

BINDING OF IONIC SURFACTANTS ON OPPOSITELY CHARGED POLYELECTROLYTES OBSERVED BY FLUORESCENCE METHODS*

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Abstract Our recent studies concerning the binding of ionic surfactants on oppositely charged polyelectrolytes observed with fluorescence techniques are reviewed. The cationic surfactants cetyltrimethylammonium bromide (CTAB), dodecyltrimethylammonium chloride (DTAC), and nonionic surfactant octaethylene glycol monododecyl ether ($C_{12}E_8$) were allowed to bind on anionic poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) and its pyrene and/or naphthalene labeled copolymers. The relative excimer emission intensity I_E/I_M of a cationic probe 1-pyrenemethylamine hydrochloride (PyMeA·HCl) and the non-radiative energy transfer (NRET) I_{Py}/I_{Np} of naphthalene to pyrene for labeled polyelectrolytes were chosen to monitor the binding process and the conformation change of surfactant-bound polyelectrolytes. The 1:1 aggregation of polyelectrolyte-CTAB with respect to the charge was found as long as the CTAB concentration was slightly higher than its critical aggregation concentration (CAC). The intermolecular NRET indicated that the CTAB-bound polyelectrolytes aggregated together through the hydrophobic interaction between the CTAB tails. However, neither 1:1 polyelectrolyte-DTAC aggregation nor intermolecular aggregation of DTAC-bound polyelectrolyte was observed owing to its weaker hydrophobicity of 12 carbon atoms in the tail, which is shorter than that of CTAB. As known from the fluorescence results, nonionic surfactant $C_{12}E_8$ did not bind on the anionic polyelectrolytes, but the presence of PAMPS promoted the micelle formation for $C_{12}E_8$ at the CAC slightly below its critical micelle concentration (CMC). The solid complex of dansyl labeled AMPS copolymer-surfactant exhibited a decrease in local polarity with increasing charge density of the polyelectrolyte or with alkane tail length of the surfactant. SAXS suggested a lamella structure for the AMPS copolymer-surfactant solid complexes with a long period of 3.87 nm for CTAB and 3.04 nm for DTAC, respectively.

Keywords Polyelectrolyte, Surfactant, Binding, Fluorescence technique, Complex

INTRODUCTION

Recently, the binding process and complex structure of ionic surfactants with oppositely charged polyelectrolytes have been intensively studied due to their fundamental and applicational interest^[1, 2]. The binding process in aqueous solution is considered to consist of two steps: initial binding of surfactant molecules to the charged sites on the polymer chain and propagating aggregation of surfactant molecules to form micelle-like structure in a highly cooperative manner^[3, 4]. The driving force is the electrostatic attraction between charged groups on the polyelectrolyte and ionic heads of the surfactant molecules as well as the hydrophobic interaction between the bound surfactant alkyl tails and between hydrophobic moieties of the polymer and the surfactant tails. Therefore, the surfactant structure, especially the alkyl tail length and the head-group charge, plays a very important role in the binding process and the polyelectrolyte conformation and aggregation after binding. Solid polyelectrolyte-surfactant complexes are easily produced by precipitation from aqueous solution of polyelectrolytes and surfactants^[2]. The most attractive finding from the polyelectrolyte-surfactant complex is its highly ordered

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structure^[5]. Another characteristic factor of the complex is the equivalence of the stoichiometric composition of the polyelectrolyte to the surfactant with respect to charge^[6]. Considering the polyelectrolyte-surfactant complex, one question is whether the 1:1 stoichiometric polyelectrolyte-surfactant complex forms in dilute solution or during the precipitation process. Another question is about the change in polyelectrolyte chain conformation and aggregation during binding with surfactant in dilute solution, which concerns the formation of the ordered structure in the solid complex.

Fluorescence techniques, including the fluorescence label and probe, are powerful tools in investigating the polyelectrolyte-surfactant binding^[7, 8]. Pyrene chromophore is frequently used for this purpose due to its special photophysical properties and high efficiency of excimer formation^[9, 10]. The intensity ratio I_1/I_3 of the first (375 nm) to the third (386 nm) emission peak of pyrene is sensitive to the polarity of its microenvironment. It is generally known that I_1/I_3 is lower in less polar media^[11, 12]. The emission intensity ratio I_E/I_M of I_E at 480–490 nm for the excimer to I_M at 395 nm for the monomer of pyrene can indicate the spatial stacking of pyrene residues^[10]. The fluorescence anisotropy ratio r is measured to monitor the mobility of the probe, which is defined as:

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \quad (1)$$

where $I_{\parallel}$ and $I_{\perp}$ are emission intensities measured parallel and perpendicular to the polarizing direction of excitation, respectively. The efficiency of nonradiative energy transfer (NRET) from the energy donor to the energy acceptor depends sensitively on their separation distance^[13]. NRET between energy donor and energy acceptor covalently attached to the same or different polymer chains provides a sensitive tool to probe changes in chain conformation and aggregation^[13–15]. Naphthalene and pyrene are often used as the energy donor and acceptor, respectively, because of their large spectral overlap, and naphthalene can be selectively excited at a wavelength of 290 nm. This pair provides a useful “spectroscopic ruler” to study the polymer conformational changes on the scale of a few nanometers (because the Förster radius R_0 is 2.86 nm for NRET from 1-methylnaphthalene to pyrene^[16]). The occurrence of NRET is experimentally indicated by an increase in pyrene emission with excitation of naphthalene.

