Effect of Hydrophobic Side Chain on Poly(carboxyl acid) Dissociation and Surfactant Binding

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ABSTRACT: Copolymers consisting of acrylic acid (AA) and 12-acryloyldodecanoic acid (ADA) [poly(ADA-*co*-AA)] were synthesized, and their dissociation behaviors and binding characteristics with ionic surfactant, dodecylpyridinium chloride, were investigated. The dissociation is strongly suppressed in the presence of ADA, and when the ADA molar fraction (F_{ADA}) is 0.5, the copolymer exhibits a distinct two-stage dissociation associated with AA and ADA. The binding process is also changed by the presence of ADA. When the ADA content is low, the surfactants bind cooperatively to form a stoichiometric complex. An increase in ADA content brings about noncooperative and nonstoichiometric complexion. The initiation constant (K_0) for an isolated surfactant binding to poly(ADA(F_{ADA} = 1.0)) is more than 3 orders of magnitude larger than that of poly(AA(F_{ADA} = 0)), indicating that the initiation of the binding is associated not only with the electrostatic interaction but also with the hydrophobic interaction between the alkyl chains of surfactant and ADA. The structure of surfactant−poly(ADA-*co*-AA) complexes changes from micelle-like to lamellar-like with the increase in F_{ADA}.

1. Introduction

Ionic surfactant binding to solvated and cross-linked polyelectrolytes having opposite charges on side chains as well as backbones has been extensively studied.[1−5] Three kinds of surfactant binding were observed: (1) stoichiometric and cooperative, (2) stoichiometric but noncooperative, and (3) nonstoichiometric but cooperative.[6] These different binding behaviors are determined by the structure of the ionic surfactant, the hydrophobicity, and the charge density of the polyelectrolytes.

Polyelectrolytes having a high charge density form a stoichiometric complex with ionic surfactant. For example, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) forms a stoichiometric complex cooperatively with ionic surfactants with long alkyl chains. The side-by-side hydrophobic interaction among the alkyl chains of the surfactant molecules gives rise to a micellar-like structure within the polymer system.[7,8]

The noncooperative and stoichiometric binding is demonstrated by the binding of tetraphenylphosphonium chloride (TPPC) with poly(2-acrylamido-2-methyl-1- propanesulfonic acid) (PAMPS). The bulky hydrophobic moiety of the TPPC surfactant interferes with the cooperative binding.[9]

The nonstoichiometric but cooperative binding is observed in amphiphilic polymers such as *x*,*y*-ionene bromide (*x*,*y*-IB) (x = 6, 12; y = 4, 6, 12) polymers and copolymers consisting of *N*-isopropylacrylamide and 2-acrylamido-2-methyl-1-propanesulfonic acid [poly(NIPA-*co*-AMPS)].[10,11] Two-step surfactant binding occurs, and soluble complexes are formed due to the extra binding of surfactant to the polyelectrolytes.

In this paper, we prepared copolymers of acrylic acid (AA) and the hydrophobic 12-acryloyl-dodecanoic acid (ADA) (poly(ADA-*co*-AA)) to investigate the effect of hydrophobic long side chain on the ionization and surfactant binding processes by studying the interaction with *N*-dodecylpyridinium chloride (C_{12}PyCl). X-ray diffraction analysis revealed that the structure of surfactant−poly(ADA-*co*-AA) complex changes from micelle-like structure to lamellar-like structure with increasing amount of hydrophobic long alkyl side chain.

2. Experimental Section

Materials. Acrylic acid (AA) (Tokyo Kasei Co. Ltd.) was distilled at 30 °C under 900 Pa before used. α,α′-Azobis(isobutyronitrile) (AIBN) (Tokyo Kasei Kogyo Co. Ltd.) used as a radical initiator and *N*,*N*′-methylenebis(acrylamide) (MBAA) (Wako Pure Chemical Industries Ltd.) used as a cross-linking reagent were recrystallized from ethanol solution. *N*-Dodecylpyridium chloride (C_{12}PyCl) and acryloyl chloride were purchased from Tokyo Kasei Co. Ltd. 12-Hydroxydodecanoic acid was purchased from Aldrich Co. Ltd.

