# Study of the Effect of Polyion Charge Density on Structural Properties of Complexes between Poly(acrylic acid) and Alkylpyridinium Surfactants<sup>†</sup>

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Received: October 28, 2002; In Final Form: March 7, 2003

Structural properties of complexes of poly(acrylate) anion (PA) and the cationic surfactants dodecylpyridinium (DPC) and cetylpyridinium chloride (CPC) were investigated by synchrotron X-ray scattering at various degrees of neutralization  $\alpha_N$  of poly(acrylic acid) (HPA) and at a fixed surfactant:polymer molar ratio. In all scattering curves, one broad (PA-DPC complexes, all  $\alpha_N$ -values, and PA-CPC complexes,  $\alpha_N = 0$ ) or several sharp peaks (PA-CPC complexes,  $\alpha_N > 0$ ) were observed, pointing to a high degree of ordering in these systems. The fundamental type of organization of surfactant is in the form of polymer-induced micelles that are clustered around the polymer. The multiple reflections in the case of PA-CPC complexes point to a Pm3n cubic structure. The calculated values of structural parameters indicate a larger degree of ordering in complexes at low  $\alpha_N$ -values (i.e., at  $\alpha_N < 0.5$ ) than that at higher ones. This suggests that the binding of the surfactant by the polyelectrolyte is influenced by factors other than the charge density of polyion. At low  $\alpha_N$ -values, the micelles are attracted by the polymer mainly through hydrophobic interactions. However, pH measurements have demonstrated that a nonnegligible contribution to attractive surfactant-polymer interactions at  $\alpha_{N}$ values close to 0 comes also from a small but pronounced increase of polymer charge upon surfactant binding. The presence of surfactant gives rise to a nearly 5-fold increase in the degree of ionization of HPA at  $\alpha_N$ 0. This increase becomes less pronounced with increasing  $\alpha_N$  and is negligible for  $\alpha_N \ge 0.5$ . From the position of the peaks in the scattering curves, the characteristic distance  $\bar{a}$  in the complexes was derived. It increases linearly with  $\alpha_N$ -values in PA-DPC solutions from 30.2 Å at  $\alpha_N = 0$  to 36.6 Å at  $\alpha_N = 1$ , and correspondingly,  $\bar{a}$  increases from 44.1 to 51 Å in PA-CPC solutions. The  $\bar{a}$ -value at  $\alpha_N = 0$  almost matches one diameter of a globular DPC or CPC micelle. This suggests that the polymer in a coil conformation does not contribute significantly to the intermicellar distance in complexes. It is proposed that micelles are clustered side by side around the polymer coil. The electrostatic repulsion between likely charged micelles could possibly be overcome by the rearrangement of their counterions from the site of binding with the polymer to the solution layer separating them. The  $\bar{a}$ -value at  $\alpha_N = 1$  exceeds that at  $\alpha_N = 0$  by 6.4 and 7 Å for DPC and CPC, respectively. This dimension is comparable to the radius of the PA anion, which is around 5.5 Å. This finding indicates that a layer of a fully charged polymer chain at  $\alpha_N = 1$  separates the micelles, and in this way, it contributes to the reduction in electrostatic repulsion among them. The linear variation of  $\bar{a}$  with  $\alpha_N$  is an indication of a smooth expansion of the PA chain upon neutralization.

## Introduction

Charged polyelectrolyte—surfactant systems are classified according to polyion or surfactant charge into types  $P^-\!-\!S^+$  and  $P^+\!-\!S^-.^1$  A basic feature of polyion—surfactant counterion interactions is the very strong association between oppositely charged components. This finding is not surprising, since strong electrostatic forces are in play. In addition, a cooperative process involving aggregation of alkyl chains of the bound surfactant molecules reinforces the electrostatic attraction.

A high priority in the study of polyelectrolyte—surfactant interactions is the determination of the degree of surfactant binding by polyelectrolyte.  $^{1-6}$  Most of the binding studies were carried out at low polyelectrolyte concentrations, typically at 5  $\times$   $10^{-4}$  monomol/L (as expressed in moles of monomer units of the polymer chain per volume), and at surfactant concentra-

tions determined by the region of cooperative binding to polyelectrolyte. In the presence of polyelectrolytes with high polyion charge density, the corresponding surfactant concentration range may be extremely low, in some cases 2—3 orders of magnitude below the usual cmc of surfactant in the absence of a polyelectrolyte.

Recently, an increasing amount of studies has been devoted to investigations of phase behavior  $^{7-10}$  and structural properties  $^{8-19}$  in mixed polyelectrolyte—surfactant solutions. A low concentration range that is appropriate for binding studies may present some limitations in structural investigations due to lower sensitivity of the methods involved in these studies. Therefore, the concentration of the polymeric component applied in structural studies is usually much higher, typically 100 times higher than the above value  $5\times 10^{-4}$  monomol/L. At these concentrations, a variety of surfactant organizations in conjunction with the polymer have been observed, ranging from simple micellar  $^{8-10,15-18}$  to cubic,  $^{8-10,12,14-18}$  hexagonal,  $^{8-11,13,15-17}$  lamellar,  $^{15,16,19,20}$  and even coexisting cubic and hexagonal. It is worthwhile to stress that all these structures can be found

<sup>†</sup> Part of the special issue "International Symposium on Polyelectrolytes."

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also in two-component surfactant—water concentrated phases (usually at surfactant concentrations higher than 40%).<sup>21</sup> However, in the presence of a polyelectrolyte, they appear at considerably lower total surfactant concentrations, which can be as low as a few weight percents.<sup>8–10,15–18</sup> This important distinction between two-component surfactant—water and three-component surfactant—polyelectrolyte—water systems is a consequence of a strong accumulation of oppositely charged surfactant ions in the vicinity of the polyion.<sup>4</sup> In a typical case of poly(styrenesulfonate) anion, the local concentration of monovalent surfactant ions may exceed the average concentration by a factor of about 2000 at the polyion surface.<sup>3,4</sup>

