Characterization of the Complexes of Amphiphilic Polyanions and Double-Chain Cationic Surfactants

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ABSTRACT: Coulombic complexes of amphiphilic polyanions and double-chain cationic surfactants were prepared by adding an aqueous solution of didodecyldimethylammonium bromide (DDAB) to aqueous solutions of terpolymers consisting of sodium 2-(acrylamido)-2-methylpropanesulfonate, *N*-(1-adamantyl)methacrylamide (49 mol %) or *N*-(1-naphthylmethyl)methacrylamide (59 mol %), and *N*-(1-pyrenylmethyl)-methacrylamide (1 mol %). As the contents of the adamantyl and naphthyl groups in the terpolymers are sufficiently high, the parent terpolymers adopt micellelike microphase structures in aqueous solution. Both the complexes of the adamantyl and naphthyl terpolymers with DDAB were soluble in benzene, methanol, tetrahydrofuran (THF), acetonitrile (ACN), *N*,*N*-dimethylformamide (DMF), etc. ^{1}H NMR spectra indicated that the quantitative numbers of DDAB were ionically bound to the sulfonate sites in the parent terpolymers. Dynamic light scattering data for the complex of the adamantyl terpolymer showed that the size of the complex in THF solution ranged from 6 to 15 nm in diameter, which fairly agreed with a radius of gyration estimated on the basis of GPC data. ^{1}H NMR spectra, 2D-NOESY, and spin-lattice and spin-spin relaxation times for the complex of the naphthyl terpolymer in organic solution revealed that the motions of the naphthyl residues were highly restricted, while those of the DDAB residues were much less restricted. These findings imply that the micellelike microphase structure of the parent amphiphilic polyanions formed in aqueous solution remained rather intact in the complexes even though they were dissolved in organic solvents. In benzene solution, the complex was shown to be in a particularly compact form. Fluorescence emitted by the pyrenyl probes incorporated in the complexes supported these findings.

Introduction

Complexes between polymers and surfactant molecules have extensively been studied by many investigators from theoretical and experimental points of view.[1-6] These complexes are of interest because they provide self-organized molecular assemblies which may serve as vehicles for chemical reactions relevant to biological phenomena. A number of studies in this area have been concerned with the complexation of polyelectrolytes with oppositely charged surfactants below the critical micelle concentration (cmc).[7]

Interactions between polyelectrolytes with oppositely charged particles including surfactants above the cmc are also of considerable scientific and technological interest. Dubin and co-workers[8-12] have extensively studied the complexes of polyelectrolytes with oppositely charged micelles with varying surface charge densities and shown that the complexation is a critical phenomenon governed by electrostatic interactions between polyelectrolytes and the charged surfaces of micelles.

Amphiphilic polyelectrolytes bearing sufficient amounts of hydrophobic substituent groups are known to adopt micellelike microphase structures where hydrophobic units form interior domains and charged segments form outer layers in aqueous solution.[13-22] Such micellelike microphase structures are rigid and "static" in nature[15,17,19] as compared to the dynamic nature of conventional surfactant micelles. Therefore, the hydrophobic domains in the microphase structures may be viewed as solid microparticles sustained in water by surrounding charged segments to give an apparently clear aqueous solution.

Coulombic interactions between such amphiphilic polyelectrolytes and oppositely charged surfactants below the cmc may provide new types of molecular assemblies which may have a variety of interesting features worthy of study.

We have shown that the microphase structure of an amphiphilic polyelectrolyte in aqueous solution provides a medium for photoinduced electron-transfer reactions.[23-26] A hydrophobic photodonor (photoactive electron donor) covalently incorporated in an amphiphilic polyelectrolyte can be encapsulated (compartmentalized) in a hydrophobic microdomain in aqueous solution,[24-26] and thus the photodonor can be kept in separation from hydrophilic acceptors added in the bulk aqueous phase. Rapid photoinduced electron transfer occurs from the compartmentalized photodonor to the acceptors located on the surface of the hydrophobic microdomain, whereas back electron transfer can be retarded, giving rise to a long-lived charge-separated state.[24-26]

The compartmentalization of the hydrophobic photodonor in the amphiphilic polyelectrolyte occurs only in aqueous solution, because the formation of the microphase structure and also the compartmentalization event are solely due to hydrophobic interactions.[24-26] When the amphiphilic polyelectrolyte is dissolved in polar organic solvents such as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide, and methanol, the polymer would adopt a random coil but not a microphase structure.[15,17,19] If the micellelike structure of the amphiphilic polyelectrolyte can be retained in organic solutions, such systems would offer opportunities for studies of separated donor-acceptor assembly systems in various organic media.