ADA was synthesized by esterifying acryloyl chloride with 12-hydroxydodecanoic acid in tetrahydrofuran in the present of triethylamine at 4 °C for 12 h. THF-soluble matter was collected, and the product was recrystallized from methanol and dried under vacuum. The chemical structure of the product was confirmed by ^{1}H NMR, ^{13}C NMR (JEOL GSX-400, 400 MHz), and IR spectroscopy. Details were described in a previous paper.[12]

Soluble poly(ADA-*co*-AA)s were prepared by radical polymerization in the presence of 0.5 mol % AIBN in ethanol with varying ADA composition f_{ADA} = 0, 0.17, 0.33, 0.5, and 1.0 (f_{ADA} is defined as the molar fraction of ADA in the total polymer in feed), while keeping the total monomer concentration at 2.0 M. Polymerization was carried at 58 °C for 20 h, and during this period nearly 100% of the monomer was polymerized. The obtain polymer were purified and dried in a vacuum.

Poly(ADA-*co*-AA) gels were prepared by the same procedure as the soluble poly(ADA-*co*-AA) in the presence of 2 mol % MBAA. After polymerization, the gel was immersed in a large amount of ethanol for more 3 days to remove the monomer, un-cross-linked polymer, and initiator and then immersed in water for a week until reaching an equilibrium state.

The molar fraction F_{ADA} of ADA units in the poly(AHA-*co*-AA) [or ADA units in the poly(ADA-*co*-AA) gel] was determined by ^{1}H NMR from the intensity ratio of the peaks for α-proton of ADA (2.17 ppm) and α-proton of AA (2.66 ppm), and the results are shown in Table 1.

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Table 1. Molar Fraction of ADA in Poly(ADS-*co*-AA) (F_{ADA})

f_{ADA} (in feed)	0	0.17	0.33	0.5	1.0
F_{ADA} (measd by ^{1}H NMR)		0.18	0.34	0.50	

Titration of Poly(ADA-*co*-AA) Acid. The pH measurement of aqueous solution of poly(ADA-*co*-AA) was carried out in a water-jacketed cell flashing argon gas. A Hitachi-Horiba F-5 type pH meter was used. The temperature (25 °C) of sample solution was controlled by circulation of thermostated water. Since poly(ADA) is not soluble in acidic solution, the titration was started from the alkali side. Poly(ADA-*co*-AA) was dissolved in an aqueous mixture of 20×10^{-3} L of NaCl (0.1 M) and 3.5×10^{-3} L of NaOH (0.1 M), and the concentration of the polymer was adjusted to 10^{-2} M. The titration was carried out using 10^{-1} M HCl aqueous solution.

Surfactant Binding Isotherm. The binding isotherm of surfactant with poly(ADA-*co*-AA) was established by measuring free surfactant concentration in the surfactant−polymer mixed solution using a surfactant selective membrane electrode prepared from C_{12}PyCl in poly(vinyl chloride) film. The binding isotherm of surfactant with poly(ADA-*co*-AA) gel was obtained by measuring the surfactant concentration of the surrounding solution ([NaOH] = 0.1 M, ionic strength is 0.1, pH = 11.5) via the electronic spectra of the surfactant. The detail procedures were described elsewhere.[7,8,13]

Complex Formation. The complex formation was carried out at 25 °C by mixing a relatively concentrated NaOH solution (pH = 11.5) of surfactant (concentration range from 10^{-5} to 10^{-3} M) and poly(ADA-*co*-AA) polymer (3.7×10^{-3} M) at different ratios and wait for 1 week until attaining the absorbing equilibrium state. The precipitates were collected by centrifugation (3000 rpm).