Although one cannot generalize findings obtained in the dilute regime to higher concentrations or vice versa, it is often possible to find correlations between binding parameters on one hand and structural features on the other. It is well established by now that both the degree of binding and the particular structure of a polymer-surfactant complex will depend on the structure of the molecules involved.<sup>1,7-18</sup> From the perspective of the polyelectrolyte, the charge density of the polyion, its flexibility, and the presence of hydrophobic instead of hydrophilic functional groups are the deciding parameters. From reports in the literature, the influence of the latter two parameters on structure formation can be obtained.<sup>22–24</sup> The importance of hydrophobic character of the polyion was demonstrated by binding studies involving polyvinyl-based polyelectrolytes with the same linear charge density parameter but different nature of the side groups, i.e., poly(styrenesulfonate) (PSS) and poly(acrylate) (PA). 22,24 It was shown that interactions between PSS anion and surfactant micelle are noticeably enhanced by the presence of hydrophobic benzenesulfonate repeating units.<sup>24</sup> The observed structures in PSS-surfactant complexes are also influenced by the hydrophobicity of the PSS chain. 15-17 For example, in a complex between PSS and cationic surfactant cetylpyridinium chloride (CPC), a simple micellar phase exists up to the surfactant to polyelectrolyte molar ratio S:P of approximately 0.75 (nonstoichiometric mixtures), whereas in a stoichiometric PSS-CPC complex (S:P  $\geq$  1), a hexagonal phase appears.<sup>15-17</sup> It was proposed that this very compact structure involves one PSS chain associated with several CPC micelles in such a way that the hydrophobic aromatic rings of the polyion are embedded in the micellar interior.  $^{15-17,22-24}$  On the other hand, in complexes of CPC with a hydrophilic PA anion, a cubic structure is found already at rather low surfactant content (S:P around 0.25) and is accompanied by a well-pronounced hexagonal phase when S:P approaches and exceeds  $1.^{8-10,15-17}$  The coexistence of two geometrically rather different phases is possible in the first place because the PA chain is a rather flexible one and in the second place because it is purely hydrophilic when completely ionized. It was argued<sup>10</sup> that these characteristics of the PA chain favor higher aggregate curvature and lead toward the formation of more or less discrete and nearly spherical surfactant aggregates. The other extreme in structure formation are very rigid polymer chains, e.g., various polysaccharides. 15 It is not very likely that a rigid chain could adapt to a curved surface of a spherical micellar aggregate. Rather, stiff polymer chains induce a lamellar-like arrangement of surfactant, 15 which enables them to remain in their more or less extended conformation. One may conclude that structures in polyelectrolyte—surfactant complexes can be rather diverse and may depend considerably on specific features of the chain.

The aggregate structure should depend also on the charge density of the polyelectrolyte. <sup>14</sup> One of the rare reports of charge density effects on nanostructures in polyelectrolyte—surfactant

complexes deals with a slightly cross-linked polyelectrolyte hydrogel, a copolymer of sodium methacrylate, MAA, and N-isopropylacrylamide, NIPAM. 14a The charge of this copolymer can be controlled on the basis of reactivity ratios for the two comonomers. In sequence with decreasing charge density of the poly(MAA-NIPAM) copolymer chains, the structures of the Pm3n cubic space group, the face-centered cubic close packing of spheres, and the hexagonal close packing of spheres were observed.<sup>14a</sup> The variation of the charge density by controlling the amount of two different monomer units in a copolymer presents a certain difficulty for further interpretation of the results. By varying the composition of copolymer, one changes not only the polyion charge density but also the chemical nature of the functional groups. As pointed out in the previous paragraph, this is a very important factor that influences the aggregate structure. To circumvent this difficulty, a more suitable way of controlling the charge density of polyions is by varying the degree of neutralization of, for example, weak acidic groups on the polymer backbone.<sup>4,25–29</sup> This is the strategy of the present study for which we have chosen a typical hydrophilic polymer, i.e., poly(acrylic acid), to exclude any specific interactions between surfactant micelle and the polymer. Two cationic surfactants were chosen for the study, dodecylpyridinium and cetylpyridinium chloride, DPC and CPC, respectively. The synchrotron X-ray scattering was used for the evaluation of structural characteristics of polymer-surfactant aggregate. The conclusions are corroborated by the results of pH measure-

### **Experimental Section**

**Materials.** Poly(acrylic acid), HPA, with a molar mass of 10 kg/mol was supplied from K&K Laboratories, Inc., Plainview, NY. The procedure for the purification was reported previously. From the acid form, the sodium salt NaPA was prepared by neutralization with NaOH. By mixing HPA- and NaPA-stock solutions of known concentrations, the solutions of poly(acrylate) anion with various degrees of neutralizations  $\alpha_N$  were obtained, i.e., with  $\alpha_N = 0.0, 0.25, 0.50$ , and 0.75. The results for  $\alpha = 1.0$  were taken from our previous structural studies. From the surfactants N-cetylpyridinium chloride (CPC, puriss, Kemika Zagreb, Croatia) and N-dodecylpyridinium chloride (DPC, a gift from Merck-Schuchardt) were repeatedly recrystallized from acetone and dried under vacuum at 50 °C. All solutions were prepared with ultrapure water obtained from Milli-Q-Reagent Grade Water System, Millipore.

**Preparation of Samples.** The polyelectrolyte—surfactant complex solutions were prepared by slowly adding the appropriate amount of DPC or CPC stock solutions in water to the polyelectrolyte solution with a desired  $\alpha_N$ -value at room temperature under stirring. Immediately after the addition of surfactant, most of the solutions became milk-like colloidal systems. The only cases of a clear solution were the PA-DPC and the PA-CPC ones at  $\alpha_N=0$ . The visual observation of samples showed that the turbidity of solutions increased with increasing  $\alpha_N$ -values. For  $\alpha_N=0.75$  and 1.0, a precipitate was obtained in an otherwise milky solution. The precipitation was more extensive in the case of CPC than in the case of DPC.

All solutions were studied at a constant concentration of the polymer ( $c_P = 0.05 \text{ monomol/L}$ ) and at a constant surfactant to polyelectrolyte molar ratio (S:P = 0.5). It is useful to note that the parameter S:P (= $c_S^{\text{tot}}/c_P$ , where  $c_S^{\text{tot}}$  is the total surfactant concentration in mol/L) in our study is closely related to the degree of surfactant binding by polyelectrolyte  $\beta$  (= $c_S^{\text{bound}}/c_P$ =

 $(c_{\rm S}^{\rm tot}-c_{\rm S}^{\rm free})/c_P$ ; here,  $c_{\rm S}^{\rm bound}$  and  $c_{\rm S}^{\rm free}$  free are the concentrations of polyelectrolyte-bound and free surfactant in mol/L, respectively), which is obtained from binding studies.<sup>1,2</sup> The critical micelle concentration values for DPC and CPC are in water at 25 °C equal to  $1.52 \times 10^{-2}$  and  $6.3 \times 10^{-4}$  mol/L, respectively.

The polymer concentration range is typical for structural studies as mentioned in the Introduction. The variable parameters were the degree of neutralization of poly(acrylic acid) and the simple salt concentration. The presence of a simple salt is a consequence of an ion exchange process between charged surfactant micelle and polyelectrolyte. Namely, when the surfactant aggregate binds to the polyion, it replaces its counterions (in this case Na<sup>+</sup> ions), and concurrently, when the polyion binds to the charged surfactant micelle, it replaces its counterions (in this case Cl<sup>-</sup> ions). Therefore, NaCl is released into the surrounding solution. Consequently, for  $\alpha_N \ge 0.5$  and for S:P = 0.5, assuming 100% binding of surfactant to polyelectrolyte, the concentration of NaCl is around 0.025 M. For  $\alpha_N$  < 0.5, one may assume that the amount of NaCl is approximately equal to  $\alpha_N c_P$ . In addition to this, some HCl could be present at low  $\alpha_N$ -values also. This could be a consequence of an increase in ionization of COOH groups on the polymer in the presence of surfactant, which would eventually lead to a release of a small amount of HCl into the solution. To prove this assumption, comparative pH measurements were performed in pure PA solutions at various  $\alpha_N$ -values and in PA solutions containing the surfactant. The polymer concentration and the S:P ratio in these measurements were the same as those in structural studies. The degree of neutralization was varied from 0 to 1 in steps  $\alpha_N = 0.0$ , 0.10, 0.25, 0.50, 0.75, and 1.0. The pH was measured by using a combined pH electrode from Mettler Toledo, type U402-M3-S7/60.