In a previous paper, we have reported on a photoactive molecular composite consisting of a Coulombic complex of an amphiphilic polyanion with cationic double-chain surfactants and electron acceptors.[27] Fluorescence behavior and photoinduced electron transfer of pyrenyl (Py) moieties covalently incorporated in the parent amphiphilic

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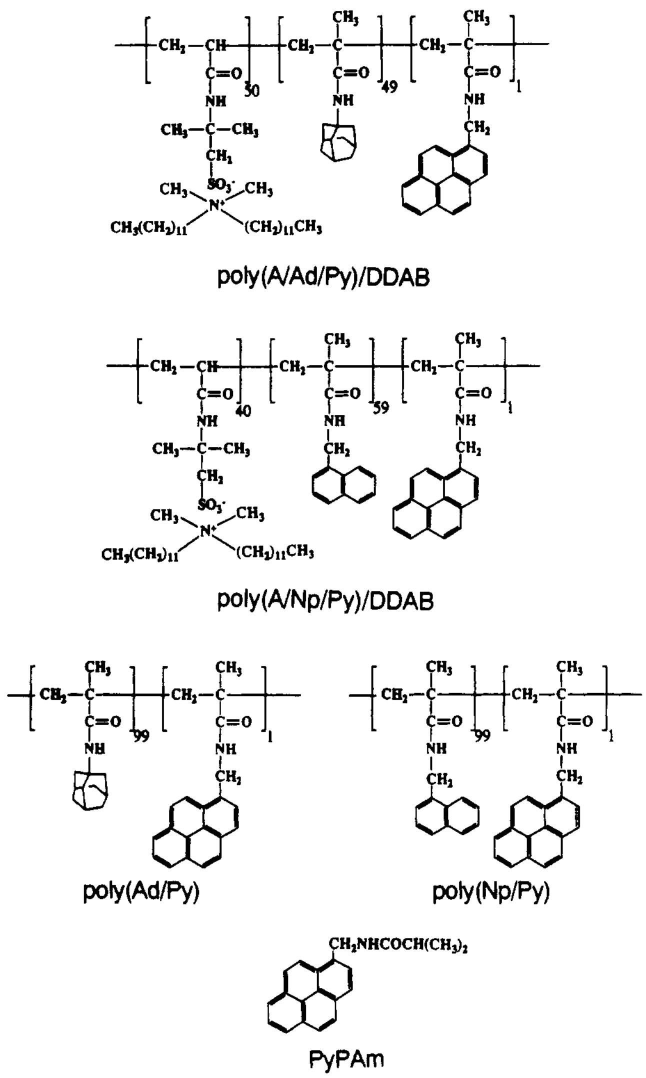
Chart I



poly(A/Ad/Py)/DDAB

poly(A/Np/Py)/DDAB

poly(Ad/Py)

poly(Np/Py)

PyPAm

polyanion suggested that the microphase structure of the parent polymer formed in aqueous solution was retained to some extent in the complex dissolved in some organic solvents.[27]

The present paper is concerned with the characterization of the Coulombic complexes of amphiphilic polyelectrolytes and double-chain surfactants. As amphiphilic polyelectrolytes, terpolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS), *N*-(1-adamantyl)methacrylamide (AdMAm) or *N*-(1-naphthylmethyl)methacrylamide (1NpMAm), and *N*-(1-pyrenylmethyl)methacrylamide (1PyMAm) were employed. Small mole fractions of the Py moieties were incorporated in the terpolymers as fluorescence probes. These terpolymers were treated with didodecyldimethylammonium bromide (DDAB) in aqueous solution to prepare complexes poly(A/Ad/Py)/DDAB and poly(A/Np/Py)/DDAB (Chart I). We studied these complexes by dynamic light scattering, GPC, fluorescence, and NMR techniques for characterization.

Experimental Section

Materials. The amphiphilic terpolymer of 50 mol % sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS), 49 mol % *N*-(1-adamantyl)methacrylamide (AdMAm), and 1 mol % *N*-(1-pyrenylmethyl)methacrylamide (1PyMAm) (poly(A/Ad/Py)) and that of 40 mol % AMPS, 59 mol % *N*-(1-naphthylmethyl)methacrylamide (1NpMAm), and 1 mol % 1PyMAm (poly(A/Np/Py)) were prepared by radical terpolymerizations of the corresponding monomers in DMF at 60 °C as reported previously.[26] The polymers were purified by reprecipitating from methanol into a large excess of ether and then dissolved in dilute aqueous sodium hydroxide at pH 11. The polymer solutions were dialyzed against pure water for a week and finally lyophilized. The terpolymer compositions were determined by the N/C and S/C ratios in combination with absorption spectroscopy to determine the mole fractions of the 1PyMAm units in the terpolymers.

