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Fluorescence and Energy Migration in the Random Copolymers of (1-Naphthylmethyl)methacrylamide and Sodium 2-(Acrylamido)-2-methylpropanesulfonate

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ABSTRACT: Random copolymers of (1-naphthylmethyl)methacrylamide (1-NpMAm) and sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) with varying compositions were synthesized. Fluorescence spectra of the copolymers in organic solution showed predominant monomer fluorescence of the naphthyl (Np) residues even when the Np content in the copolymers is as high as 58 mol %, unlike conventional random copolymers containing Np moieties. In aqueous solution, by contrast, the copolymers showed a strong preference for excimer emission. The excimer intensity increased with increasing Np content, and the copolymers with >40 mol % Np content showed almost only excimer emission. The total fluorescence quantum yield increased with increasing Np content, despite an excimer component increase, again unlike conventional random copolymers. The copolymer with 58 mol % Np content showed a rapid decay of Np monomer fluorescence with lifetimes of 28 and 268 ps, which agreed fairly well with the rise times of the excimer (29 and 278 ps) at room temperature. All these findings imply that little or no self-quenching site exists and rapid singlet energy migration occurs solely to preformed excimer sites in the copolymers with a higher Np content in aqueous solution. Efficient triplet energy migration was also observed for the copolymers in aqueous rigid solution at 77 K.

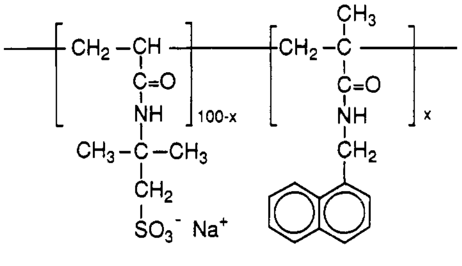
Introduction

An increasing number of studies have focused on the photophysics of aromatic chromophores covalently bound to polyelectrolytes.[1] The photophysical behavior of such amphiphilic polyelectrolyte systems in aqueous solution depends largely on polymer-chain conformation. When a chromophore loading on a polyelectrolyte is sufficiently low, the polymer would assume an expanded conformation in aqueous solution where the chromophore would be forced to be exposed to the water phase. On the other hand, when a chromophore loading is high, the polymer assumes a micellelike microphase structure in which the hydrophobic chromophores form an interior cluster and loops of charged segments form an outer layer.[2,3] In the former case, the photophysical behavior of the hydrophobic chromophore is relatively simple,[4-7] whereas in the latter case, it is rather complex.[3,8] The complexity arises mostly from chromophore interactions such as excimer formation and/or self-quenching due to interactions between excited and ground states, energy transfer and migration, and excited-state annihilation.

The understanding of such complex photophysical behavior of the amphiphilic polyelectrolyte systems and the design of the "photon-harvesting system" have been the subjects of considerable interest in recent years.[9] Since the distance between chromophores in the cluster of chromophores is very short in the amphiphilic polyelectrolyte systems, a fast energy migration can occur, but energy trapping by self-quenching sites is a crucial problem.[8a] Therefore, a key to the molecular architecture for a photon-harvesting polymer is to avoid self-quenching while maintaining a high chromophore density on the polymer.

It is important to establish the relationship between the copolymer structure and photophysical properties. The functionalization of a polyelectrolyte with an aromatic chromophore is usually performed by copolymerization of a chromophore monomer and an electrolyte monomer. Recent studies have shown that the photophysics is dependent on the monomer sequence distribution along the copolymer chain or, in other words, on whether the copolymer is random,[8a,b] block,[10] or alternating[11,12] in nature. Another important structural factor for a photoactive amphiphilic polyelectrolyte may be how a chromophore pendant is attached to the main chain, because the local motion of the pendant chromophore should rest on the nature of the spacer bond between the main chain and the chromophore.

Chart I



poly(A/Np(x))

In the present work, we synthesized random copolymers of (1-naphthylmethyl)methacrylamide (1-NpMAm) and sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) with different compositions (Chart I). Structural features for the copolymers poly(A/Np(x)) (x represents the mole percent content of the 1-NpMAm unit) are that the naphthyl (Np) residues are distributed along the polymer chain in a highly random fashion and that they are fixed to the main chain by amide bonds which restrict motion of the Np residue, owing to the rotational barrier of the spacer bond.