X-ray Diffraction. The ordered structure of poly(ADA-*co*-AA) polymer and surfactant−poly(ADA-*co*-AA) complexes as well as the their corresponding gels were analyzed by using both a small-angle X-ray diffractometer (SAXD, 40 kV, 30 mA; Shimaza XD-610, SAG-6A) and a wide-angle X-ray image diffractometer (WAXD, 40 kV, 200 mA; RIN7-2000, Rigaku Co. Ltd.). Ni-filtered Cu radiation was used.

3. Results and Discussion

3.1. Titration of Poly(ADA-*co*-AA) Polymer. Figure 1 shows the dissociation isotherms for poly(ADA-*co*-AA)s with various ADA composition. When F_{ADA} = 0, that is, the homo-PAA, the dissociation begins at pH = 4 and saturates to α = 0.8 at pH = 10 due to electrostatic repulsion between neighboring COO^- groups. On the other hand, when F_{ADA} = 1, that is, the homo-poly(ADA), no dissociation occurs until pH = 7, and only about 50% of the carboxyl groups of ADA can dissociate at pH = 10. This result shows that the long alkyl chain of ADA strongly inhibits the dissociation of the carboxyl groups of ADA. When F_{ADA} = 0.5, dissociation begins at pH = 5 and shows the same dissociation curve as that of homo-PAA up to pH = 7, indicating that the dissociation of the AA unit occurs. When pH exceeds 7, the dissociation curve is similar to that of homo-poly(ADA), indicating that dissociation of ADA begins at pH = 7. The interesting thing is that when F_{ADA} = 0.18, the dissociation starts at the same pH as that of PAA, but at high pHs it almost reaches α = 1.0, higher than that of homo-PAA. This indicates that the presence of a small amount of long alkyl chains screens the electrostatic repulsion between neighboring dissociated COO^- groups and promotes the dissociation at a high pH.

The difference in pH values of PAA and poly(ADA) at which the dissociation starts corresponds to the free energy change to replace the dodecyl group changing from a hydrophobic alkyl medium to a hydrophilic water medium, breaking the side-by-side hydrohopic interactions. Accordingly, we have

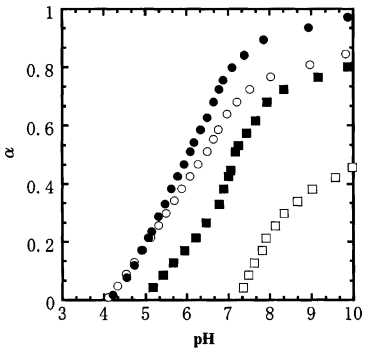

Figure 1. Relationship between pH and the degree of dissociation, α, for poly(ADA-*co*-AA) with various compositions: (○) F = 0; (●) F = 0.18; (■) F = 0.50; (□) F = 1.0.

$$\Delta F_{ADA}/k_B T = -2.3[\mathrm{pH(AA)} - \mathrm{pH(ADA)}] \approx 7 \quad (1)$$

from Figure 1. Here, ΔF_{ADA} is the hydrophobic interaction energy between alkyl chains of ADA. k_B and T are the Boltzmann constant and absolute temperature, respectively. The value thus obtained is approximately in agreement with that in the literature for an alkyl chain with 12 carbons.[14]

3.2. Surfactant Bindings. a. Competition between Dissociation and Surfactant Binding. As described in the previous section, only half of the carboxyl groups (α = 0.5) of poly(ADA) dissociates even at a pH as high as 10 due to the strong hydrophobicity of the alkyl chains. Positively charged surfactant would bind with the ionized ADA group not only through the electrostatic but also through the hydrophobic interactions between alkyl chains of surfactant and the ADA. The surfactant binding eliminates the next-neighbor repulsion between ionized groups and would promote further dissociation. The following two equilibriums would exist in solution:

$$-\mathrm{COOH} \overset{K_a}{\longleftrightarrow} -\mathrm{COO^-} + \mathrm{H^+}$$

$$-\mathrm{COO^-} + \mathrm{S^+} \overset{K}{\longleftrightarrow} -\mathrm{COOS(complex)}$$