The Coulombic complex of poly(A/Np/Py) and didodecyldimethylammonium bromide (DDAB), poly(A/Np/Py)/DDAB, was prepared as follows. To a 300-mL aqueous solution containing 0.139 g (0.30 mmol) of DDAB was added dropwise a 50-mL aqueous solution containing 0.171 g of poly(A/Np/Py) at 40 °C with stirring. White fine particles thus formed were collected by centrifugation and suspended in deionized water. The suspension was dialyzed against deionized water for several days to remove the remaining salt (NaBr) and free DDAB. The solid particles were then recovered by freeze-drying.

The complex of poly(A/Ad/Py) and DDAB, poly(A/Ad/Py)/DDAB, was prepared in a manner similar to that above.

N-(1-Pyrenylmethyl)-2-methylpropionamide (PyPAm) was synthesized as reported previously.[27]

The copolymer of 99 mol % AdMAm and 1 mol % 1PyMAm, poly(Ad/Py), was prepared as follows. A glass ampule containing 2.71 g (12.4 mmol) of AdMAm, 0.037 g (0.125 mmol) of 1PyMAm, 0.0103 g (0.058 mmol) of 2,2′-azobis(2-methylpropionitrile) (AIBN), and 30 mL of benzene was outgassed on a vacuum line by five freeze–pump–thaw cycles and then sealed under vacuum. Polymerization was carried out at 60 °C for 12 h. The polymerization mixture was poured into a large excess of methanol to precipitate the resulting polymer. The polymer was purified by reprecipitating from chloroform into a large excess of methanol. The number-average molecular weight was determined to be $M_n = 1.1 \times 10^4$ by GPC.

The copolymer of 99 mol % 1NpMAm and 1 mol % 1PyMAm, poly(Np/Py), was prepared in a manner similar to that above.

Water was deionized by passing through a 0.1-μm filter and an ion-exchange resin column.

Measurements. Gel-permeation chromatograms were obtained with a Shimadzu LC-6A system at 40 °C. Tetrahydrofuran (THF) containing 60 mM H_3PO_4 and chloroform were used as solvents for the complexes and for a related model copolymer poly(Ad/Py), respectively. Standard polystyrenes were used to calibrate molecular weight.

Proton NMR spectra were obtained with a JEOL EX-270 spectrometer using a deuterium lock at a constant temperature of 298 K during the whole run. For two-dimensional (2D) nuclear Overhauser enhancement spectroscopy (NOESY), a data set was obtained with 512 data points for each dimension and with 32 accumulations per experiment. Three contour levels were plotted in a sequence of ×(1/4), ×(1/2), and 1 as the maximum threshold value. The contour maps were symmetrized after the Fourier transformations. Proton spin–lattice relaxation times (T_1) were determined by using a simple inversion–recovery technique with a 180°–τ–90° pulse sequence.[28–30] Proton spin–spin relaxation times (T_2) were determined by using the Carr–Purcell–Meiboom–Gill (CPMG) method.[31]

Particle size distribution was measured with an Otsuka Electronics DLS-700 dynamic light scattering spectrophotometer at 40 °C.

Fluorescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer. Sample solutions were deaerated by bubbling with argon gas for 15 min prior to measurements.

Results and Discussion

The amphiphilic terpolymers employed in the present study have completely random sequence distributions of the monomer units. The mole percent content of each monomer unit is indicated in Chart I. We ascertained, in a separate experiment, that the monomer combinations of AMPS and each of the methacrylamides used in this study provided "ideal copolymerization" systems; i.e., the copolymer composition was found to be proportional to

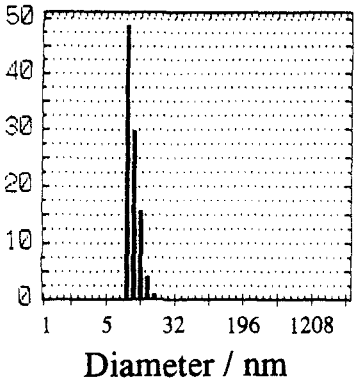


Figure 1. Histogram of the size distribution (number) for the parent terpolymer poly(A/Ad/Py) in aqueous solution. The concentration of the polymer was 0.0032 g/mL.

the monomer composition in feed, allowing us to prepare completely random terpolymers of well-defined composition.[26]

The contents of the hydrophobic units in the parent terpolymers poly(A/Ad/Py) and poly(A/Np/Py) (Chart I) are sufficiently high to form micellelike microphase structures in aqueous solution. Figure 1 shows a histogram for the particle size distribution of the parent terpolymer poly(A/Ad/Py) in aqueous solution measured by a dynamic laser light scattering spectrophotometer. The particle size of poly(A/Ad/Py) in aqueous solution was distributed between ca. 6 and 13 nm in diameter.