Experimental Section

Materials. 1-NpMAm was synthesized as follows. To a stirred solution of 16.1 g (0.102 mol) of 1-naphthylmethylamine and 12.4 (0.123 mol) of triethylamine in 500 mL of benzene was added dropwise 12.8 g (0.123 mol) of methacryloyl chloride in 50 mL of benzene over a period of 30 min under cooling in an ice bath.

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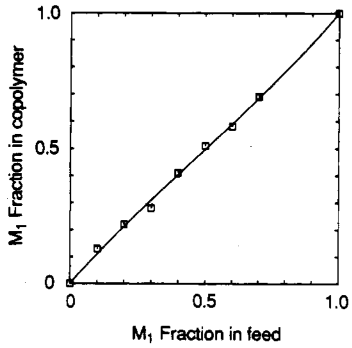

Figure 1. Relationship between the mole fraction of 1-NpMAm (M_1) in copolymer and that in a monomer feed for the copolymerization of 1-NpMAm and AMPS in DMF at 60 °C.

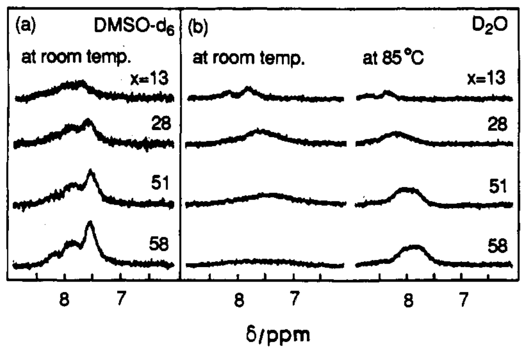

Figure 2. ^{1}H NMR spectra of poly(A/Np(x)) with different contents of the 1-NpMAm units observed in DMSO-d_6 at room temperature and in D_2O at room temperature and 85 °C.

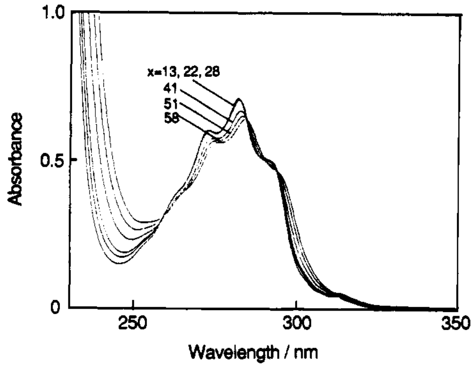

Figure 3. Absorption spectra of poly(A/Np(x)) with various Np contents in aqueous solution.

After the reaction mixture stirred for 12 h at room temperature, it was filtered to remove triethylamine hydrochloride. The filtrate was washed with aqueous solutions of 1 N HCl, saturated NaCl, 1 M $NaHCO_3$, and saturated NaCl successively. The organic layer was dried with $MgSO_4$ overnight. The solvent was evaporated under a reduced pressure to give a crude product which was recrystallized from n-hexane three times to give 17.4 g (75.4%) of white needles (mp 105 °C): ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 5.0 (d, 2 H), 5.3 (s, 1 H), 6.2 (s, 1 H), 7.4–8.2 (m, 7 H). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.04: H, 6.14; N, 6.21.

2-(Acrylamido)-2-methylpropanesulfonic acid (AMPS) was a gift from Nitto Chemical Industry Co. and was used without further purification.

Copolymers. Copolymers of 1-NpMAm and AMPS with different compositions were prepared as follows. A glass ampule containing 20 mmol of the total monomers of AMPS and 1-NpMAm in a known molar ratio, 0.5 mol % (on the basis of the total monomers) 2,2′-azobis(isobutyronitrile) (AIBN), and 40 mL of N,N-dimethylformamide (DMF) was outgassed on a vacuum line by five freeze–pump–thaw cycles and then sealed under vacuum. Copolymerization was carried out at 60 °C for 15–40 h. The mixture was poured into a large excess of ether to precipitate polymers which were purified by reprecipitating from methanol into a large excess of ether. The polymers were dissolved in dilute aqueous NaOH. The alkaline solution, whose pH was adjusted to 11, was dialyzed against pure water for several days and then lyophilized.