The purpose of our recent work was to further systematically clarify the binding of ionic surfactants on the oppositely charged polyelectrolytes by fluorescence methods. We investigated the binding process of cationic surfactants cetyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium chloride (DTAC), nonionic surfactant octaethylene glycol monododecyl ether ($C_{12}E_8$) on a strong polyanion poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS). The relative excimer emission intensity I_E/I_M of a cationic pyrene probe 1-pyrenemethylamine hydrochloride ($\text{PyMeA} \cdot \text{HCl}$), NRET efficiency expressed by $I_{\text{Py}}/I_{\text{Np}}$ of pyrene to naphthalene labeled on PAMPS copolymers and relative fluorescence intensity I_1/I_3 and fluorescence anisotropy r of the pyrene label were utilized for this purpose^[17–19]. We also determined the solid structure of strong polyelectrolyte-surfactant complexes with the emission maximum blue-shift of dansyl label and X-ray diffraction and scattering^[20].

CTAB BINDING ON PAMPS

Emission Spectrum of Cation Probe

For easy understanding of the binding information given by the pyrene probe $\text{PyMeA} \cdot \text{HCl}$, we investigated its emission spectra in aqueous solutions without mixing polyelectrolyte with surfactant. $\text{PyMeA} \cdot \text{HCl}$ in water will dissociate into a cation probe PyMeAH^+ and an anion Cl^- . The emission spectrum of PyMeAH^+ in aqueous solution at different concentrations exhibits the characteristic monomer emission of four peaks at 375, 380, 386, 395 nm and a shoulder at 415 nm without any sign of excimer, owing to the electrostatic repulsion between the cations^[21]. For the same reason, no excimer of PyMeAH^+ is formed in the aqueous solution of cationic surfactant CTAB, even at a concentration higher than CTAB's critical micelle concentration (CMC). The relative intensity of I_1/I_3 for the cationic pyrene probe in CTAB solution is kept at a constant 2.94, higher than the value of 2.39 in

the CTAB micelle^[17]. These results mean that this pyrene probe cannot enter the CTAB micelle in aqueous solutions.

On the other hand, this cationic probe PyMeAH^+ can bind on anionic polyelectrolytes by electrostatic attraction. The emission spectra of PyMeAH^+ in the presence of PAMPS are compared with those of PyMeAH^+ without PAMPS in Fig. 1. A typical pyrene excimer emission with a broad, structureless band centered at 485 nm can be found from the curve b for the PAMPS concentration of 1×10^{-4} mol/L in the repeat unit. This is due to the binding of PyMeAH^+ on the polyelectrolyte, which results in an increase in the local concentration of the probe along the polyelectrolyte chain and promotes the excimer formation and fluorescence quenching to the monomer emission. At a little higher PAMPS concentration (2.5×10^{-3} mol/L, curve c), the probe cation can be redistributed to all the polymer chains owing to the increased number of available binding sites, sulfonate groups, in the polymer. This is evidenced by a decrease in the intensity of excimer emission.

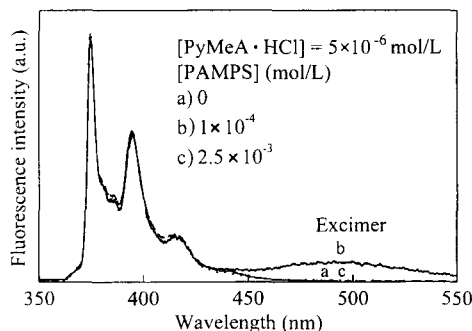


Fig. 1 Emission spectra of cationic probe PyMeAH^+ in aqueous solutions of PAMPS at indicated concentrations

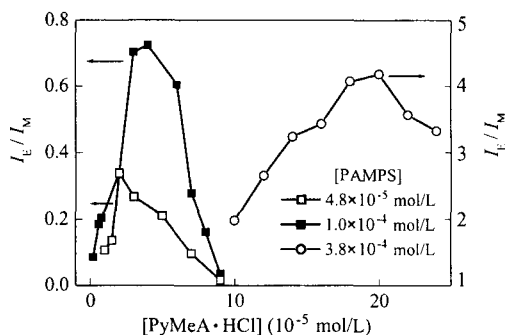


Fig. 2 Emission intensity ratio I_E/I_M as a function of PyMeAH^+ concentration in aqueous solutions of PAMPS with indicated concentration

Figure 2 shows the dependence of I_E/I_M on $\text{PyMeA} \cdot \text{HCl}$ concentration at given PAMPS concentrations of 4.8×10^{-5} , 1×10^{-4} and 3.8×10^{-4} mol/L, respectively. First, I_E/I_M increases with the increase in probe concentration because more probe cations are provided for binding on PAMPS chains to form more excimers. At the maximum of I_E/I_M , the binding of PyMeAH^+ on PAMPS is saturated. Then, I_E/I_M decreases with a further increase in the probe concentration since excess PyMeAH^+ is dissolved in water leading to an increase in the emission intensity I_M of the monomer. The maximum value for the probe to be bound on a polyelectrolyte chain (*i.e.*, saturation binding) can be estimated from the probe concentration corresponding to the I_E/I_M maximum. From Fig. 2, one can determine that the number of AMPS repeat units corresponding to the binding of one PyMeAH^+ probe cation is about 2.4 at the saturation binding on PAMPS. This fact indicates that the binding of the probe cation PyMeAH^+ does not neutralize all of the charges of the PAMPS and cannot undergo 1:1 stoichiometric electrostatic aggregation with the PAMPS charges. We assumed a binding equilibrium model that semi-quantitatively described the I_E/I_M curves in Fig. 2^[22]. According to the counterion condensation theory, about 63 mol% of the sulfonate groups on PAMPS should be condensed by counterions to form loose ion pairs^[23]. The previous fact indicates that the probe cation PyMeAH^+ only occupies about 42 mol% ($1/2.4$) of charged sites of the PAMPS chain, the remaining 21 mol% charged sites, which should be condensed, have to be occupied by protons. The relative number of the bound cations of the probe PyMeAH^+ and the protons may be altered by the chain structure and stereo barrier.