In Figure 2 are shown particle size distributions of the complex poly(A/Ad/Py)/DDAB (chart I) as prepared in an aqueous solution. Figure 2a shows the size distribution measured immediately after a DDAB aqueous solution was added to a poly(A/Ad/Py) aqueous solution. As soon as DDAB was added, the complex was separated out as particles with diameters ranging from 60 to 250 nm. The solution became turbid, but no precipitation occurred. As can be seen from parts a and b of Figure 2, the particles of the complex were stable in aqueous media for a long period of time; i.e., no coagulation of the particles occurred, and the particle size of the as-prepared complex persisted for more than 12 days in aqueous media.

The complexes thus prepared were soluble in common organic solvents with a range of polarities such as benzene, toluene, THF, chloroform, methanol, ACN, and DMF. Figure 3 shows the particle size distribution of poly(A/Ad/Py)/DDAB in THF solution. The size was found to be distributed between ca. 6 and 15 nm. It is to be noted that the particle size of the complex in THF was quite similar to that of the parent terpolymer in aqueous solution. Figure 4 represents a GPC elution curve for poly(A/Ad/Py)/DDAB in THF, from which the number-average molecular weight was estimated to be $M_n = 3.9 \times 10^4$ with standard polystyrenes. The radius of gyration of the complex was calculated to be ca. 6 nm (ca. 12 nm in diameter) from the polystyrene equivalent molecular weight, which is in fair agreement with the light scattering data given in Figure 3.

Structural features of the parent amphiphilic terpolymers used in the present study are that the hydrophobic pendants are connected to the polymer main chain by rotationally hindered amide bonds. The parent terpolymers form micellelike hydrophobic self-aggregates in aqueous solution, in which the Py probes are tightly encapsulated.[26] The aggregates are stabilized by hydrophobic interactions among the hydrophobic pendants. Hydrogen bonding between the spacer amide bonds may contribute to strengthening the microphase structure as discussed previously.[19,20] Since the complexes were prepared in aqueous solution, the microphase structures should be retained at least in the as-prepared complexes. It should be interesting, however, to examine whether the microphase structures can be retained even after the complexes were dissolved in organic solvents.

^{1}H NMR spectroscopy provides qualitative information about the motional restrictions owing to the aggregation of the hydrophobic residues.[32,33] Considerable line broadening of the NMR resonance peaks for the protons of the hydrophobic residues occurred when the hydrophobic residues were aggregated in aqueous solution.[15,17,19]

Figure 5 shows the ^{1}H NMR spectra of poly(A/Np/Py)/DDAB (Chart I) measured in various organic solvents. From the integrated peak intensities for the resonances of the naphthyl and DDAB protons in the NMR spectrum of poly(A/Np/Py)/DDAB in DMF-d_7, the residual molar ratio of naphthyl/DDAB was found to be 4:6, indicating that almost quantitative numbers of DDAB molecules were ionically bound with the SO_3^- groups in poly(A/Np/Py) which consists of 40 mol % of AMPS and 59 mol % of 1NpMAm units.

As can be seen from Figure 5, the resonance peaks due to the naphthyl protons at ca. 8 ppm were much broader than those due to the aliphatic protons in the DDAB residues. It is important, however, to note that the resonance line widths were different for different solvents used. In benzene-d_6, the resonance lines were markedly broader than those in ACN-d_3 and in DMF-d_7. The peaks due to the naphthyl protons in poly(A/Np/Py)/DDAB in benzene-d_6 were as broad as those of the parent terpolymer in D_2O. The resonance peaks due to the protons in the DDAB residues in poly(A/Np/Py)/DDAB in ACN-d_3 and DMF-d_7 showed no significant line broadening, except for

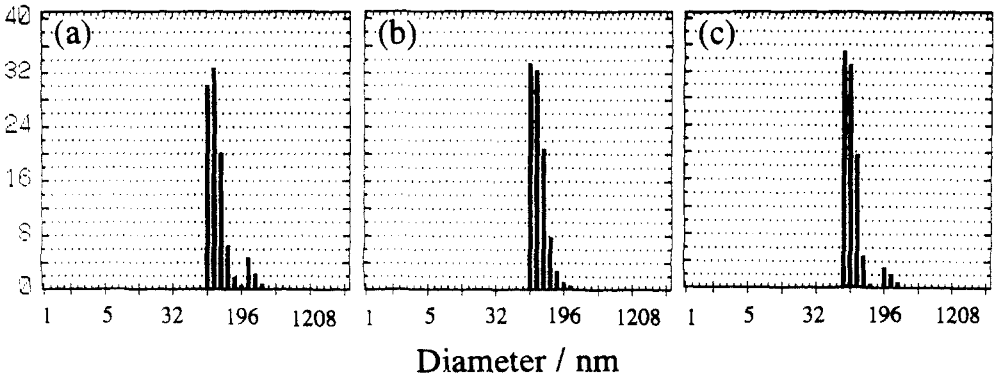


Figure 2. Histograms of the size distributions (number) for as-prepared complex poly(A/Ad/Py)/DDAB in aqueous media: immediately after a 0.3 g/L DDAB aqueous solution was added to a 0.3 g/L poly(A/Ad/Py) aqueous solution (a), after standing for 4 h (b), and after standing for 12 days (c).