The copolymer composition was determined by the N/C and S/C ratios.

Measurements. Absorption spectra were recorded on a Shimadzu UV-2100 spectrophotometer.

Fluorescence and phosphorescence spectra were recorded on a Shimadzu RF-02A spectrofluorometer. For measurement of fluorescence quantum yields (ϕ_F) of the copolymers, 1-methylnaphthalene in cyclohexane (ϕ_F = 0.21)[13] or anthracene in 95% ethanol (ϕ_F = 0.27)[13] was used as a standard. The area under the fluorescence peak of the standard was compared with that of a copolymer sample. Corrections for the inner filter adsorption and for the change in the refractive index were also made.[14]

Time-dependent fluorescence was measured by using a correlated single-photon-counting technique as reported previously.[15] All the sample solutions for the spectroscopic measurements were deaerated by bubbling with Ar gas for 30 min.

Results and Discussion

Copolymer composition data for the copolymerization of (1-naphthylmethyl)methacrylamide (M_1) and 2-(acrylamido)-2-methylpropanesulfonic acid (M_2) in DMF at 60 °C are presented in Figure 1. The monomer reactivity ratios were determined by fitting the composition data to the copolymer composition equation. Initial parameters for the computation were determined by the conventional Fineman–Ross plot. The best fit curve is given in Figure 1. The monomer reactivity ratios that gave the best fit were r_1 = 0.85 ± 0.08 and r_2 = 0.87 ± 0.07. These values indicate that the distribution of the monomer units in the copolymer is highly random.

The ability of the AMPS charged segments to solubilize sequences of the 1-NpMAm units into water is very high; i.e., the copolymers with <58 mol % 1-NpMAm content were completely soluble in water. However, the copolymer containing a 69 mol % 1-NpMAm unit was insoluble in water.

^{1}H NMR spectroscopy provides qualitative information on the self-aggregation of hydrophobic residues in an amphiphilic polyelectrolyte.[2a,b] In Figure 2 are compared NMR peaks due to naphthyl (Np) protons in poly(A/Np(x)) (Chart I) of different Np contents. The NMR spectra of poly(A/Np(x)) were measured in DMSO-d_6 and in D_2O at a constant polymer concentration (7 wt %) under the same instrumental conditions. In DMSO-d_6, the peak intensity increased systematically with increasing Np content in the copolymer. In D_2O, by contrast, the intensity decreased with increasing Np content at room temperature, owing to line broadening. This marked motional broadening of the Np proton resonances indicates that the motion of the naphthalene ring is highly restricted in the hydrophobic self-aggregate at room temperature. When the temperature was raised, however, the NMR peak intensity in D_2O began to increase at about 70 °C and the peak became apparent at 85 °C as shown in Figure 2. Hydrophobic interaction is characterized by the formation of organized water structures around hydrophobic groups.[16,17] At a higher temperature the water structures are destroyed, and thereby the hydrophobic aggregate is destabilized. Hence, the packing of the Np residues in the aggregate is loosened, and therefore the restriction to the motion is alleviated at a higher temperature.

Absorption spectra of poly(A/Np(x)) with different Np contents in aqueous solution are compared in Figure 3. There was no significant difference in the spectra among the copolymers of <28 mol % Np content. However, the

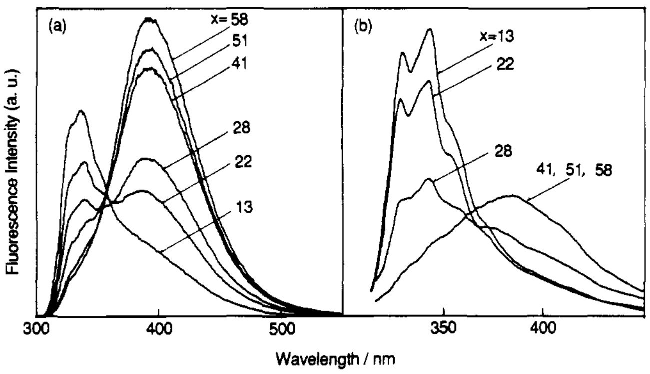

Figure 4. Fluorescence spectra of poly(A/Np(x)) with various Np contents in aqueous solution: (a) at room temperature, (b) at 77 K. Excitation wavelength, 290 nm.