**Synchrotron Measurements.** Small-angle X-ray experiments were performed on SAXS/WAXD beam line BM26 (DUBBLE) at the European Synchrotron Radiation Facility (ESRF, Grenoble).31 The monochromatic incident light from the radiation spectrum of the source was obtained by using an energy tunable double-crystal Si(111) monochromator with saggital focusing on the second crystal to give an intense monochromatic X-ray beam in the range from 5 to 30 keV. The beam had a fixed exit height and a transmission bandwidth of  $\Delta \lambda/\lambda \approx 2 \times 10^{-3}$ . The samples were illuminated with 10 keV X-rays selected by the monochromator. The Si mirror was used to focus the beam vertically and to suppress higher harmonics coming out of the monochromator. The optical bench of the SAXS instrument allowed variation of the sample-to-detector distance from 1.0 to 8.0 m, covering the scattering vector  $|\mathbf{q}|$  (=  $q = (4\pi/\lambda)\sin\theta$ , where  $\lambda$  is the wavelength and  $2\theta$  is the scattering angle) in the range from 0.002 to 0.5  $Å^{-1}$ . The beam line is equipped with a two-dimensional gas-filled wire chamber SAXS detector. Silver behenate was used as a low-angle diffraction standard to check the proper alignment and to calibrate the q-axis.<sup>32</sup> The SAXS data were normalized to the intensity of the primary beam and corrected for the detector response. The background scattering due to the solvent was subtracted from the scattering curves by taking into account the differences in the absorption of the solution and the solvent. For the preliminary treatment of the data, the software packages BSL33 and FIT2D34 were used. The samples for measurements were filled in a thermally isolated sample holder. All measurements were performed at 25 °C.

General Remarks on Structural Parameters from Scattering Curves of Polyelectrolyte-Surfactant Solution. It has been shown<sup>15,16,35</sup> that the appearance of diffraction peaks in the SAXS profiles of polyelectrolyte-surfactant complexes is an indication of a high degree of order in the system. The value of the scattering vector corresponding to the peak maximum  $q_{\rm m}$  determines the mean characteristic distance  $\bar{a}$  between the neighboring scattering units by an expression  $\bar{a} = 2\pi/q_{\rm m}$ . Not only is the position of the maximum a convenient measure of order but so is its width. It is well-known that the powder or diffraction patterns of solid crystalline structures are composed of sharp lines (Bragg peaks) from which the lattice type of a substance and the lattice constant can be determined. On the other hand, in the case of liquids and assemblies of chain molecules, not possessing strict periodicity, the diffraction peaks become broadened. Scherrer showed<sup>36</sup> that line broadening is related to the mean long-range order L in a given sample and may be estimated from Bragg peaks by the equation:

$$L = \frac{\lambda}{\beta_{\rm S} \cos \theta} \tag{1}$$

where  $\beta_S$  is the full width (in radians) at a half-maximum intensity of the peak observed at a mean scattering angle of  $2\theta$ and  $\lambda$  is the wavelength of the incident beam. The value of  $\beta_{\rm S}$ is obtained by modeling the Bragg peak in SAXS curves using a Gaussian function. From eq 1, the spatial scale, over which the supramolecular self-assemblies in a system are periodically ordered, can be estimated.

Additional structural parameters that can be evaluated from SAXS curves are the "interaction radii"  $r_{\rm m}$  of scattering entities, which defines the region of interaction between the scattering units and the degree of disorder  $\Delta/\bar{a}$ . They are given by eqs 2 and  $3:^{35}$ 

$$r_{\rm m} = \left(\frac{\pi}{2.5}\right)^2 \frac{\lambda}{\beta_{\rm S}} \tag{2}$$

$$\Delta/\bar{a} = \frac{1}{\pi} \sqrt{\frac{\beta_{\rm S} \bar{a}}{\lambda}} \tag{3}$$

In eq 3,  $\Delta$  is the width of fluctuations in characteristic distances  $\bar{a}$  resulting from the thermal motion. There are some important turning points in the value of parameter  $\Delta/\bar{a}$ . "Gas"-type scattering with no maximum in the scattering curve occurs if the degree of disorder  $\Delta/\bar{a}$  exceeds 0.25–0.3, whereas for  $\Delta/\bar{a}$  $\approx$  0.2, one already observes a strong first maximum.<sup>35</sup> Formally speaking, the reduction in  $\Delta/\bar{a}$ -values (very sharp peaks and consequently small  $\beta_{S}!$ ) would bring us to the crystalline lattice; however, only high values of this parameter are characteristic for real objects.35

## **Results and Discussion**

pH Measurements. In Table 1 are reported changes in pH of poly(acrylate) solution at various α<sub>N</sub>-values upon addition of DPC or CPC. The data in columns 2, 4, and 6 clearly show that the addition of surfactant causes a substantial drop in pH of pure PA solution. On average, CPC causes a larger change than DPC in accordance with the stronger binding of this surfactant to the polyion.<sup>3,4</sup> For  $\alpha_N \geq 0.5$ , the lowering of the pH is in the range from 0.05 to 0.2 and from 0.3 to 0.6 for DPC and CPC, respectively. To a first approximation, this is independent of  $\alpha_N$  in this  $\alpha_N$ -range. However, for  $\alpha_N=0.0$ , 0.10, and 0.25, the corresponding change in pH is considerably higher and increases with increasing  $\alpha_N$ -values. In the case of  $\alpha_N = 0.25$ , the pH is lowered by around 1.2 and 1.6 pH units for DPC and CPC, respectively. This confirms the assumption that the addition of an oppositely charged surfactant increases

TABLE 1: Experimental pH Values and the Calculated Degrees of Ionization  $\alpha$  (Equation 4) in Solutions of Pure Poly(acrylate) Anion (PA) and in Poly(acrylate)—Surfactant Solutions, PA—DPC and PA—CPC, at Various Degrees of Neutralization  $\alpha_N$  and for Constant  $c_P=0.05$  monomol/L and S:P =  $0.5^a$ 

	PA		PA-DPC		PA-CPC	
$\alpha_{N} \\$	pН	α	pН	α	pН	α
0.00	3.05	0.018	2.35	0.089	2.40	0.080
0.10	4.13	0.101	2.68	0.142	2.61	0.149
0.25	5.10	0.250	3.92	0.252	3.46	0.257
0.50	6.35		6.30		6.02	
0.75	7.18		6.97		6.60	
1.00	9.27		9.10		8.94	

 $^{\it a}$  Values of  $\alpha$  are reported only for low degrees of neutralization (see text).

the degree of ionization of unneutralized or partly neutralized poly(acrylic acid).