1:1 Aggregation of CTAB and PAMPS Observed with PyMeAH^+

According to the observation described above, the excimer emission of PyMeAH^+ can only be observed when bound on PAMPS chains at suitable concentration. The relative emission intensity I_E/I_M can be used to detect the binding state of PyMeAH^+ on the PAMPS, which will be affected by competitive binding of the cationic surfactant CTAB. For measuring the fluorescence spectra of pyrene in polyelectrolyte-surfactant solutions,

concentrated aqueous solutions of PAMPS, CTAB and PyMeA·HCl were prepared separately. Then, desired amounts of each concentrated solution were placed in a volumetric flask and diluted to the test concentration. The polyelectrolyte concentration is expressed by the molar concentration of the repeat unit AMPS. All solutions were kept for more than 12 h to insure the binding equilibrium. They were stirred for 1 min prior to recording the spectrum. The excitation wavelength was 340 nm. I_E/I_M for PyMeAH⁺ in the presence of PAMPS is shown in Fig. 3 as a function of CTAB concentration. The data on the ordinate indicate the I_E/I_M value in PAMPS solutions without CTAB. With increasing CTAB concentration, the I_E/I_M value at a given PAMPS concentration first increases and then decreases after a maximum. Addition of the initial amounts of CTAB leads to coiling of the polyelectrolyte chain, which in turn enhances the excimer formation between bound probes. This coiling resulted mainly from the charge neutralization, with the polymer becoming increasingly hydrophobic owing to surfactant binding.

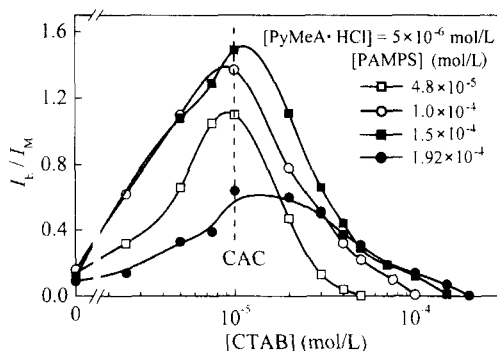


Fig. 3 I_E/I_M of pyrene probe cation PyMeAH⁺ as a function of CTAB concentration in aqueous PAMPS solutions at the concentrations indicated with $[\text{PyMeA} \cdot \text{HCl}] = 5 \times 10^{-6} \text{ mol/L}$. The data at the ordinate were determined without CTAB.

Because the pyrene probe used in this work is also a cationic species, addition of the cationic surfactant CTAB induces competitive binding of CTAB with the probe cation at the anionic sites of PAMPS. There should be equilibrium in the bound composition of CTAB and PyMeAH⁺·HCl controlled by the free-energy change during the binding process. When the CTAB concentration is beyond its critical aggregation concentration (CAC), this binding equilibrium greatly shifts towards the aggregation of PAMPS and CTAB. Thus, the bound PyMeAH⁺ is gradually replaced by CTAB from the binding site owing to the favorable binding free-energy contributed from the electrostatic attraction between surfactant cation and polyanion as well as hydrophobic bonding among the alkyl tails of the surfactant. As a result, the I_E/I_M decreases when the CTAB concentration is beyond the CAC. Finally, the pyrene probe cation is almost completely removed from the polyanion and is dispersed in solution separately, which makes I_E/I_M approach zero at higher CTAB concentrations. Hayakawa *et al.* also found that the bound probe cation proflavine was expelled from the anionic polymer pectate by the competitive binding of cationic surfactant dodecyltrimethylammonium bromide (DTAB)^[24].

There are two kinds of pyrene excimers, *i.e.*, the static excimer and the dynamic excimer. The former occurs if the pyrene groups are in juxtaposition due to ground-state aggregation of pyrene groups. The latter is formed through the excitation of isolated pyrene groups and subsequent diffusional encounter with ground-state pyrene. The blue-shift of the excimer emission and excitation spectra indicate the existence of preassociation of the bound pyrene probes and a decrease in the amount of static excimer induced by CTAB binding^[17].

The I_E/I_M maximum corresponds the CAC at which the CTAB begins to aggregate as proposed by Chandar *et al.*^[25]. The CAC value for CTAB in dilute aqueous solutions of PAMPS was estimated from the maximum of I_E/I_M . For all PAMPS concentrations tested, the CAC is the same at $1 \times 10^{-5} \text{ mol/L}$, 2 orders of magnitude smaller than the CMC of about $1 \times 10^{-3} \text{ mol/L}$ for CTAB in water without polyelectrolyte. The CAC

should depend on the polyelectrolyte concentration because it alters the number of anionic binding sites and the distribution of the surfactant cation on the polymer chains. Hansson and Almgren found that the CAC for DTAB bound on poly(acrylic acid) (PAA) increased from 10^{-5} to 10^{-4} mol/L as the PAA concentration increased from 10^{-4} to 10^{-2} mol/L^[26]. However, the PAMPS concentration range in this work is too narrow to observe an obvious dependence of polyelectrolyte concentration. The PAMPS concentration is limited by the intensity requirement of excimer emission I_E , and the precipitation of polyelectrolyte-surfactant complexes appearing at high CTAB concentrations.

If we look at Fig. 3 carefully we can find that the CTAB concentration at which I_E/I_M equals zero, $[CTAB]_0$, varies with the polyelectrolyte concentration, $[PAMPS]$. The relation between $[CTAB]_0$ and $[PAMPS]$ is illustrated in Fig. 4. The result that $[CTAB]_0$ is equal to $[PAMPS]$ within experimental precision is surprising. This phenomenon has also been observed on using different probe concentrations (Fig. 4) and different molecular weights of PAMPS samples (Fig. 5). This finding means that the probe cations are thoroughly excluded from the binding sites of polyelectrolyte by the surfactant cations and the sulfonate groups of PAMPS are all occupied by CTAB cations. It is well known that the equivalent stoichiometry with respect to the charge is usually obtained in the solid complex of the polyelectrolyte and surfactant^[2]. The present fact indicates that the stoichiometric complex of polyelectrolytes and oppositely charged surfactants forms in a surfactant-polyelectrolyte solution as long as the surfactant concentration is higher than its CAC. Besides the cooperative driving force, the lower stereo barrier of the linear surfactant tail seems to be another reason for this.