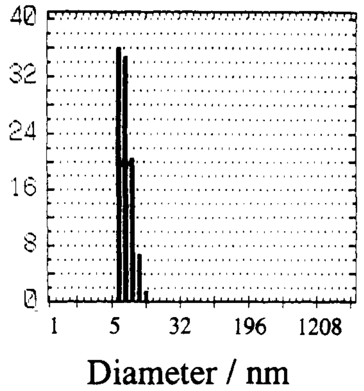


Figure 3. Histogram of the size distribution (number) for the complex poly(A/Ad/Py)/DDAB in THF solution.

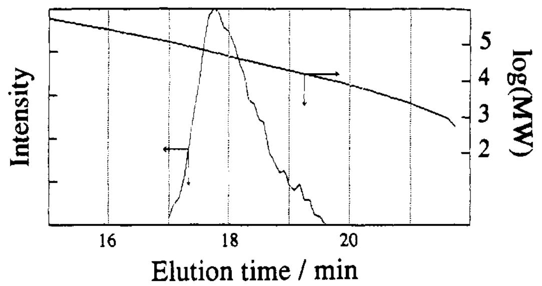


Figure 4. GPC elution curve for the complex poly(A/Ad/Py)/DDAB in THF. A calibration curve obtained with standard polystyrenes is also indicated.

a slight change in chemical shift, as compared with those of DDAB itself shown in Figure 5a. In benzene-d_6, however, the DDAB peaks in the complex were much broader than those in ACN-d_3 and DMF-d_7. These findings suggest that, in the complex in benzene solution, the naphthyl groups are still densely packed as reminiscent of the hydrophobic aggregate of the parent terpolymer in aqueous solution, leading to a compact conformation of the complex. Furthermore, the quaternary ammonium cation of DDAB and the sulfonate anion would form a contact ion pair in nonpolar solvents such as benzene, giving rise also to a compact conformation. A conceptual illustration of a local structure of the complex is shown in Figure 6.

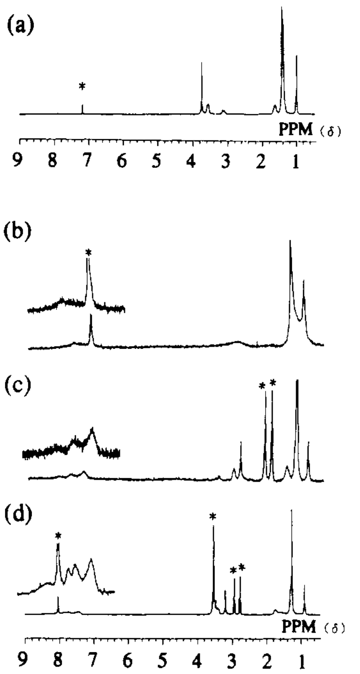


Figure 5. ^{1}H-NMR spectra of DDAB and poly(A/Np/Py)/DDAB: DDAB in benzene-d_6 (a); poly(A/Np/Py)/DDAB in benzene-d_6 (b), poly(A/Np/Py)/DDAB in ACN-d_3 (c), and poly(A/Np/Py)/DDAB in DMF-d_7 (d) at room temperature. Asterisks represent peaks due to solvents.

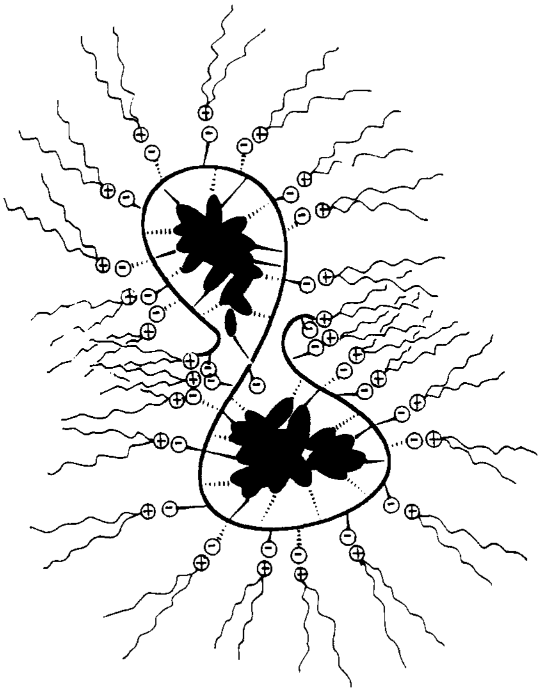


Figure 6. Conceptual illustration of a local structure of the complex.