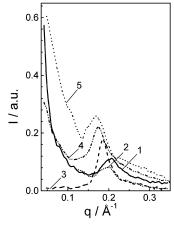
The distinction between the degree of neutralization  $\alpha_N$  and the degree of ionization  $\alpha$  is negligible at high  $\alpha_N$ -values, but for low  $\alpha_N$ -values, it needs to be taken into account. From the electroneutrality condition, the following expression is derived:

$$\alpha = \alpha_{\rm N} + \frac{[\text{H}^+] - [\text{OH}^-]}{c_{\rm P}} \tag{4}$$

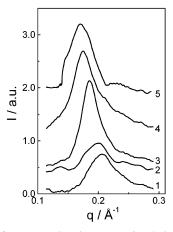
where [H<sup>+</sup>] and [OH<sup>-</sup>] are calculated from the measured pH. Applying eq 4 to pure HPA ( $\alpha_N = 0.0$ ) at  $c_P = 0.05$  monomol/ L, one obtains the degree of ionization as  $\alpha = 0.018$  (cf. Table 1), indicating that nearly 2% of COOH groups are ionized. Upon addition of surfactant, the degree of ionization of HPA ( $\alpha_N$  = 0.0) increases to approximately 0.09 and 0.08 in the case of DPC and CPC, respectively (cf. Table 1). This is a nearly 5-fold increase. Upon the increase of the degree of neutralization of poly(acrylic acid) to 0.1, the increase in the ionization degree upon addition of surfactant is around 1.5-fold for both surfactants, whereas for  $\alpha_N = 0.25$ , an increase of only 1% and 3% is found in the case of DPC and CPC, respectively. For  $\alpha_N \ge$ 0.50, there is no longer any significant difference between  $\alpha$ and  $\alpha_N.$  Therefore, these  $\alpha\text{-values}$  are not reported in Table 1. One can conclude that the surfactant has a substantial influence on the dissociation behavior of poly(acrylate anion) at low  $\alpha_{N}$ values.

It has to be noted that the influence of surfactant on degree of ionization of weak polyacids was observed before. 20c,26-28 It has been shown, also by pH measurements, that the degree of dissociation in solutions of unneutralized poly(acrylic acid) increases upon addition of tetradecyltrimethylammonium<sup>26</sup> or cetyltrimethylammonium bromide,28 TTAB or CTAB, respectively. In accordance with the pH results, Kiefer et al. 26a,b found out that the onset of binding of TTAB to PA at α-values below 0.4 shifts to lower free TTAB concentrations with decreasing  $\alpha$ , whereas for  $\alpha > 0.4$  it is independent of  $\alpha$ . Concurrently, the cooperativity of binding for  $\alpha$  < 0.4 increased with decreasing  $\alpha$ . 26a,b It was argued 26a,b that this could be a consequence of changes in polymer conformation and possibly hydrophobicity of the backbone that occur at these low degrees of ionization. As demonstrated by pH measurements reported herein, it could be also a consequence of a considerable increase in charge of the polyion at low  $\alpha$ -values that is caused by the binding of highly charged micelles.<sup>26c</sup>

**Small-Angle X-ray Scattering.** Figure 1 shows SAXS profiles obtained in solutions of poly(acrylate) anion and dodecylpyridinium chloride (PA-DPC) at various degrees of



**Figure 1.** SAXS patterns in PA-DPC solutions at different degrees of neutralization  $\alpha_N$  of poly(acrylic acid): curves 1-5 with  $\alpha_N=0.0$ , 0.25, 0.50, 0.75, and 1.0 (the last one is taken from ref 16a), respectively.



**Figure 2.** Interference maxima in PA-DPC solutions corrected for the background scattering (the numbering of curves is the same as that in Figure 1). For clarity, the curves are displaced by an appropriate integer.

neutralization of the polyacid. The curve for  $\alpha_{\text{N}}=1.0$  is taken from our previous studies. 16,17 All curves for PA-DPC solutions display one broad diffraction maximum in the q-range from about 0.21 to 0.17  $\text{Å}^{-1}$ . The position of the maximum gradually shifts to lower  $q_{\rm m}$ -values with increasing  $\alpha_{\rm N}$ . This is more evident from Figure 2, where the interference maxima after the correction for the background scattering are shown. As a consequence of the decrease in  $q_{\rm m}$ , the corresponding characteristic distances  $\bar{a}$  between the scattering units increase with increasing  $\alpha_N$ -values from 30.2 to 36.7 Å. By taking into consideration the length of an extended dodecyl (C12) chain embedded in a micellar core (i.e.,  $l_{C_{12}} = 15.42 \text{ Å}^{16,37,38}$ ), these ā-values are comparable to one diameter of a spherical DPC micelle (30.84 Å). Consequently, the appearance of a maximum in scattering curves is attributed to the micelle-like aggregation of DPC and to a subsequent side-by-side ordering of these micelles in the vicinity of the polymer. 15-17

The  $q_{\rm m}$ -values and the distances  $\bar{a}$  obtained in PA-DPC solutions as a function of  $\alpha_{\rm N}$  are reported in Table 2 together with the structural parameters calculated from eqs 1-3. It can be seen that the mean long-range order L and the interaction radius  $r_{\rm m}$  increase with increasing degree of neutralization in the  $\alpha_{\rm N}$ -range  $0.0 \le \alpha_{\rm N} \le 0.5$ . On the other hand, for  $\alpha_{\rm N} = 0.75$  and 1.0, they drop again and become practically equal to the value obtained for  $\alpha_{\rm N} = 0.0$ . A similar observation applies to the degree of disorder  $\Delta/\bar{a}$  in the system, which is reported

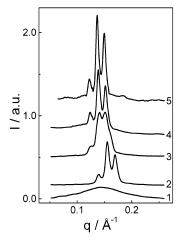


Figure 3. SAXS patterns in PA-CPC solutions at different degrees of neutralization  $\alpha_N$  of poly(acrylic acid): curves 1–5 with  $\alpha_N = 0.0$ , 0.25, 0.50, 0.75, and 1.0 (the last one is taken from refs 15 and 16a), respectively. For clarity, the patterns are displaced by an appropriate

TABLE 2: Structural Parameters in PA-DPC Solutions as a Function of Degree of Neutralization  $\alpha_N$  Obtained from the Peaks in the SAXS Curves:  $c_P = 0.05$  monomol/L and

$\alpha_{N}$	$q_{ m m}$ / $ m \AA^{-1}$	$\beta_{ m s}  imes 10^3/{ m rad}$	$\bar{a}/\mathrm{\mathring{A}}$	L/Å	$r_{ m m}/{ m \AA}$	$\Delta/\bar{a}$
0.00	0.2081	9.209	30.2	135	213	0.151
0.25	0.1983	6.906	31.7	180	284	0.134
0.50	0.1877	6.419	33.5	193	305	0.133
0.75	0.1791	8.554	35.1	145	229	0.157
1.00	0.1719	8.597	36.7	144	228	0.161

TABLE 3: Position of Maxima and Characteristic ā-Spacings Obtained from the SAXS Patterns in PA-CPC Solutions as a Function of Degree of Neutralization  $\alpha_N$ :  $c_P =$ 0.05 monomol/L and S:P = 0.5

		$q_{ m m}/{ m \AA}^{-1}$			$\bar{a}/\mathrm{\mathring{A}}$	
$\alpha_{N} \\$	1. max	2. max	3. max	1. max	2. max	3. max
0.00	0.1426			44.1		
0.25	0.1398	0.1554	0.1694	44.9	40.4	37.1
0.50	0.1272	0.1410	0.1507	49.4	44.6	41.7
0.75	0.1246	0.1390	0.1517	50.5	45.2	41.4
1.00	0.1230	0.1370	0.1490	51.0	45.9	42.0

in the last column of Table 2. The values of the latter parameter are below 0.2 ( $\Delta/\bar{a}$  is between 0.13 and 0.16) and first decrease with increasing  $\alpha_N$ , while, for  $\alpha_N = 0.75$  and 1.0, they increase again and acquire approximately the same values as those at  $\alpha_N = 0.0$ . The decrease in ordering at higher  $\alpha_N$ -values (higher polyion charge densities!) is in contrast with intuitive expectations and it repeatedly suggests that lower charge densities are more favorable for interactions of PA with surfactants.<sup>26</sup> This observation is in agreement with pH measurements reported above. Further conclusions that follow from structural parameters in Table 2 will be presented later on.