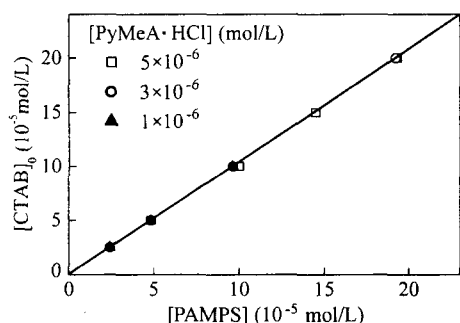


Fig. 4 CTAB concentration at which I_E/I_M is zero determined with the probe concentration $[PyMeA \cdot HCl]$ indicated plotted against the PAMPS concentration

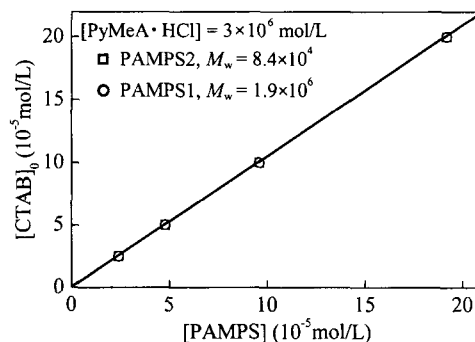


Fig 5 CTAB concentration at which I_E/I_M is zero determined with different PAMPS molecular weights indicated plotted against the PAMPS concentration

Chandar *et al.* studied the binding of DTAB on PAA using the I_E/I_M maximum of pyrene labels^[25]. In that case, the pyrene aggregation at high DTAB concentration is solubilized in a relatively less-polar microenvironment created by associated surfactants, resulting in a decrease in I_E/I_M . However, I_E/I_M never becomes zero even at a surfactant concentration 10 times as high as ours, because the pyrene label cannot be removed from the polyelectrolyte chains.

Summarizing the above observations, we propose an aggregation model for the binding of ionic surfactant molecules on an oppositely charged polyelectrolyte in dilute solutions, which is schematically presented in Fig. 6. When the CTAB concentration is below the CAC, all the cations condense randomly on the polyanion PAMPS to occupy about 63 mol% of the binding sites as required by the counterion condensation. Binding of CTAB and $PyMeAH^+$ makes the chain hydrophobic and coiling and promotes the static excimer formation. Above the CAC, the aggregates of CTAB exclude pyrene cations from the binding sites. A decrease in the extent of ground-state pyrene aggregation occurs. At the final stage, all charged sites of the polyelectrolyte are bound with surfactants, forming the 1:1 stoichiometric polyelectrolyte-surfactant complex. The probe cations are dissolved in solvent again and the excimer formation is prevented by electrostatic repulsion.

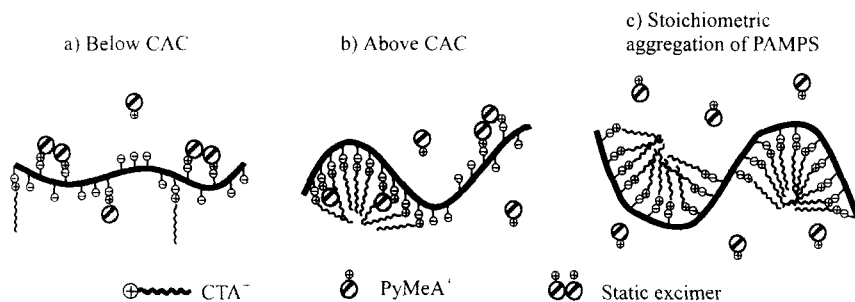


Fig. 6 Schematic representation of the aggregation of polyelectrolyte-surfactant, (a) below the CAC, (b) above the CAC, (c) formation of stoichiometric aggregation. The proton and bromide anions are ignored for simplicity.

With increasing [CTAB] in PAMPS aqueous solution, the value of the relative emission intensity I_1/I_3 for the pyrene probe slightly decreases from 2.50 for [CTAB] = 0 to a minimum of 2.39 at the CAC, then recovers to a value of 2.52 at [CTAB]₀. This indicates that the probe PyMeAH^+ is primarily exposed to water again after the formation of the 1:1 stoichiometric aggregation between CTAB and PAMPS.

SURFACTANT STRUCTURE EFFECTS ON BINDING

Observation with Cationic Pyrene Probe

In order to study the effects of surfactant structure on the binding process and conformation of the surfactant bound polyelectrolyte we chose CTAB and DTAC with 16 and 12 carbon atoms in the tail, respectively, to change the hydrophobic interaction and C_{12}E_8 to test the electrostatic attraction. The excimer emission of cationic pyrene probe PyMeAH^+ was used again in the same way as above.

Figures 7(a) and 7(b) show the I_E/I_M of $\text{PyMeA}^+ \cdot \text{HCl}$ as a function of surfactant concentration of DTAC and C_{12}E_8 , respectively, with different PAMPS concentrations. The data on the ordinate indicate the I_E/I_M value in PAMPS solutions without surfactants. All curves in Fig. 7(a) for the cationic surfactants are similar to those in Fig. 3 for CTAB binding but quite different from those in Fig. 7(b) for the nonionic surfactant. With increasing cationic surfactant concentration, the I_E/I_M value at a given PAMPS concentration first increases and then decreases, showing a maximum on each curve. The relative intensity of I_E/I_M for DTAC binding is different from that for CTAB binding at high surfactant concentrations. As mentioned above, binding of CTAB will exclude the bound cationic probe completely from PAMPS chains and lead to $I_E/I_M = 0$, where the CTAB concentration just equals to the concentration of PAMPS repeat units. This fact manifests the formation of 1:1 aggregation of CTAB and PAMPS at surfactant concentrations a little higher than its CAC. The binding of DTAC does not decrease I_E/I_M exactly to zero, even at concentrations up to 1×10^{-3} mol/L as shown by the enlarged inset in Fig. 7(a), which is about one order of magnitude higher than the used PAMPS concentrations. This would be attributed to the lower hydrophobicity of DTAC with the tail of 12 carbon atoms, shorter than that of 16 carbon atoms in CTAB. Thus, the hydrophobic aggregation force of bound DTAC is not strong enough to remove the bound PyMeAH^+ from the polyelectrolyte completely.