spectra were broadened with a significant red shift when the Np content exceeded 41 mol %. This is due in part to the hydrophobic microenvironments of the Np chromophores and also to the electronic perturbation of the π-electron system of the Np rings arising from the hydrophobic self-aggregation.

The chromophore self-aggregation in aqueous solution is more clearly reflected in the steady-state fluorescence spectra. Figure 4a shows the fluorescence spectra of poly(A/Np(x)) of different Np contents in aqueous solution at room temperature. The fluorescence spectra depend markedly on the copolymer composition. As the Np content increased from 13 to 28 mol %, fluorescence due to the monomeric Np moieties peaking at 337 nm decreased, and excimer fluorescence peaking at 390 nm increased systematically. The copolymers of >41 mol % Np content showed a marked tendency for emitting strong excimer fluorescence which dominated the monomer emission.

In rigid aqueous solution at 77 K, the Np monomer fluorescence markedly decreased as the Np content in the copolymer increased as shown in Figure 4b. It should be noted that the copolymers with >41 mol % Np content showed practically only excimer emission even in rigid solution at 77 K, although the intensity was much weaker than that at room temperature. Moreover, the excimer at 77 K was blue-shifted by about 10 nm from the excimer peak observed at room temperature. The blue-shifted excimer emission is attributable to a preformed excimer with configurational constraints leading to a deviation from the full overlap between the two naphthalene rings.[10]

Since the fluorescence spectra given in Figure 4a were measured at the same molar concentration of the Np residue, a relative fluorescence intensity can approximately be related to a relative fluorescence quantum yield. Total fluorescence quantum yields for the copolymers containing 13 and 58 mol % Np units were estimated to be $\phi_F = 0.09$ and 0.16 at room temperature, respectively. An important observation in the present study is that the total fluorescence quantum yield was increased as the excimer component increased with incrasing Np content at room temperature. This is rather unusual as compared with the tendency shown by polymer-bound aromatic chromophores studied up to now, as discussed below.

In vinylic polymers containing a large number of pendant chromophores, in general, the chromophore groups are close enough to electronically interact, but because of the conformational constraints they cannot necessarily achieve the proper orientation to emit excimer fluorescence. Thus, an electronic interaction in a singlet-excited and ground-state chromophore pair, whose geometrical orientation is not suitable to form an excimer, would result in shortening of the fluorescence lifetime. This is an origin of self-quenching. Consequently, if the number of excimer-forming sites increases as a result of the increased chromophore density in a polymer system, the number of self-quenching sites also tends to increase, leading to a decrease in the total fluorescence quantum yield. For example, in the case of the random copolymers of 2-vinylnaphthalene (2VN) and acrylic acid (AA), which we previously investigated,[11a] the total fluorescence quantum yields for the copolymers with 4 and 44 mol % 2VN content in aqueous solution at pH 6 were $\phi_F = 0.12$ and 0.056, respectively. The 2VN–AA random copolymer with 4 mol % 2VN content exhibited only monomeric Np fluorescence, while that with 44 mol % 2VN content showed dominant excimer emission at pH 6.

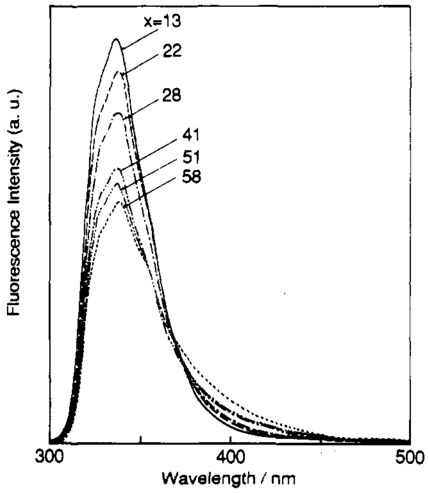

Figure 5. Fluorescence spectra of poly(A/Np(x)) with various Np contents in DMF/methanol (90/10, v/v) at room temperature. Excitation wavelength, 290 nm.