The scattering curves for PA-CPC solutions at experimental conditions identical to those in PA-DPC ones are shown in Figure 3. Only for  $\alpha_N = 0.0$  is one broad maximum obtained in this case, whereas for  $\alpha_N > 0.0$  three rather sharp diffraction peaks appear. Their positions in  $q_{\rm m}$ -values are reported in Table 3. Because of low  $\beta_s$ -values in PA-CPC case (sharp peaks!), the L and  $r_{\rm m}$  increase considerably in comparison with the values found in PA-DPC solutions. At the same time, the degree of disorder  $\Delta/\bar{a}$  becomes smaller than 0.1 (cf. eq 3 and the corresponding comments on  $\Delta/\bar{a}$ -values). It has been stated before that one cannot encounter extremely low values of  $\Delta/\bar{a}$ 

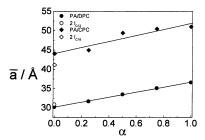


Figure 4. Characteristic distance  $\bar{a}$  in PA-surfactant solutions as a function of  $\alpha_N$ : ( $\bullet$ ) PA-DPC and ( $\diamond$ ) PA-CPC; the open symbols (O) and ( $\diamondsuit$ ) denote the lengths of two dodecyl ( $C_{12}$ ) and two cetyl (C<sub>16</sub>) chains, respectively.

(or high values of L and  $r_{\rm m}$ ) in a real system; therefore, these values are not given in Table 3. Rather, the characteristic distances  $\bar{a}$  for each diffraction peak are reported in addition to  $q_{\mathrm{m}}$ -values. The values of  $\bar{a}$  obtained from the first diffraction line increase from 44.1 Å at  $\alpha_N = 0.0$  to 51.0 Å at  $\alpha_N = 1.0$ . Similarly to the PA-DPC case, these dimensions are close to the diameter of a globular CPC micelle, which is estimated at 41.12 Å. This estimation is based on the value for the length of an extended cetyl (C16) chain embedded in a micellar core (i.e.,  $l_{C_{16}} = 20.56 \text{ Å}^{15-17,37,38}$ ).

The appearance of multiple peaks in scattering profiles in Figure 3 points out that we are faced with a much more ordered, as a matter of a fact, crystalline-like, arrangement of surfactant in PA-CPC solutions as compared with those in the PA-DPC solutions. This is a consequence of the well-known increase of attractive polymer-surfactant interactions with increasing length of the surfactant hydrocarbon tail.  $^{1-4}$  The  $q_{\rm m}$ -values for the three most intense peaks have the  $\sin^2\theta$ -values in the ratio 4:5:6. Together with much weaker diffraction peaks that could be identified in the scattering profiles of Figure 3, and by comparison with previous results in PA-surfactant systems, 15-17 it was concluded that they indicate a Pm3n cubic structure. 10,15-18,21,39 In previous reports<sup>10,16</sup> the resolution of the SAXS profiles for  $PA(\alpha=1)$ -CPC complexes at S:P > 1 was much better (see, for example, Figure 8 in refs 16a and 16b and Figure 4 in ref 10). Up to 12 spectral lines identical with a  $\sin^2 \theta$  sequence 2:4:5:6:8:10:14:16:20, etc., were identified. They are consistent with the extinctions expected for the Pm3n space group.21e In all these cases, the first diffraction order is not seen, presumably because it is too weak and too close to the beam to be observed. The same structure was observed in a single crystal of N<sub>2</sub> at 49 kbar and 299 K.<sup>21e</sup> It is believed that this cubic phase is composed of slightly elongated but still discrete globular micelles in a body-centered cubic arrangement. 10,21 The lattice constant for the cubic phase in PA-CPC solutions in the present study was calculated from the first diffraction line.<sup>39</sup> Its lowest value is 88.2 Å at  $\alpha_N = 0.0$ , and the highest one is 102.5 Å at  $\alpha_{\rm N} = 1.0$ .

It is important to note some additional structural features that are common to both PA-DPC and PA-CPC solutions. In both cases, the characteristic distance  $\bar{a}$  increases with increasing  $\alpha_N$ . The dependence of  $\bar{a}$  on  $\alpha_N$  is shown in Figure 4, and it clearly demonstrates that the increase is linear. For comparison, the lengths of two extended dodecyl ( $2l_{C_{12}} = 30.84 \text{ Å}$ ) and cetyl  $(2l_{C_{16}} = 41.12 \text{ Å})$  chains embedded in a micellar core are also shown in Figure 4 (see open symbols). The  $\bar{a}$ -value at  $\alpha = 0.0$ almost coincides with the length of two alkyl chains. The value of  $\bar{a}$  at  $\alpha_N = 1.0$  exceeds the one at  $\alpha = 0.0$  by approximately 6.4 and 7 Å in DPC and CPC complexes, respectively. These differences are comparable with the radius of the PA anion, which is around 5.5 Å. $^{15-17,30}$  Similarly, the lattice constant of the Pm3n cubic phase at  $\alpha_N = 0.0$  (88.2 Å) is only a little larger (for 6 Å) than two diameters of a CPC micelle. The overall increase of the lattice constant with increasing  $\alpha_N$  (from 88.2 to 102.5 Å) is around 14 Å, which is two times the corresponding increase in  $\bar{a}$  (see above). Repeatedly, this increase can be attributed to the contribution of the PA chain to the cell constant; in this case, it is close to two PA diameters.

At this point it is appropriate also to recall the  $\bar{a}$ -values obtained for complexes of DPC and CPC with a completely neutralized PA anion, i.e., with NaPA at  $\alpha_{\rm N}=1.0$ , at variable S:P-values (S:P increasing from 0 to more than  $1^{15-17}$ ). The observed distances  $\bar{a}$  did not change in dependence on the amount of the surfactant present in the system (S:P-value!) in this case. They were equal to 36.5-36.9 Å and to 51.0-51.4 Å in NaPA-DPC and NaPA-CPC complexes, respectively. This shows that  $\bar{a}$  is not influenced by the amount of surfactant bound to the completely ionized PA anion. <sup>26c</sup> The independence of  $\bar{a}$  on S:P as observed in this case is, however, not a general observation. For polyelectrolytes with a pronounced hydrophobic character (e.g., polystyrenesulfonate; PSS,  $\alpha=1$ ) it has been observed <sup>15,16</sup> that distance  $\bar{a}$  increases with increasing S:P.