The curves in Fig. 7(b) for the C_{12}E_8 binding are completely different. The I_E/I_M keeps low values, close to those in PAMPS solutions without C_{12}E_8 , when the C_{12}E_8 concentration is lower than 2.5×10^{-5} mol/L. In these cases C_{12}E_8 neither binds on PAMPS nor forms micelles. At the same time, the probe cation binds to PAMPS individually and separately as if there were no surfactant in the solution. Then, I_E/I_M begins to increase at a C_{12}E_8 concentration of 2.5×10^{-5} mol/L and reaches a maximum at 10^{-4} mol/L. The concentration at the turning point is a little higher than 8×10^{-5} mol/L, the CMC for C_{12}E_8 ^[27]. As known from experiments, the PyMeAH^+ probe at the concentration of 2.5×10^{-5} mol/L cannot form excimer in the absence of micelle, but can enter the C_{12}E_8 micelle to form excimer^[18]. Therefore, the increase I_E/I_M with C_{12}E_8 concentration is an indication of micelle formation. It is worth noting that this C_{12}E_8 concentration of micelle formation is lower than its CMC. This means

that the CAC for $C_{12}E_8$ in the presence of polyelectrolyte is somewhat lower than the CMC, though the $C_{12}E_8$ is a nonionic surfactant. In other words, the micelle formation of $C_{12}E_8$ seems to be promoted by PAMPS. When the surfactant concentration increases beyond 10^{-4} mol/L, there are enough $C_{12}E_8$ micelles to induce a dilution for $PyMeAH^+$ and then to decrease the excimer quantity. At present we have no reasonable explanation for this promotion effect. Saito found the conformation change in PAA chains to be induced by adding nonionic poly(oxyethylene) (PEO) surfactants and suggested that hydrophobic attraction of the surfactants to PAA and hydrogen bonding between the acidic groups of the polymer and the head-groups of the surfactants contributed to this change^[28, 29].

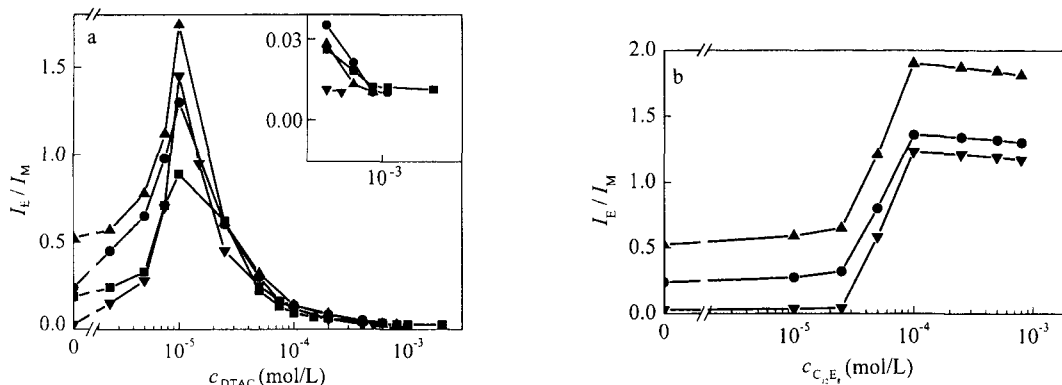


Fig. 7 The I_E/I_M of pyrene probe cation $PyMeAH^+$ as a function of surfactants concentration in aqueous PAMPS solutions with $[PyMeA \cdot HCl] = 3 \times 10^{-6}$ mol/L

(a) DTAC; (b) $C_{12}E_8$; [PAMPS]: ▼ 2.4×10^{-5} ; ▲ 4.8×10^{-5} ; ● 9.6×10^{-5} ; ■ 1.9×10^{-4} mol/L

The inset in (a) is an enlargement for the higher c_{DTAC} about 10^{-3} mol/L.

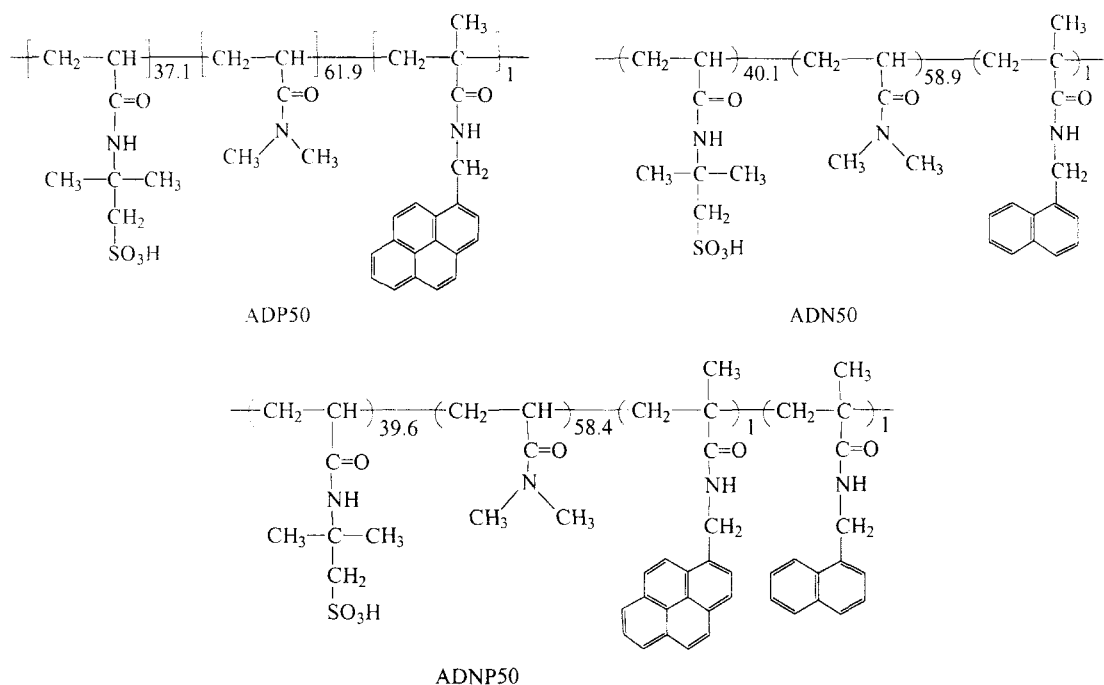
Observations with NRET of Labeled Polyelectrolytes