The fluorescence behavior of the present copolymers at room temperature differs remarkably from that of the 2VN–AA random copolymers in that the poly(A/Np(x)) with >41 mol % Np content shows a much stronger excimer emission with a higher total fluorescence quantum yield; $\phi_F = 0.16$ for poly(A/Np(58)) (poly(A/Np(x)) with 58 mol % Np content). It should be noted that there seems to exist an isoemissive point at about 360 nm, though it is not very clear, in the fluorescence spectra of the present copolymers at room temperature as shown in Figure 4a. All these findings suggest that there is little or no self-quenching occurring at room temperature even though the Np residues are highly crowded in the hydrophobic aggregate of the present copolymers. In aqueous rigid solution at 77 K, however, the total fluorescence quantum yield decreased as the excimer component increased.

Fluorescence spectra of the present copolymers in organic solution were remarkably different from those in aqueous solution. Figure 5 compares the fluorescence spectra of poly(A/Np(x)) with different Np contents in DMF/methanol (90/10, v/v). The copolymers exhibited predominantly monomeric Np fluorescence even when the Np content is as high as 58 mol %. This sharp contrast in the fluorescence behavior of poly(A/Np(x)) in water and in DMF/methanol arises from the difference in the polymer conformation. The copolymers assume a microphase-separated structure in aqueous solution, while they assume a random-coil structure in organic solution.

It is commonly known that random copolymers containing a relatively large mole fraction of the Np residues show excimer fluorescence in organic solution. Guillet et al.[3a] reported that a copolymer of 16 mol % 1-naphthyl-

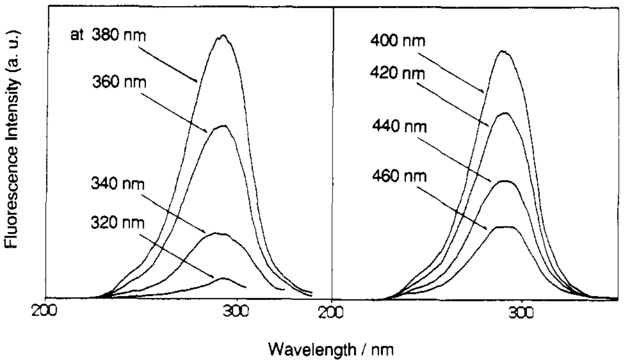

Figure 6. Excitation spectra of poly(A/Np(58)) in aqueous solution at room temperature. Wavelengths at which fluorescence was monitored are indicated in the figure.

methyl methacrylate and 84 mol % AA units showed a significant excimer emission in 1,4-dioxane. Bai et al.[12a] compared the fluorescence behavior of alternating and random copolymers of 2VN with methacrylic acid (MA) and with methyl methacrylate (MMA) and found that the alternating copolymers had essentially no excimer fluorescence, while the random copolymers with 43–45 mol % 2VN content exhibited significant excimer emission both in water and in tetrahydrofuran.[12a] In our earlier work, we also found that a DMF solution of a random copolymer containing 44 mol % 2VN and 56 mol % methyl acrylate units showed a strong excimer emission.[11a]

In contrast to these earlier results, the present copolymers showed a strong preference for monomeric fluorescence in organic solution; i.e., even the copolymer with 58 mol % Np content showed a strong monomer emission with a small shoulder due to an excimer in DMF/methanol. We attribute these findings to the geometrical constraints imposed on the Np pendant groups by the spacer bonds. A structural feature of poly(A/Np(*x*)) is that the Np pendant groups are combined with the backbone by amide bonds. A high rotational barrier of the amide bond due to a partial double-bond character as well as hydrogen bonding between the neighboring spacer amide bonds will restrict the motional freedom of the pendant chromophore. Hence, an arrangement of the Np pendants to properly orient for excimer conformation is likely to be disfavored.