Here, K is the overall binding constant. This indicates that the surfactant binding would promote the dissociation. To quantitatively characterize the polymer dissociation process in the presence of surfactant concentration, we have studied the change in α caused by surfactant addition by measuring the pH changes. Figure 2 shows the degree of dissociation (α) as a function of the surfactant concentration in feed. The pH does not dramatically change upon inducing the surfactant for polymers of F_{ADA} = 0 and 0.5. However, in the case of F_{ADA} = 1.0, the degree of dissociation increases abruptly at the surfactant concentration of 10^{-3} M and attains to 1.0. This experimentally demonstrates that surfactant binding to dissociated carboxyl groups of poly(ADA), naturalizing the charge, substantially enhances further dissociation and surfactant binding.

b. Binding Isotherms. Binding isotherms of surfactant to the poly(ADA-*co*-AA)s with various ADA compositions are shown in Figure 3a−d (left vertical axes). Here β is the molar ratio of bound surfactant to total

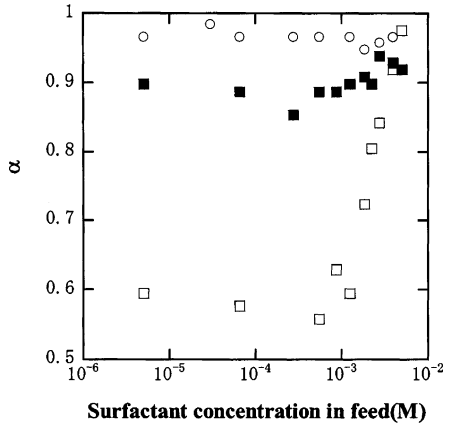

Figure 2. Relationship between α of poly(ADA-*co*-AA) and the concentration of surfactant in feed: (○) $F = 0$; (■) $F = 0.5$; (□) $F = 1.0$.

carboxyl acid groups of the polymer, and C_s is the free surfactant concentration at equilibrium state. When $F_{ADA} = 0$, surfactant binding abruptly increases at $C_s = 5 \times 10^{-5}$ M and then saturates to $\beta = 1$ at a higher surfactant concentration, showing a stoichiometric and cooperative binding. This result is the same with the complex formation between C_{12}PyCl and PAMPS reported.[15] By incorporating a small amount of ADA ($F_{ADA} = 0.18$), the surfactant binding starts at a lower surfactant concentration than that of $F_{ADA} = 0$, i.e., 10^{-6} M, but with a less cooperative binding. When $F_{ADA} = 0.5$ and 1, the binding starts at a surfactant concentration even lower than 1×10^{-7} M and continues binding through a wide range of concentrations. These results show that introduction of hydrophobic long alkyl group on the side chain of poly(ADA-*co*-AA)s reduces the surfactant concentration at which the binding starts, but the cooperativity of the binding substantially decreases. Furthermore, the surfactant binding changes from stoichiometric to nonstoichiometric when the ADA is introduced to the copolymer, as shown in Figure 3.

Upon surfactant binding, the complexes precipitate from the solution. Figure 3a,c,d (right vertical axes) shows the yield of precipitated surfactant−poly(ADA-*co*-AA) complex for $F_{ADA} = 0$, 0.50, and 1.0, respectively. Since no precipitate is formed when $F_{ADA} = 0.18$, the transmittance of the complex solution is shown in Figure 3b. The yield of the complex is defined as a ratio in percent of weight of precipitate formed to that of the calculated amount supposing an equimolar complex formation.

When $F_{ADA} = 0$, a stoichiometric complex was formed, and the complex is insoluble in water because of the increase in the hydrophobic nature due to the neutralization of the charge of PAA.

When $F_{ADA} = 1.0$, the precipitate appears at $\beta \approx 0.7$, and the amount of the precipitate increases until β is about 1 (Figure 3d). However, with the further increase in β, the amount of precipitate dissolves. The extra binding of surfactant is apparently due to the hydrophobic interaction between the stoichiometric complex and the surfactant, which in turn enhances the hydrophilicity of the complex and results in the dissolving of the complex.