NRET between energy donor and energy acceptor covalently attached to the same or different polymer chains can probe changes in chain conformation and aggregation^[13–15]. For this purpose three pyrene and/or naphthalene labeled AMPS copolymers were prepared as illustrated in Scheme 1, assigned as ADP50, ADN50, and ADNP50 with mole fraction of AMPS of 0.37, 0.40, and 0.40 and weight-averaged molecular weight of 4.7 , 6.0 , and 7.0×10^4 , respectively. The desired amounts of copolymer and surfactant concentrated solutions were mixed in a volumetric flask and diluted to test concentrations. The excitation wavelength was 290 nm. The energy transfer efficiency was characterized by the emission intensity ratio I_{Py}/I_{Np} for pyrene at 396 nm to naphthalene at 338 nm.

The I_{Py}/I_{Np} due to NRET is plotted as a function of surfactant concentration c_{Surf} in Figs. 8 and 9 for the solution of doubly labeled sample ADNP50 and for the solution of a mixture of the naphthalene labeled ADN50 and pyrene labeled ADP50, respectively. The former mainly reflects the intramolecular NRET while the latter is induced merely by the intermolecular NRET. With increasing surfactant concentration, the I_{Py}/I_{Np} in Fig. 8 for CTAB binding slowly increases below its CAC, then rapidly increases above its CAC, and finally decreases after formation of the 1:1 surfactant-polyelectrolyte aggregation. At the same time, I_{Py}/I_{Np} in Fig. 9 for CTAB binding abruptly increases as CTAB concentration is beyond 4×10^{-5} mol/L and reaches a maximum where c_{Surf} equals the concentration of the charge sites of the polyelectrolyte. The binding of CTAB on the labeled polyelectrolytes makes the chain more hydrophobic and curlier, increasing the intramolecular NRET. The intermolecular hydrophobic aggregation occurs between CTAB-bound polyelectrolyte chains after micelle formation on the chain, resulting in an increase in the intermolecular NRET.

Because the alkyl tail of DTAC is short and its hydrophobicity is weaker than that of CTAB, the I_{Py}/I_{Np} in Fig. 8 for intramolecular NRET caused by DTAC binding is low, the maximum value being about half of that for CTAB. The I_{Py}/I_{Np} versus c_{Surf} curves in Fig. 9 obviously illustrate that the DTAC-bound polyelectrolyte chains cannot form intermolecular aggregates, so that after the formation of micelle-like aggregates, the I_{Py}/I_{Np} recovers

the value without DTAC due to the isolation by the free DTAC in the solution.



Scheme 1 Chemical formula of pyrene and/or naphthalene labeled polyelectrolyte samples

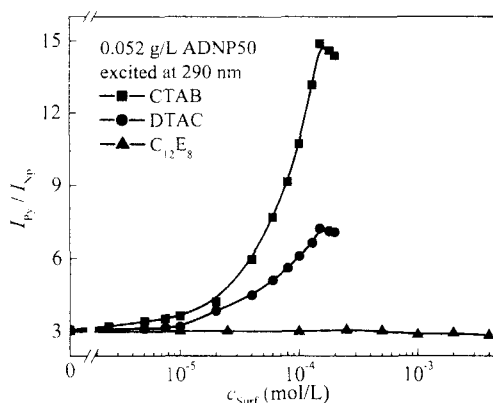


Fig. 8 The I_{py}/I_{Np} due to NRET as a function of surfactant concentration c_{surf} in aqueous solutions of doubly labeled ADNP50 at 0.052 g/L

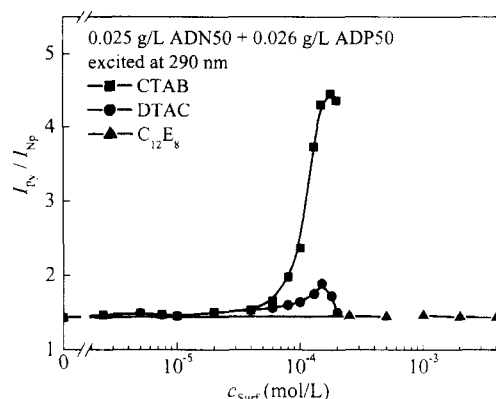


Fig. 9 The I_{py}/I_{Np} due to NRET as a function of surfactant concentration c_{surf} in the mixed solution of naphthalene labeled ADN50 at 0.025 g/L and pyrene labeled ADP50 at 0.026 g/L

The neutral surfactant $C_{12}E_8$ cannot bind on the polyelectrolytes, its presence has no obvious effect on either the intramolecular or the intermolecular NRET as seen from Figs. 8 and 9.