To clarify the difference in the compactness of the complex in different solvents, 2D-NOESY spectra were compared. The 2D-NOESY technique provides qualitative information about the spatial proximities of protons in a molecule. Figure 7 compares NOESY spectra of the parent terpolymer poly(A/Np/Py) in DMF-d_7 and in D_2O at room temperature. Clearly, cross peaks appeared owing to dipolar interactions between the naphthyl and methyl and/or methylene protons in D_2O, but such cross peaks were absent in DMF-d_7, indicating a compact conformation in aqueous solution. Figure 8 compares NOESY spectra for poly(A/Np/Py)/DDAB in DMF-d_7 and in benzene-d_6. The NOESY of the complex in benzene-d_6 showed spectra very similar to those of the parent terpolymer in D_2O. Strong cross peaks occurred between the resonances of the naphthyl and aliphatic protons in the complex in benzene-d_6, while weaker cross peaks were observed in DMF-d_7. It should be noted that the methyl protons at the ends of the DDAB tails peaking at ca. 0.9 ppm were not included in the cross peaks with the naphthyl protons for the complex in benzene-d_6 (Figure 8b). This suggests that the cross peaks observed for the complex in benzene may be attributed to the same type of cross interactions existing in the parent terpolymer in aqueous solution. In other words, the complex in benzene may possess naphthyl aggregates formed in aqueous solution. Considering that hydrogen bonding is strengthened in nonpolar media, hydrogen bonding among the spacer amide bonds existing in the microphase structure of the parent terpolymer in aqueous solution may still be retained in the complex in benzene. It may be reasonable to consider that the hydrogen bonding is responsible for retaining the naphthyl aggregates even in the complex in organic solution.

The NMR relaxation techniques provide useful tools to study local segment motions in polymers.[28-30] In Table I are listed the measured spin–lattice relaxation time (T_1) and spin–spin relaxation time (T_2) for the parent terpolymer poly(A/Np/Py), a related model copolymer poly-

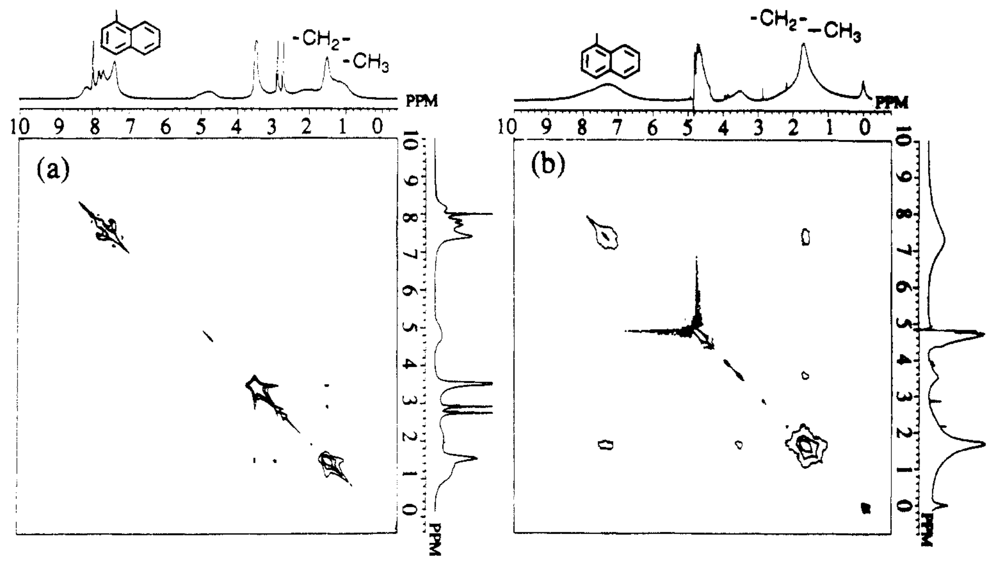


Figure 7. 2D-NOESY contour plots for the parent terpolymer poly(A/Np/Py) in DMF-d_7 (a) and in D_2O (b).