When $F_{ADA} = 0.50$ (Figure 3c), the two-stage binding appears also, but the complex is not resoluble completely upon extra binding in the experimental range. Our previous study shows that surfactants have an alkyl chain shorter than C12 could not form resoluble complex with the polymer, indicating that the hydrophobic interaction is not strong enough to form extra binding in these cases.[11]

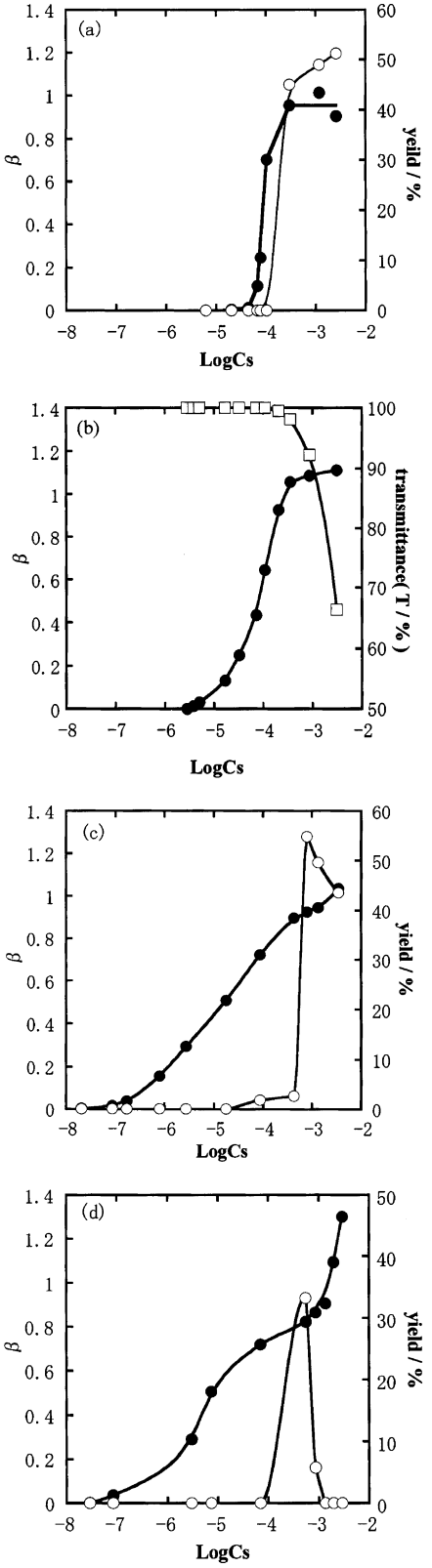

Figure 3. Binding isotherms (left vertical axis) and yields of precipitated complex (a, c, d) or transmittance of complex (b) (right vertical axis). Concentration of poly(ADA-*co*-AA): 3.7×10^{-3} M. (a) $F_{ADA} = 0$; (b) $F_{ADA} = 0.18$; (c) $F_{ADA} = 0.50$; (d) $F_{ADA} = 1.0$. (●) β; (○) yield; (□) transmittance.

Table 2. Interaction Parameters of C_{12}PyCl with Poly(ADA-*co*-AA)

	$F_{ADA} = 0$	$F_{ADA} = 0.18$	$F_{ADA} = 0.50$	$F_{ADA} = 1.0$
K (M^{-1})	1.0×10^4	1.3×10^4	6.0×10^4	1.0×10^5
K_0 (M^{-1})	41	430	4.4×10^4	7.4×10^4
u	242.1	30.2	1.35	1.35
$\Delta F_c/kT$	−5.5	−3.4	−0.3	−0.3
$\Delta F_i/kT$	−6.7	−9.1	−13.7	−14.2

As has been described in the Introduction section, three kinds of surfactant binding were proposed: (1) stoichiometric and cooperative, (2) stoichiometric but noncooperative, and (3) nonstoichiometric but cooperative. In the present work, the binding changes from stoichiometric and cooperative to nonstoichiometric and noncooperative with the increase of ADA of poly(ADA-*co*-AA)s. The latter behavior is, therefore, observed for the first time.