Observations with Pyrene Label on Polyelectrolyte

If the excitation wavelength is 340 nm, only the emission of pyrene can be detected because naphthalene cannot be excited at this wavelength. In Fig. 10, the I_1/I_3 of pyrene labels for ADNP50 in aqueous solutions is plotted against the surfactant concentration c_{surf} . The I_1/I_3 value is almost constant at about 1.53, when $c_{surf} \leq 1 \times 10^{-5}$ mol/L for CTAB or DTAC, then decreases with increasing c_{surf} and achieves values of 1.45–1.46 when $c_{surf} \geq 1.5 \times 10^{-4}$ mol/L. This degree of I_1/I_3 reduction in CTAB or DTAC solutions suggests that the pyrene label does

not enter the micelle-like aggregation of surfactant on polyelectrolyte (if it is the case, I_1/I_3 should be about 1.25^[25]) and the decrease of I_1/I_3 is due to increasing hydrophobicity of the local environment surrounding the polyelectrolyte chains with binding cationic surfactants. Morishima *et al.* considered that the pyrene label was prevented from penetrating into the hydrophobic core of the micelle by constraint exerted by the polymer chain^[30].

To monitor the mobility of the pyrene labels, the fluorescence anisotropy r was measured. Fig. 11 shows the plots of r as a function of surfactant concentration, the excitation wavelength is 340 nm. We can see an abrupt increase in fluorescence anisotropy r for the CTAB binding and a maximum at $[CTAB] = 1.5 \times 10^{-4}$ mol/L. The increase in fluorescence anisotropy indicates that the depolarization of the probe is restricted due to the increase in microenvironmental viscosity around the pyrene. The I_1/I_3 data tell us that the pyrene label does not enter the CTAB micelle on the polyelectrolyte, so that the increase in r is deduced by the intermolecular aggregation between CTAB-bound polyelectrolyte chains induced by the hydrophobic interaction between the CTAB tails. The fluorescence anisotropy r for the DTAC binding increases slightly with surfactant concentration. This means no intermolecular aggregation between the DTAC-bound polyelectrolyte chains, which is consistent with the NRET result in Fig. 9.

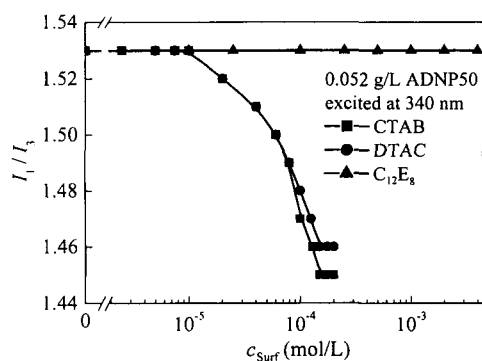


Fig. 10 The I_1/I_3 of pyrene labels of doubly labeled ADNP50 in aqueous solutions of indicated concentration against surfactant concentration c_{Surf}

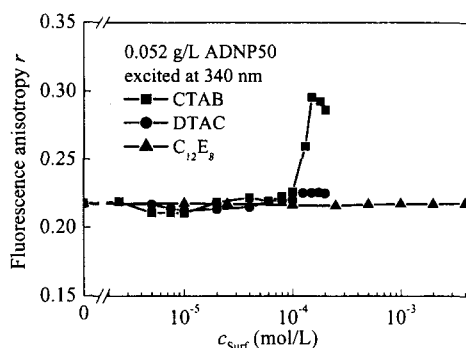


Fig. 11 Fluorescence anisotropy r of pyrene for ADNP50 in aqueous solutions against surfactant concentration c_{Surf}

The I_1/I_3 and r for the ADNP50 solutions with $C_{12}E_8$ are constant over the entire range of surfactant concentration and denotes no surfactant binding on the polyelectrolyte.

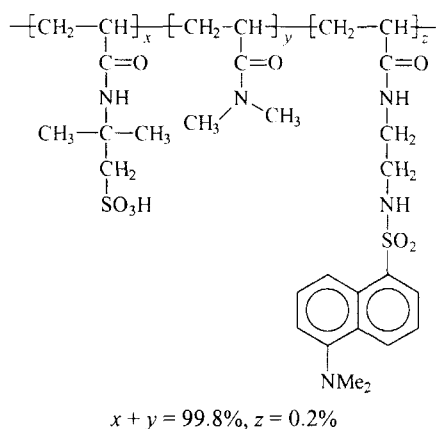
SOLID POLYELECTROLYTE-SURFACTANT COMPLEX

Fluorescence of Dansylated Solid Complex

Dansyl labeled polyelectrolyte samples of ADDan series as shown in Scheme 2 with different mole fractions of AMPS monomer F_{AMPS} were used in investigating the solid structure of the polyelectrolyte-surfactant complex to avoid the self-associating tendency of pyrene labels. The dansyl emission at about 510 nm is due to the twisted intramolecular charge transfer (TICT) related to the torsional motion of the dimethylamino group round the naphthyl plane^[31-33]. The wavelength of the dansyl emission maximum λ_{em} decreases when its microenvironment becomes less polar and the emission intensity for the TICT state increases with enhancement of the torsional mobility^[34].

Solid complexes of polyelectrolyte-surfactant were obtained following Antonietti and Conrad's method. The aqueous solutions of polyelectrolyte and surfactant were mixed to produce the complex precipitate, which was purified by repeat precipitation from methanol into water. The films of the complexes were prepared by casting from the chloroform solutions. All solid complex films of dansyl labeled polyelectrolytes with DTAC (C12) or CTAB (C16) are soft, highly transparent, and deformable. The thermogravimetry (TG) chart indicates that these

complexes are stable below 200°C.