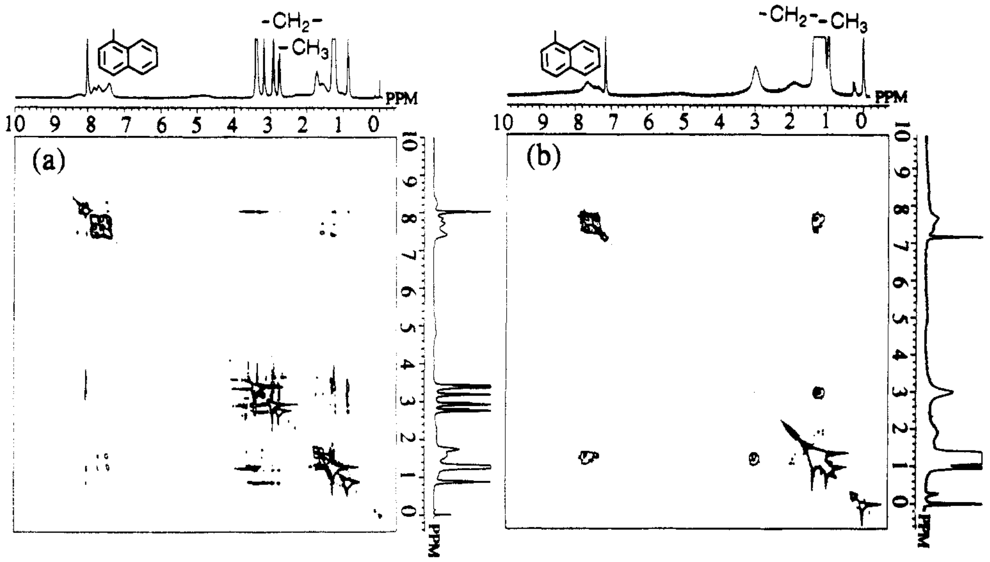


Figure 8. 2D-NOESY contour plots for the complex poly(A/Np/Py)/DDAB in DMF-d_7 (a) and in benzene-d_6 (b).

Table I
Values of T_1 and T_2 for the Protons of the Naphthyl Residues and the DDAB Methylene Groups

		T_1 (ms)		T_2 (ms)	
sample	solvent	naphthyl	DDAB	naphthyl	DDAB
poly(A/Np/Py)	D_2O	726		4	
poly(A/Np/Py)	DMF-d_7	854		45	
poly(Np/Py)	benzene-d_6	1107		131	
poly(A/Np/Py)/ DDAB	benzene-d_6	598	655	11	137
poly(A/Np/Py)/ DDAB	DMF-d_7	712	792	26	737

(Np/Py) (Chart I), and the complex poly(A/Np/Py)/DDAB in various solvents. The value of T_2 for the naphthyl resonance in poly(A/Np/Py) in D_2O was found to be very small, being 1 order of magnitude smaller than that observed in DMF. This is in agreement with the finding that the naphthyl protons in poly(A/Np/Py) exhibited much broader resonance lines in D_2O than in DMF-d_7, as can be seen from Figure 7. These findings are consistently indicative of highly restricted mobility of the naphthyl residues owing to hydrophobic aggregation in aqueous solution.

It is important to point out that T_2 values for the naphthyl resonances in poly(A/Np/Py)/DDAB in benzene-d_6 and in DMF-d_7 were much smaller than that for poly(Np/Py) in benzene-d_6. These T_2 values for poly(A/Np/Py)/DDAB were also smaller than T_2 for poly(A/Np/Py) in DMF-d_7. This suggests that the motion of the naphthyl groups in the complex in organic solution is still restricted as reminiscent of the parent terpolymer in aqueous solution. A very small T_2 value of 11 ms for the naphthyl resonance for poly(A/Np/Py)/DDAB in benzene is indicative of considerably restrained naphthyl motions, similar to those in poly(A/Np/Py) in D_2O, being consistent with the broad resonance line of the naphthyl peaks shown in Figure 5. The much larger T_2 values for the aliphatic protons of the DDAB residues in poly(A/Np/Py)/DDAB indicate that the motions of the aliphatic double chains in DDAB are much less restrained in the complex.

The T_1 values for the naphthyl resonances in poly(A/Np/Py)/DDAB in benzene-d_6 and in DMF-d_7 were smaller than that for poly(Nd/Py) in DMF-d_7, which is consistent with the tendency observed for T_2. The T_1 value for the parent terpolymer in DMF-d_7 was a little smaller than that of the model copolymer in benzene-d_6, while it was larger than that of the complex in DMF-d_7. This tendency is qualitatively consistent with that observed for T_2. However, the T_1 value for the parent terpolymer in D_2O was a little larger than those of the complex in benzene-d_6 and in DMF-d_7, whereas T_2 exhibited an opposite tendency. The spin-lattice relaxation occurs most efficiently

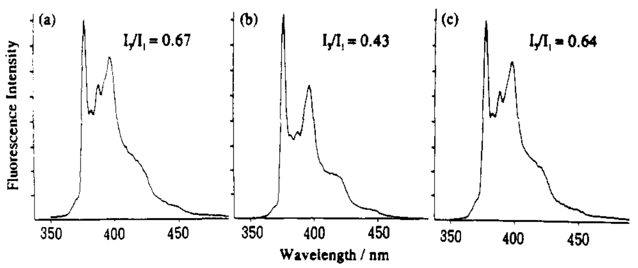


Figure 9. Fluorescence spectra of the model compound PyPAm in benzene (a) and in DFM (b) and the model copolymer poly(Ad/Py) in benzene (c). The I_3/I_1 ratios are indicated in the figure.