Consequently, one can conclude that the characteristic distance  $\bar{a}$  is determined mainly by two factors: (i) by the size of the surfactant aggregate (its hydrocarbon chain length and the aggregation number) and (ii) by the thickness of the polymer chain, in the case that chain wraps around the aggregate. In view of this, the increase of  $\bar{a}$  with  $\alpha$  for PA—surfactant systems in this study could be interpreted as being a consequence of a variable micellar size and/or a gradual inclusion of the polyion chain between polymer-induced surfactant micelles. First, the small difference between the observed values of  $\bar{a}$  in aggregates at  $\alpha = 0.0$  (30.2 and 44.1 Å for PA-DPC and PA-CPC, respectively) and the calculated values for one micellar diameter (30.84 and 41.12 Å for a spherical DPC and CPC micelle, respectively) is discussed. This difference could be attributed to a different aggregation number of the surfactant micelle in the presence and in the absence of a polymer. That is, it has been found by Fundin et al.<sup>28</sup> that micelles of cetyltrimethylammonium bromide, CTAB, which form in the presence of poly(acrylic acid) at  $\alpha = 0.0$ , are smaller than the free ones. For example, aggregation number of CTAB in a 70 mM HPA solution with S:P = 0.5 is around 62, <sup>28</sup> whereas in a polymer free 20 mM CTAB solution without added salt it is 107.28 In our case we have observed two trends: a small decrease in the size-dependent parameter  $\bar{a}$  is seen for the PA induced DPC micelle, whereas for the CPC one a small increase in  $\bar{a}$  is found. both in comparison with the size of the free micelle.

Next, the observed increase of  $\bar{a}$  with  $\alpha_N$  could also be ascribed to an increase in the micellar aggregation number with increasing degree of ionization of the polymer. However, it has been shown by a fluorescence study from Kiefer et al.26a of solutions of partly or completely ionized PA and TTAB that there is only little difference in aggregation numbers as a function of  $\alpha$ . For example, at  $\alpha = 0.26$  and at a degree of binding  $\beta$  around 0.42 (close to the S:P-value in our study!), the aggregation number N is around 53, at  $\alpha = 0.51$  and  $\beta \approx$ 0.60, it is around 48, whereas at  $\alpha = 1.0$  and  $\beta = 0.42$ , a value of 59 is obtained for N. <sup>26a</sup> These results suggest, as proposed by the authors, <sup>26a</sup> that the surfactant aggregate size in PA-TTAB complexes is independent of charge density within experimental error. It has to be noted at this point that in contrast to the micellar aggregation number the overall composition of the PA-surfactant complex does depend on α. It has been shown<sup>20c</sup> that insoluble (S:P = 1) complexes formed between

PA and dodecyltrimethylammonium bromide, DTAB, at low pH are 6-fold enriched in polyelectrolyte, whereas at neutral or basic pH they contain polyelectrolyte and surfactant in an equivalent ratio. No attempt was made in this study in order to determine the dependence of the composition of PA—surfactant complexes on  $\alpha$ .

In agreement with our observations on the constancy of distances  $\bar{a}$  in dependence on S:P at  $\alpha_N = 1.0$  (see discussion above), Hansson and Almgren<sup>6</sup> have demonstrated by fluorescence measurements in solutions of PA and DTAB that the aggregation number of NaPA induced DTAB micelle is rather insensitive to the S:P ratio. All these observations lead one to conclude that there is no general understanding on how the polymers influence the aggregation numbers of surfactants. In all three situations, a constant aggregation number, 6,26a and both an increase<sup>25</sup> and a decrease<sup>28,40</sup> in this parameter for the polymer-induced micelles as compared to the ordinary ones, have been observed. Furthermore, as far as we could ascertain, there are no systematic studies correlating micellar aggregation numbers with the actual diameter of a globular micelle in solution. Consequently, we assume in the following discussion that the larger part of the observed increase of  $\bar{a}$  with  $\alpha_N$  in our systems comes from the contribution of the polyion to this characteristic dimension. Changes in surfactant aggregation number, if any, should have only a minor contribution to the overall variation in  $\bar{a}$ .

With this in mind, the following interpretation of the increase of  $\bar{a}$  with  $\alpha_N$  in PA-DPC and in PA-CPC solutions is proposed. At  $\alpha_N = 0.0$ , the pure polymer is nearly uncharged (self-ionization is responsible for less than 2% of the total charge of the fully ionized polyacrylate anion; cf., pH measurements) and adopts a random coil conformation.<sup>41</sup> It has been shown<sup>42</sup> that surfactants interact in a cooperative way with polymers even if they bear no charge. A characteristic feature of this cooperative binding is that surfactant forms micelles near the polymer coil (not in bulk solution) at total surfactant concentration that is usually lower than its critical micelle concentration, cmc.<sup>42</sup> Important driving forces responsible for this association can be rather strong hydrophobic interactions between surfactant micelles and the polymer backbone. 43 It seems that hydrophobic interactions, although short-ranged, are able to compensate for the weaker electrostatic stabilization of the surfactant aggregate. However, electrostatic interactions also play an important role at low  $\alpha_N$ -values. Upon the addition of surfactant, the degree of ionization of HPA is increased from 2% to nearly 10%. This small but pronounced increase in polymer charge is an additional contributing factor in the process of cooperative binding of surfactant to polymer. Interestingly, Fundin et al.<sup>28</sup> have shown by measuring hydrodynamic radius of the polymer-surfactant complex in a system PA-CTAB that in the first stage of surfactant binding the polymer coil initially shrinks in order to bring the ionized carboxyl groups close enough for the interaction of the bound surfactant to occur. The hydrodynamic radius of PA-CTAB reaches a minimum value<sup>28</sup> at around surfactant to polymer molar ratio (S:P) equal to 0.5, which the same as that in our study.

To recap, one may visualize the polymer chain in a random-coil conformation merely as a site in solution around which surfactant self-assembles into a cluster of several micelles. The characteristic distance  $\bar{a}$  in this case corresponds to a center-to-center separation between two adjacent micelles. This is (see Tables 2 and 3) very close to one micellar diameter. A schematic representation of the mutual arrangement of the polymer chain and the surfactant aggregates at  $\alpha_N=0.0$  is given in Figure 5a.

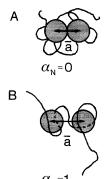


Figure 5. Schematic representation of a structural element in the polyion-surfactant complex at two values of the degree of neutralization  $\alpha_N$  of the polyion, i.e., (a) at  $\alpha_N=0.0$  and (b) at  $\alpha_N=1.0$ ; the characteristic distance  $\bar{a}$  within the aggregates is denoted by an arrow.