Scheme 2. Chemical formula of Dansyl labeled polyelectrolyte sample

Figure 12 depicts the emission wavelength λ_{em} of these polyelectrolyte-surfactant films as a function of F_{AMPS} , representing the charge density of the polyelectrolyte. At the same charge density, the λ_{em} value for ADDan-C16 is lower than that for ADDan-C12, suggesting that the polarity of the former is lower than that of the latter. For the complexes with a given surfactant, λ_{em} decreases with increasing charge density, showing the decrease in microenvironmental polarity of highly charged polyelectrolytes. These observations seem to reveal that the polyelectrolyte with higher charge density can form less polar micelle-like aggregations when bound by the oppositely charged surfactant. This may be attributed to the increase in the aggregation number with the charge density as reported by Anthony and Zana for solutions^[35] and by Zhou et al. for collapsed gels^[36]. The λ_{em} value of the ADDan polyelectrolyte solids without surfactants is about 510 nm^[32], while λ_{em} becomes less than 475 nm for the polyelectrolyte-surfactant complex, showing that the local polarity surrounding the dansyl label is greatly reduced by forming the micelle-like aggregation with surfactant molecules.

The fluorescence anisotropy r for our complex films is also summarized in Fig. 12. The limiting value of r for dansyl groups is 0.325 in the system without molecular torsion and energy migration^[37]. The small r -value for the complexes manifests the high mobility of chromophore segments owing to the embedment of alkyl tails of surfactants. With increasing F_{AMPS} , r for ADDan-C16 complexes quickly decreases, while that for ADDan-C12 complexes exhibits only a slight decline. The reason for the charge density dependence of r is similar to that for the change of micelle polarity with the charge density as discussed above. The higher rate of r decreasing with F_{AMPS} for ADDan-C16 than for ADDan-C12 indicates that the longer alkane tail in C16 is more effective in building hydrophobic aggregation surrounding the chromophore.

Solid Structure of Complexes

The WAXD results indicate that ADDan-C12 and ADDan-C16 solid complexes are amorphous unstructured materials with a halo at $2\theta = 19.7^\circ$. SAXS profiles for ADDan-C16 and ADDan-C12 complexes are illustrated in Fig. 13. Owing to the low S/N ratio, only one narrow peak can be identified from each curve, corresponding to a long-range ordered structure analogous to a smectic phase with the long period d of 3.87 nm for C16 complexes and 3.04 nm for C12 complexes, respectively. According to the interpretation proposed by Antonietti *et al.*^[38, 39], we adopt the lamella structure for these polyelectrolyte-surfactant complexes as presented in Fig. 14. The lamella is a combination of layers of polyions and alkane tails and the long period is related to the length and orientation of alkane tails of the surfactant. From the results of Antonietti *et al.*^[40] and Ponomarenko *et al.*^[41] the thickness d_1 of the polyion layer $d_1 = 1.40$ nm is used for our complexes. Consequently, the observed thickness d_2 for the

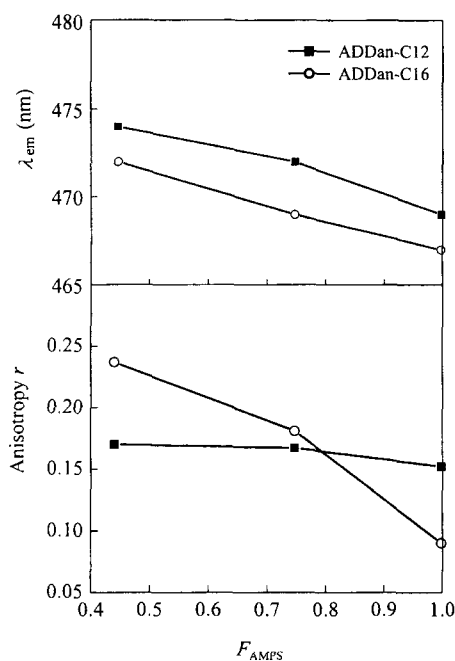


Fig. 12 AMPS mole fraction F_{AMPS} dependence of λ_{em} (upper panel) and fluorescence anisotropy r (lower panel) of dansylated polyelectrolyte-surfactant complex solid films ADDan-C12 (■) and ADDan-C16 (□)

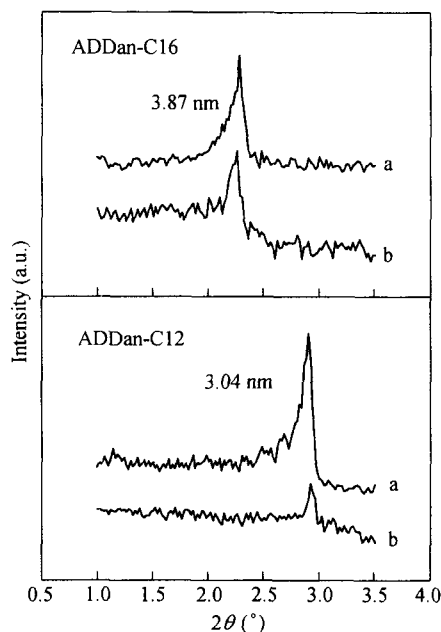


Fig. 13 SAXS profiles of dansylated polyelectrolyte-surfactant complex solid films ADDan100-C16 (a in upper panel), ADDan45-C16 (b in upper panel), ADDan100-C12 (a in lower panel), and ADDan45-C12 (b in lower panel)

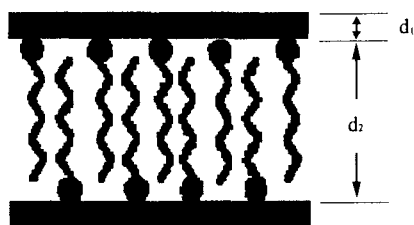


Fig. 14 Schematic representation of the lamella structure for polyelectrolyte-surfactant complex solid films

alkane tail layer is 2.47 nm for C16 complexes and 1.64 nm for C12 complexes, respectively. For a completely stretched alkane chain, the increment of one carbon is expected to increase about 0.125 nm in the long period if the chain is perpendicular to the lamella. Therefore, these observed d_2 values are larger than those calculated from the carbon number of the corresponding alkanes, indicating the interpenetrating finger packing of the surfactant tails.

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