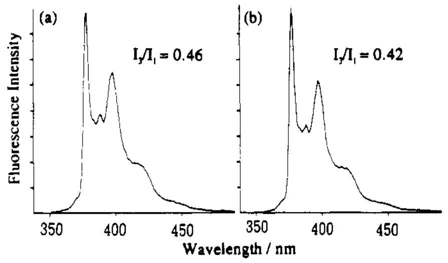


Figure 10. Fluorescence spectra of the complex poly(A/Ad/Py)/DDAB in benzene (a) and in DMF (b). The I_3/I_1 ratios are indicated in the figure.

through molecular motion whose frequency is comparable to the NMR frequency.[34] Therefore, T_1 decreases with a decrease in molecular motion, reaches a minimum, and then increases with a further decrease in the molecular motion. The large T_1 value observed for the naphthyl resonance in the parent terpolymer in D_2O, in spite of the very small T_2 value, is attributable to the relaxation in the highly restricted motion.

Fluorescence emitted from the pyrene probes provides useful information about the nature of their local environments. It is known that the ratio of the third to first vibrational fine structure, I_3/I_1, of the pyrene fluorescence is dependent on local environmental polarity, the I_3/I_1 ratio being higher in less polar media.[35]

As references, fluorescence spectra of a small molecular weight model compound PyPAm (Chart I) in benzene and in DMF and of a related model copolymer poly(Ad/Py) (Chart I) in benzene are exhibited in Figure 9. The I_3/I_1 ratios for PyPAm and poly(Ad/Py) were 0.67 and 0.64, respectively, in benzene, and the ratio for PyPAm in DMF was 0.43. These values clearly reflect solvent polarities. Figure 10 compares fluorescence spectra emitted by the Py probes in poly(A/Ad/Py)/DDAB in benzene and in DMF. In benzene, the value of I_3/I_1 for poly(A/Ad/Py)/DDAB (0.46) was much smaller than those for PyPAm (0.67) and poly(Ad/Py) (0.64), while in DMF the complex and PyPAm showed almost the same values. These findings indicate that the Py probes in the complex experience micropolarities which are different from solvent polarities and that they are confined to polar microenvironments even though the complex is dissolved in benzene.

The fluorescence spectrum of poly(Ad/Py) was very similar to that of PyPAm in benzene as can be seen from Figure 9, indicating that the Py residues in the reference copolymer experience solvent bulk polarity, although the microenvironment around the Py chromophores are crowded with a large number of adamantyl groups and spacer amide bonds in the copolymer.

In poly(A/Np/Py)/DDAB and poly(A/Ad/Py)/DDAB, the Py residues are surrounded by a large number of hydrophobic groups and also by ion-pair groups. Therefore, the Py residues may not be exposed to the solvent phase but experience a polar microenvironment owing to the surrounding ion pairs in the complex even though they are in benzene solution.

Conclusions

The Coulombic complexes poly(A/Ad/Py)/DDAB and poly(A/Np/Py)/DDAB were prepared from the corresponding parent amphiphilic terpolymers poly(A/Ad/Py) and poly(A/Np/Py) by treatment with double-chain cationic surfactant DDAB in aqueous solution. The complexes were soluble in common organic solvents with a range of polarities. The size of the complex in THF solution, measured by a dynamic light scattering technique, ranged from 6 to 15 nm in diameter, being consistent with a radius of gyration approximately calculated on the basis of GPC data. ^{1}H-NMR line broadening, 2D-NOESY, and T_1 and T_2 data for poly(A/Np/Py)/DDAB in organic solutions revealed that the motions of the naphthyl residues were strongly restricted, while those of the aliphatic tails in the DDAB residues were much less restricted. These findings imply that the micellelike microphase structure of the parent amphiphilic terpolymers formed in aqueous solution remained intact, if not completely, in the complexes even though they were dissolved in organic solvents. The complex was found to adopt a particularly compact form in benzene presumably because of stronger hydrogen bonding among the spacer amide bonds and more contact ion pairs between the cationic head of DDAB and the sulfonate group in the parent terpolymer in benzene than in polar solvents. Fluorescence emitted by the pyrenyl probes incorporated in the complexes supported these findings.

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