For simplicity, counterions are omitted in this scheme. It should be stressed that the scheme in Figure 5a does not imply a real physical contact between micelles; rather, its intention is to point out that the polymer chain does not contribute significantly to the separation distance between adjacent micelles. In part, the repulsive interactions between charged micellar aggregates are compensated by the condensation of surfactant counterions (i.e., Cl<sup>-</sup> ions) to the surface of the aggregate. The phenomenon of ion binding is well-known for free micelle formation.44 Another important moment in overcoming the repulsive electrostatic forces between likely charged micelles is the observed change in the degree of ionization of HPA and additional coiling of the chain.<sup>28</sup> According to this, the polymer can adopt a local charge density only at the site of surfactant binding, whereas the rest of the chain remains essentially uncharged and still coiled. The redistribution of surfactant and polymer counterions from the contact site with the locally charged polymer into the solution layer separating the adjacent micelles may lead to additional screening of electrostatic repulsion.

The opposite case is the situation at  $\alpha_N = 1.0$ . A fully charged PA chain powerfully attracts charged surfactant micelles. To screen the repulsion between the charged headgroups of the surfactant, the flexible PA chain makes loops around the micelles and in this way acts as a polymeric counterion in place of the simple chloride ones<sup>10</sup> (see Figure 5b). It has been shown<sup>24,42b</sup> that the entropy gain due to the release of condensed counterions from the micelle and from the polyion presents an important driving force for complex formation. If one presumes that the diameter of the DPC or CPC micelle is to a first approximation the same as the micelles' diameters in polymer solutions at  $\alpha_N = 0.0$  and at  $\alpha_N = 1.0$  (see the discussion above), then the larger  $\bar{a}$ -value can be attributed to the incorporation of the polyion chain between two neighboring surfactant micelles.

The solutions with  $\alpha_N$ -values between 0 and 1 can be interpreted as intermediate cases, where the increasing involvement of the polyelectrolyte chain in the complexes with increasing  $\alpha_N$ -values leads to a gradual increase in  $\bar{a}$ . The almost perfectly linear dependence of  $\bar{a}$  on  $\alpha_N$  is an indication of a smooth transition from a coiled conformation of poly(acrylic acid) at  $\alpha_N = 0.0$  to an extended one at  $\alpha_N = 1.0$ . This property of poly(acrylic acid) is well-known and was concluded on the basis of titration curves in the earlier studies of solution behavior of HPA.45 Different behavior could be expected for polymer chains that display a conformational transition upon increasing their degree of ionization. An example of such a polymer, with a structure very similar to that of HPA, is poly(methacrylic acid).46 Structural studies in this direction are in progress.

#### **Conclusions**

In this work we have studied the effect of the polyion charge density on structures that appear in solutions of poly(acrylate) anion and two alkylpyridinium surfactants, dodecyl- and cetylpyridinium chloride. The structures were investigated by synchrotron X-ray scattering. Parallel to this, pH measurements were carried out to study the influence of surfactant on the degree of ionization of the polymer. It was demonstrated that the ionization degree of COOH groups of the polymer increases upon surfactant binding. The increase is more pronounced at lower charge densities of the polyion. It is increased nearly 5-fold at  $\alpha_N = 0$ , only by a few percent at  $\alpha_N = 0.25$ , and becomes negligible at higher α<sub>N</sub>-values. In conjunction with results of pH measurements, the structural parameters, i.e., the mean long-range order L, the interaction radius  $r_{\rm m}$ , and the degree of disorder  $\Delta/\bar{a}$ , in PA-DPC complexes point to a larger degree of ordering at lower  $\alpha_N$ -values ( $\alpha_N \leq 0.5$ ) than that at higher ones ( $\alpha_N = 0.75$  and 1.0). This is in accordance with earlier reported results where it was found that lower charge densities are more favorable for cooperative surfactant interactions with the polymer. In addition to an increased hydrophobic character of the polymer at low  $\alpha_N$ -values, the reason for increased attractive interactions could be also a substantial increase of the ionization degree of the polymer in the presence of surfactant at these low  $\alpha_N$ -values.

Several additional conclusions can be drawn from structural studies. The first step in polyelectrolyte—surfactant complexation is micelle-like aggregation of surfactant. At low values of  $\alpha_N$ , micelles are pulled together via weak but important electrostatic interactions with the polymer and via far more important hydrophobic ones. When the charge content of the polyion is low (PA-CPC,  $\alpha_N = 0.0$ ) or when cooperative polyelectrolytesurfactant interactions are weaker (PA-DPC, all  $\alpha_N$ -values), the micellar aggregates do not form higher order crystallinelike organizations. On increasing the attractive electrostatic interactions between charged components and for surfactants with a longer hydrocarbon tail (PA-CPC, nonzero  $\alpha_N$ -values), the mutual aggregation between PA and surfactant leads to a formation of a highly ordered cubic structure of the Pm3n space group. The characteristic distance  $\bar{a}$  in PA—surfactant solutions increases in a linear manner with increasing  $\alpha_N$ . This is a result of a smooth expansion of the PA chain from a coiled form at  $\alpha_N = 0.0$  to an extended one at  $\alpha_N = 1.0$ . Such a conformational change enables a gradual incorporation of the PA chain between the micelles. It could be argued that the increase of  $\bar{a}$  with  $\alpha_N$ results from an increase in aggregation numbers of the polymerinduced micelles upon increasing the degree of neutralization of the polymer. Although the latter possibility could make a small contribution to the increase in  $\bar{a}$ -values, we believe, in view of the agreement of the overall increase in  $\bar{a}$  with dimensions of the PA anion and after critically reviewing the literature data, that the main reason for the observed linear behavior of  $\bar{a}$  with  $\alpha_N$  is the above-mentioned intrinsic property of the PA chain.

Acknowledgment. The author is indebted to Prof. Harry Reynaers for making this work possible and to Dr. Elisabeth Theunissen for her help with the X-ray scattering experiments. The team members of the SAXS beam line at DUBBLE, ESRF, Grenoble, is acknowledged for their experimental support.

#### References and Notes

(1) (a) Kwak, J. C. T., Ed. Polymer-Surfactant Systems; Surfactant Science Series 77; Marcel Dekker: New York, 1998. (b) Goddard, E. D.,