The binding process of cationic surfactant onto anionic polymer can be characterized by two processes.[16] One is the initiation process that a surfactant binds to an isolated binding site, usually via electrostatic complex formation, and the other is propagation process (or cooperative process) that a hydrophobic interaction between adjacently bound surfactant molecules. On the basis of Zimm−Bragg theory[17] for helix−coil transition, Satake and Yang derived the following expression to characterize the cooperativity of binding:[18]

$$K = K_0 u = 1/(C_s)_{0.5} \tag{2}$$

and u is determined from the slope of the binding isotherm at half-bound point.[19]

$$(\mathrm{d}\beta/\mathrm{d} \ln C_s)_{0.5} = \sqrt{u}/4 \tag{3}$$

where K_0 is the binding constant of a surfactant molecular bound to an isolated binding site on a polymer and u is the cooperative parameter characterizing the interaction between the adjacent bound surfactant; $(C_s)_{0.5}$ is the surfactant concentration at half-binding. Thus, K can be calculated as the value of the reciprocal of the equilibrium free surfactant concentration (C_s) at $\beta = 0.5$.

Thermodynamic binding parameters calculated from the binding isotherms (Figure 3) according to eqs 2 and 3 are shown in Table 2. It shows that the overall binding constant (K) increases to some extent with the increase in F_{ADA}, while the initiation binding constant K_0 substantially increases with the increase in F_{ADA}, and K_0 of poly(ADA) is more than 3 orders of magnitude larger than that of poly(AA). This indicates that the initiation process of the surfactant binding is associated not only with the electrostatic interaction between charges but also with the hydrophobic interaction between the alkyl chains of ADA and surfactant. The same phenomenon was also quantitatively confirmed with increase in the hydrophobicity of the chain backbone of polycation.[11] In contrast, a significant decrease in cooperativity u is observed with increasing F_{ADA}. This indicates that the presence of the long alkyl side chain inhibits the surfactant successive binding with copolymer to form continuous sequences. The fact that only about 50% of the carboxyl groups of ADA are in the dissociated form ever at pH = 10 might attributed to such a nonsuccessive sequence.

Using the nearest-neighbor interaction model originally employed for polyelectrolyte titration by Marcus,[20] we have developed a general formula for the ionic surfactant binding to polyelectrolyte as follows:[14]

$$\ln C_s v_c = (\Delta F_i + \Delta F_c)/k_B T - 1 + \ln \frac{\sqrt{4\beta(1-\beta)[\exp(-\Delta F_c/k_B T) - 1] + 1} + 2\beta - 1}{\sqrt{4\beta(1-\beta)[\exp(-\Delta F_c/k_B T) - 1] + 1} + 1 - 2\beta} \tag{4}$$

Here, ΔF_i is the free energy change due to an isolated binding (initiation), and ΔF_c is that through the next-neighbor interaction between bound surfactants (cooperation). v_c is the molar volume of solvent. Equation 4 indicates that the binding isotherm of the surfactant onto the linear polyelectrolyte consists of two terms: the first term characterizes the transition concentration (initiation process), and the second term characterizes the steepness of the transition (cooperative process). The transition concentration of the binding is determined by the sum of the isolated binding energy and lateral interaction energy, while the transition steepness (cooperativity) of the binding is determined by the lateral interaction energy, which is obtained from the slope of the binding curve at $\beta = 0.5$.

