular structures were formed.

Although no highly ordered supramolecular structure was formed inside the PAA gel−$C_{10}$TA complex due to the relatively weak hydrophobicity of PAA chains, an increase in the hydrophobicity of the surfactant, by increasing the alkyl chain length to $n \geq 12$, could still lead to the formation of highly ordered structures inside the PSCs. Figure 6 shows SAXS profiles of PAA gel−$C_n$TA complexes at $n = 12−16$. Similar to the results from PMAA gel−$C_n$TA complexes at $n = 12−16$, the interactions of fully charged PAA gels with $C_n$TA cations ($n = 12−16$) also produced complexes with a highly ordered *Pm3n* cubic structure.

**PSS−$C_n$TA Complexes.** To examine the flexibility effect of polyelectrolyte chains on the formation of nanostructures inside the resulting PSCs, we also chose relatively rigid PSS as polyelectrolyte chains that were complexed with $C_n$TAB surfactants. The SAXS profiles of PSS−$C_n$TA ($n = 14−18$) complexes in Figure 7 explicitly show sharp diffraction peaks with a spacing ratio of $1:3^{1/2}:4^{1/2}:7^{1/2}$, indicating a structure of 2D hexagonal close packing of cylinders. This structure was quite different from the 3D *Pm3n* cubic structure observed in PMAA−$C_n$TA complexes; namely, *Pm3n* cubic showed structural elements of both spheres and short rods, while the 2D hexagonal structure showed only rods. The structure difference between the two complexes could be ascribed to the difference in flexibility of the PSS chains and the PMAA chains. The flexible PMAA chains were relatively easy to bend. Thus, the $C_n$TA ions bound by PMAA chains could form spherical micelles inside the resulting PSCs. In contrast, the PSS chains were far stiffer due to the phenyl side group. The arrangement

of the $C_nTA$ ions bound by PSS chains could only follow the rigid polymer backbone to form the structural element of cylinders. This flexibility effect of the polyelectrolyte chain on the nanostructures of PSCs was further evidenced by other experimental results.[12−14] For example, the PSCs formed by flexible poly(2-acryamido-2-methylpropanesulfonate) chains with alkylpyridinium showed a *Pm3n* cubic structure,[12] while the PSCs formed by relatively rigid PDADMA chains with $SC_nS$ (n ≥ 12) showed a 2D hexagonal structure.[13,14]

Finally, we like to mention that the 2D hexagonal structures observed in our water-equilibrated PSS−$C_nTA$ complexes were also different from the layered structures observed in the corresponding solid-state complexes.[6] The structure difference could be related to the "relative bulkiness" of the polar and the apolar moieties of the surfactant molecules. Reducing the water content would lead to a decrease in the polar to apolar volume ratio of $C_nTA$ cations. Eventually, the dehydration of the 2D hexagonal phase made the $C_nTA$ ions have so small an interfacial curvature that the hexagonal phase gave way to the lamellar phase.

## Conclusions

The investigation on the formation and transition of highly ordered structures, including *Pm3n* cubic, FCC, HCP, and 2D hexagonal packing of cylinders observed in PMAA gel−$C_n$-TA, P(MAA/NIPAM) copolymer gel−$C_nTA$, PAA gel−$C_nTA$, and PSS−$C_nTA$ complexes, made us draw the following conclusions. (1) The alkyl chain length of surfactant could significantly affect the formation and transition of highly ordered structures inside polyelectrolyte gel−surfactant complexes. The longer the alkyl chain length of the surfactant, the stronger the hydrophobic interactions between surfactants and polymer chains and the smaller of the volume ratio of polar-to-apolar moieties of surfactant, both of which determine the self-assembly behavior of surfactant inside the resulting complexes. The mesh size of polyelectrolyte gel would also hinder the long alkyl chains of surfactant to form well-ordered structures. (2) Both electrostatic interactions and hydrophobic interactions were very important to induce the highly ordered self-assembly of surfactant molecules. The longer the surfactant alkyl chain length, the lower the charge density and the weaker the hydrophobicity of polyelectrolyte chains were required to form highly ordered structures. (3) The flexibility of polyelectrolyte chains could affect the shape of structural elements formed by the self-assembly of polymer-bound surfactant molecules. The surfactant molecules bound by stiff polymer chains prefer to form the structural element of cylinders, while those bound by more flexible polymer chains can form spheres.

## References and Notes

(1) Ober, C. K.; Wegner, G. *Adv. Mater.* **1997**, *9*, 17.

(2) *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabham, K. P., Eds.; CRC Press: Boca Raton, FL, 1993.

(3) Fundin, J.; Brown, W.; Vethamuthu, S. M. *Macromolecules* **1996**, *29*, 1195.

(4) Gershon, H.; Ghirlando, R.; Guttman, S. B.; Minsky, A. *Biochemistry* **1993**, *32*, 7143.

(5) Crowell, K. J.; Macdonald, P. M. *J. Phys. Chem. B* **1997**, *101*, 1105.

(6) Antonietti, M.; Conrad, J.; Thunemann, A. *Macromolecules* **1994**, *27*, 6007.

(7) Antonietti, M.; Kaul, A.; Thunemann, A. *Langmuir* **1995**, *11*, 2633.

(8) Antonietti, M.; Maskos, M. *Macromolecules* **1996**, *29*, 4199.

(9) Antonietti, M.; Burger, C.; Effing, J. *Adv. Mater.* **1995**, *7*, 751.

(10) Antonietti, M.; Radloff, D.; Wiesner, U.; Spiess, H. W. *Macromol. Chem. Phys.* **1996**, *197*, 2713.

(11) Khandurina, Yu, V.; Dembo, A. T.; Rogacheva, V. B.; Zezin, A. B.; Kabanov, V. A. *Polym. Sci.* **1994**, *36*, 189.

(12) Okuzaki, H.; Osada, Y. *Macromolecules* **1995**, *28*, 380.

(13) Chu, B.; Yeh, F.; Sokolov, E. L.; Starodoubtsev, S. G.; Khokhlov, A. R. *Macromolecules* **1995**, *28*, 8447.

(14) Yeh, F.; Solokov, E. L.; Khokhlov, A. R.; Chu, B. *J. Am. Chem. Soc.* **1996**, *118*, 6615.

(15) Sokolov, E. L.; Yeh, F.; Khokhlov, A. R.; Chu, B. *Langmuir* **1996**, *12*, 6229.

(16) Brazel, C. S.; Peppas, N. A. *Macromolecules* **1995**, *28*, 8016.

(17) Zhou, S.-Q.; Burger, C.; Yeh, F.; Chu, B. *Macromolecules* **1998**, *31*, 8157.

(18) Chu, B.; Harney, P. J.; Li, Y.; Linliu, K.; Yeh, F.; Hsiao, B. S. *Rev. Sci. Instrum.* **1994**, *65*, 597.

(19) Tardieu, A.; Luzzati, V. *Biochim. Biophys. Acta* **1970**, *219*, 11.

(20) Eriksson, P.; Lindblom, G. *J. Phys. Chem.* **1985**, *89*, 1050.

(21) Eriksson, P.; Lindblom, G.; Arvidson, G. *J. Phys. Chem.* **1987**, *91*, 846.

(22) Roelants, E.; De Schryver, F. C. *Langmuir* **1987**, *3*, 209.