- Ananthapadmanabahn, K. P., Eds. *Interactions of Surfactants with Polymers and Proteins*; CPC Press: Boca Raton, 1993.
- (2) (a) Hayakawa, K.; Kwak, J. C. T J. Phys. Chem. 1982, 86, 3866.
  (b) Hayakawa, K.; Santerre, J. P.; Kwak, J. C. T Macromolecules 1983, 16, 1642.
  (c) Malovikowa, A.; Hayakawa, K.; Kwak, J. C. T J. Phys. Chem. 1984, 88, 1930.
  (d) Hayakawa, K.; Kwak, J. C. T J. Phys. Chem. 1983, 87, 506
- (3) Škerjanc, J.; Kogej, K.; Vesnaver, G. J. Phys. Chem. 1988, 92, 6382.
- (4) Kogej, K.; Škerjanc, J. Surfactant Binding to Polyelectrolytes. In *Physical Chemistry of Polyelectrolytes*; Radeva, T., Ed.; Surfactant Science Series 99; Marcell Decker: New York, 2001; Chapter 21, p 793.
  - (5) Hansson, P.; Almgren, M. Langmuir 1994, 10, 2115.
  - (6) Hansson, P.; Almgren, M. J. Phys. Chem. 1995, 99, 16684.
- (7) Thalberg, K.; Lindman, B.; Karlström, G. J. Phys. Chem. 1990, 94, 4289.
- (8) Ilekti, P.; Piculell, L.; Tournilhac, F.; Cabane, B. J. Phys. Chem. B 1998, 102, 344.
- (9) Ilekti. P.; Martin, T.; Cabane, B.; Picelell, L. J. Phys. Chem. B 1999, 103, 9831.
- (10) Svensson, A.; Picullel, L.; Cabane, B.; Ilekti, P. J. Phys. Chem. B 2002, 106, 1013.
  - (11) Carnali, J. O. Langmuir 1993, 9, 2933.
  - (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) (a) Zhou, S.; Burger, C.; Yeh, F.; Chu, B. *Macromolecules* **1998**, *31*, 8157. (b) Zhou, S.; Yeh, F.; Burger, C.; Chu, B. *J. Phys. Chem. B* **1999**, *103*, 2107.
- (15) Kogej, K.; Evmenenko, G.; Theunissen, E.; Škerjanc, J.; Berghmans, H.; Reynaers, H.; Bras, W. *Macromol. Rapid Commun.* **2000**, *21*, 1226.
- (16) (a) Kogej, K.; Evmenenko, G.; Theunissen, E.; Berghmans, H.; Reynaers, H. *Langmuir* **2001**, *17*, 3175. (b) Kogej, K.; Theunissen, E.; Reynaers, H. *Langmuir* **2002**, *18*, 8799.
- (17) Kogej, K.; Theunissen, E.; Reynaers, H. Acta Chim. Slov. 2001, 48, 353.
  - (18) Hansson, P. Langmuir 1998, 14, 4059.
- (19) Mironov, A. V.; Starodoubtsev, S. G.; Khokhlov, A. R.; Dembo, A. T.; Yakunin, A. N. *Macromolecules* **1998**, *31*, 7698.
- (20) (a) Khandurina, Yu. V.; Dembo, A. T.; Rogacheva, V. B.; Zezin, A. B.; Kabanov, V. A. *Polym. Sci.* **1994**, *36*, 189. (b) Khandurina, Yu. V.; Rogacheva, V. B.; Zezin, A. B.; Kabanov, V. A. *Polym. Sci.* **1994**, *36*, 195. (c) Ibragimova, Z. Kh.; Kasaikin, V. A.; Zezin, A. B.; Kabanov, V. A. *Polym Sci. U.S.S.R.* **1986**, *28*, 1826.
- (21) (a) Balmbra, R. R.; Clunie, J. S.; Goodman, J. F. *Nature* **1969**, 222, 1159. (b) Luzzati, V.; Reiss-Husson F. *Nature* **1966**, 210, 1351. (c) Luzzati, V.; Tardieu, A.; Gulik-Krzywicki, T.; Rivas, E.; Reiss-Husson F. *Nature* **1968**, 220, 485. (d) Jordan, T. H.; Streib, W. E.; Smith, H. W.; Lipscomb, W. N. *Acta Crystallogr.* **1964**, 17, 777. (e) Don, B. T.; Mills, R. L.; Schiferl, D.; Schwalbe, L. A. *Acta Crystallogr.* **1981**, *B37*, 8.

- (22) Gao, Z.; Wasylishen, R. E.; Kwak, J. C. T. J. Colloid Interface Sci. 1988, 126, 371.
  - (23) Macdonald, P. M.; Tang, A., Jr. Langmuir 1997, 13, 2259.
  - (24) Kogej, K.; Škerjanc, J. Langmuir 1999, 15, 4251.
  - (25) Chu, D.; Thomas, J. K. J. Am. Chem. Soc. 1986, 108, 6270.
- (26) (a) Kiefer, J. J.; Somasundaran, P.; Ananthapadmanabhan, K. P. In *Polymer solutions, Blends, and Interfaces*; Noda, I., Rubingh, D. N., Eds.; Elsevier: Amsterdam, 1992; Vol. 11, pp 423–44. (b) Kiefer, J. J.; Somasundaran, P.; Ananthapadmanabhan, K. P. *Langmuir* 1993, *9*, 1187. (c) Feldshtein, M. M.; Zezin, A. B. *Mol. Biol.* 1974, *8*, 114.
  - (27) Shimizu, T. Colloids Surf., A 1994, 84, 239.
- (28) Fundin, J.; Hansson, P.; Brown, W.; Lidegran, I. *Macromolecules* **1997**, *30*, 1118.
  - (29) Kogej, K.; Škerjanc, J. Acta Chim. Slov. 1999, 46, 269.
  - (30) Škerjanc, J. Biophys. Chem. 1974, 1, 376.
  - (31) Bras, W. J. Macromol. Sci., Phys. 1998, B37, 557.
- (32) Huang, T. C.; Toraya, H.; Blaton, T. N.; Wu, Y. J. Appl. Crystallogr. 1993, 26, 180.
  - (33) Mant, G. R. Daresbury Laboratory. Private communication.
  - (34) Hammersley, A. ESRF, Grenoble. Private communication.
- (35) Vainshtein, B. K. Diffraction of X-rays by Chain Molecules; Elsevier: New York, 1996; Chapter 5, p 203.
  - (36) Scherrer, P. Göttinger Nachrichten 1918, 2, 98.
- (37) Tanford, C. The Hydrophobic Effect: Formation of Micelles and Biological Membranes; Wiley: New York, 1973; p 52.
  - (38) Škerjanc, J.; Kogej, K.; Cerar, J. Langmuir 1999, 15, 5023.
- (39) Klug, H. P.; Alexander, L. E. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials; Wiley: New York, 1974; p 419.
- (40) Abiun, E. B.; Scaiano, J. C. J. Am. Chem. Soc. 1984, 106, 6274.
- (41) Flory, P. J. Statistical Mechanics of Chain Molecules; Interscience: New York, 1969.
- (42) (a) Jones, M. N. *J. Colloid Interface Sci.* **1967**, *23*, 36. (b) Goddard, E. D. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabahn, K. P., Eds.; CPC Press: Boca Raton, 1993; p 123 and references therein.
- (43) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabahn, K. P., Eds.; CPC Press: Boca Raton, 1993; Chapter 5, p 203.
- (44) Hunter R. J. Foundations of Colloid Science; Claredon Press: Oxford, 1987; Vol. 1, Chapter 10, pp 564-625.
- (45) (a) Arnold, R. J. Colloid Sci. 1957, 12, 549. (b) Mandel, M.; Leyte, J. C. J. Polymer Sci. 1962, 56, S25. (c) Anufrieva, E. V.; Birshtein, T. M.; Nekrasova, T. N.; Ptitsyn, O. B.; Sheveleva, T. V. J. Polym. Sci. Part C 1968, 16, 3519.
- (46) (a) Eliassaf, J.; Silberberg, A. *Polymer* **1962**, *3*, 555. (b) Leyte, J. C.; Mandel, M. *J. Polym. Sci.*, *Part A* **1964**, 2, 1879. (c) Nagasawa, M.; Murase, T.; Kondo, K. *J. Phys. Chem.* **1965**, *69*, 4005. (d) Creszenci, V. *Adv. Polym. Sci.* **1968**, *5*, 358.