From eq 4, a relationship between u and ΔF_c, K_0, and ΔF_i can be derived:

$$u = \exp(-\Delta F_c/k_B T) \tag{5}$$

$$K_0 = e v_c \exp(-\Delta F_i/k_B T) \tag{6}$$

The ΔF_i and ΔF_c values calculated by eqs 5 and 6 from the data in Table 2 are also shown in Table 2. The initiation energy ΔF_i of poly(ADA) is much higher than that of PAA while the cooperative energy, which indicates the lateral interaction between bound surfactants, of PAA is much higher than that of poly(ADA). For PAA, ΔF_i, the initiation energy, is equal to ΔF_e, the electrostatic interaction energy between the ionic head of C_{12}PyCl and the ionized carboxyl groups. For poly(ADA), however, ΔF_i is the sum of the electrostatic interaction energy, ΔF_e, and the hydrophobic interaction energy between surfactant tail and the alkyl side chain of ADA, $\Delta F_h'$, that is

$$\Delta F_i = \Delta F_e \quad \text{(PAA)} \tag{7}$$

$$\Delta F_i = \Delta F_e + \Delta F_h' \quad \text{(poly(ADA))} \tag{8}$$

From Table 2, we have

$$\Delta F_e/k_B T = -6.7,$$

$$\Delta F_h'/k_B T = -14.2 - (-6.7) = -7.5$$

The value of $\Delta F_h'/k_B T = -7.5$ is in agreement with the hydrophobic interaction energy between alkyl chains of 12 carbons estimated from the titration in the previous section ($\Delta F_h/k_B T = -7$). The cooperative energy of PAA ($\Delta F_c/k_B T = -5.5$) is due to the hydrophobic interaction between next-neighbor bound surfactants. Since the alkyl tail of C_{12}PyCl has 12 carbons, $\Delta F_c/kT = -5.5$ is smaller than what is expected.

3.3. Structures of Polymer Complexes. WAXD patterns of poly(ADA-*co*-AA)s with $F_{ADA} = 0$ and 0.18 show no diffraction peak, indicating that these polymer are amorphous, while those with $F_{ADA} = 0.34$, 0.50, and 1.0 showed WAXD peaks with a d_1 spacing of 0.41 nm. This d_1 spacing is attributed to side-by-side packing of

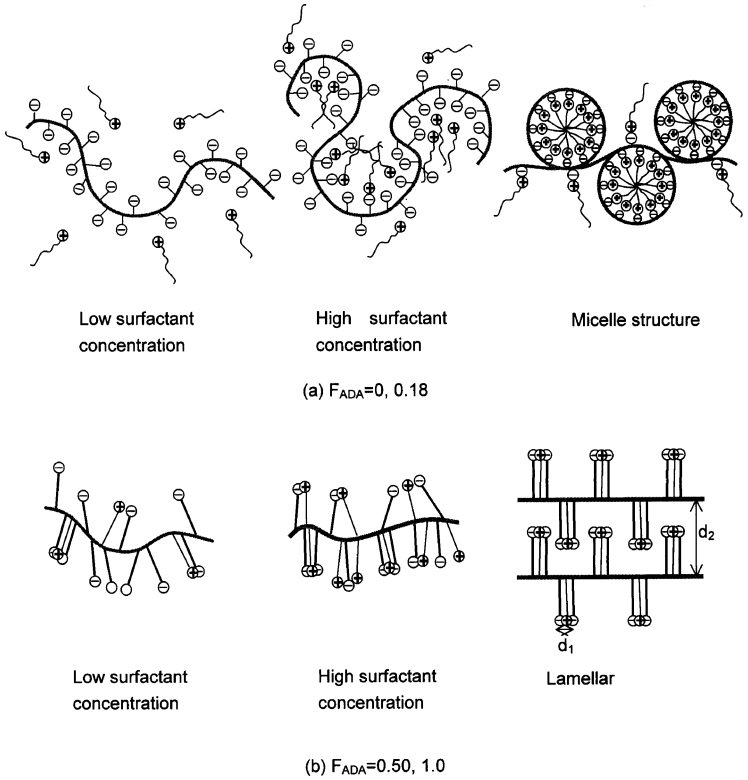

Figure 4. Schematic illustration of change in structure of surfactant−poly(ADA-*co*-AA) complex with F_{ADA}.

Table 3. Results of X-ray Diffraction

		wide angle		small angle	
		θ	d_1 (nm)	2θ	d_2 (nm)
$F_{ADA} = 1.0$	polymer	10.8	0.41		
	complex	10.8	0.41	3.37	2.62
$F_{ADA} = 0.50$	polymer	10.8	0.41		
	complex	10.8	0.41	3.24	2.73
$F_{ADA} = 0.34$	polymer	10.7	0.42		
	complex	10.7	0.42	2.77	3.20
$F_{ADA} = 0.18$	polymer				
	complex			2.73	3.24
$F_{ADA} = 0$	polymer				
	complex			2.72	3.25

hydrophobic long alkyl side chains.[21] The SAXD pattern of poly(ADA-*co*-AA)s shows no diffraction peaks at any F_{ADA}, indicating these copolymers have no long-range ordering. The chemically cross-linked poly(ADA-*co*-AA) gel with various F_{ADA} in the dry state showed the same results as those of dry copolymers.

The structure of the precipitated complex around $\beta = 1$ is analyzed by WAXD and SAXD. When $F_{ADA} = 0$ and 0.18, the complex shows no diffraction peaks, while those of $F_{ADA} = 0.34$, 0.50, and 1.0 show WAXD peaks with a spacing $d_1$of 0.41 nm (Table 3). The diffraction should be attributed to the hexagonal packing of the longer alkyl side chains of hydroxydodecanoic acid residues.[12]

SAXD analysis demonstrates that the complexes with $F_{ADA} = 0$, 0.18, 0.34, 0.50, and 1.0 show diffraction peaks at $2\theta = 2.72°$, 2.73°, 2.77°, 3.24°, and 3.37°, corresponding to a lattice spacing (d_2) of 3.25, 3.24, 3.20, 2.73, and 2.62 nm, respectively (Table 3). This indicates that the d_2 of the complexes decreases with increasing the amount of ADA. For surfactant−poly(AA) complexes, since only a long-range ordering with a spacing $d_2 =$ 3.25 nm which is slightly smaller than 2 times the extended length of C_{12}PyCl (1.8 nm) is observed, the surfactant−PAA complex also forms a micelle-like structure, such as that of PAMPS.[7,8,13] The structure of the complex with $F_{ADA} = 0.18$ is the same as that of $F_{ADA} = 0$ for the same reason. The complexes with $F_{ADA} = 0.34$, 0.50, and 1.0 show short-range and long-range orderings, indicating lamellar structures are formed in these complexes, although the secondary reflection peak of the lamellar structure is not observed due to the weakness of the diffraction peak. Since the d_2 spacing ($d_2 = 2.73$ nm for $F_{ADA} = 0.50$, $d_2 = 2.62$ nm for $F_{ADA} = 1.0$) of the lamellar structure is much shorter than the double extended length of C_{12}PyCl (1.8 nm) or the side chain of ADA (1.75 nm), the complex might form an interpenetrated structure as schematically shown in Figure 4. For the complex with $F_{ADA} = 0.34$, WAXD data show a hexagonal packing of side chain, and SAXD data show a lattice spacing near the value of $F_{ADA} = 0$, and 0.18, a mixture of micelle structure and lamellar structure might be formed. These results show that surfactant−poly(ADA-*co*-AA) complexes change its structures from micelle-like to lamellar-like with increasing F_{ADA}, as schematically illustrated in Figure 4.

It should be noted that these structural results are in good agreement with the thermodynamic binding parameters obtained in Table 2. That is, for PAA, the initiation is due to the electrostatic interaction between the ionized surfactant and the carboxyl groups, whereupon the high cooperativity appears due to adjacent side by side interaction of bound surfactants tail to form micelles. On the other hand, for the case of poly(ADA), both the electrostatic and the hydrophobic interaction contribute to the initiation process; the hydrophobic interaction between adjacent bound surfactant is much less important, leading to a noncooperative binding.

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