Excitation spectra monitored at different wavelengths in the 320–460-nm region for poly(A/Np(58)) in aqueous solution at room temperature are compared in Figure 6. Regardless of the wavelength at which the excitation spectra were monitored, the observed spectra were essentially identical in both spectral shape and peak wavelength (ca. 285 nm), implying that light-absorbing species are monomeric Np chromophores. Namely, there was no indication of the presence of ground-state Np dimers to give excimer emission by direct excitation.

The intensity of excimer fluorescence cannot be explained only by the quantity of excimer-forming sites contained in a polymer. Energy migration to the excimer-forming sites has to be taken into consideration in a polymer system. The data shown in Figure 6 suggest that the light-absorbing chromophores are the same for both the monomer and excimer fluorescence, and thus the excimer emission occurs predominantly via energy migration to preformed excimer sites existing in a small quantity in the polymer.

The efficient energy migration of the singlet-excited state to the preformed excimer-forming sites is strongly implied by the time-dependent fluorescence of poly(A/Np(58)) in aqueous solution at room temperature. Figure 7 compares the time-dependent fluorescence monitored at 330 and 400 nm. The lifetimes τ_i and the relative weights of the preexponential factors a_i are listed in Table I. There was a substantial shortening of the lifetime for the Np monomer fluorescence measured at 330 nm. A large portion of the fluorescence at 330 nm decayed with lifetimes of 28 and 268 ps. An important observation to be noted here is that there were rapid rise processes with 29- and 278-ps components in the Np excimer fluorescence monitored at 400 nm whose time constants were very close to the decay constants for the Np monomer fluorescence monitored at 330 nm.

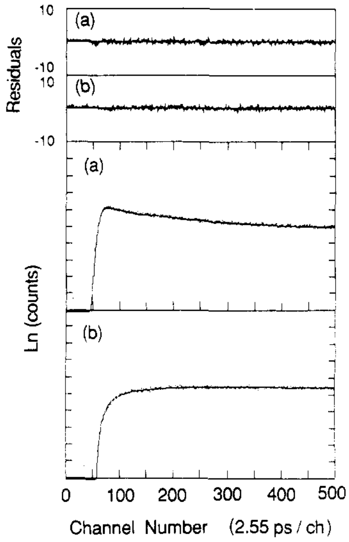

Figure 7. Comparison of (a) the decay of monomer fluorescence monitored at 330 nm and (b) the rise of an excimer at 400 nm for poly(A/Np(58)) in aqueous solution at room temperature. Excitation wavelength, 295 nm; 1 channel = 2.55 ps.

Table I
Fluorescence Decay and Rise Times for Poly(A/Np(58)) in Aqueous Solution at Room Temperature[a]

species	λ_{em}[b]/nm	fitting parameters, τ_i (ps)/a_i		
monomer	330	28/0.639	268/0.234	5830/0.127
excimer	400	29[c]/−0.169	278[c]/−0.096	4490/0.227

[a] Excitation wavelength, 290 nm. Fitting function, $I(t) = \sum a_i \exp(-t/\tau_i)$. [b] Wavelength at which fluorescence decays were monitored. [c] Rise time.

There are at least two plausible explanations for the observed rise of the excimer emission: (1) dynamic motions of a singlet-excited Np and/or adjacent ground-state Np group to bring the chromophore pair into a proper juxtaposition for the full-overlap excimer conformation; (2) rapid energy transfer to preformed excimer-forming sites in which an excimeric interaction can take place with extreme rapidity without need of chromophore motions. We would rule out the first possibility because it seems difficult to conceive that such a rapid motion of the Np groups can occur in the hydrophobic cluster of the Np groups as discussed earlier on the basis of the NMR data. Therefore, we believe that extremely fast migration of Np singlets occurs in the hydrophobic cluster of the Np residues in aqueous solution at room temperature and the migrating excitation energy is rapidly trapped solely by preformed excimer-forming sites. There seems to be no trapping by self-quenching sites.

If the excimer-forming site has the same absorption spectrum as the monomeric Np chromophore, then energy transfer to the excimer-forming site occurs with the same rate as energy hopping between the isolated Np chromophores. If energy hopping occurs by the Förster mech-

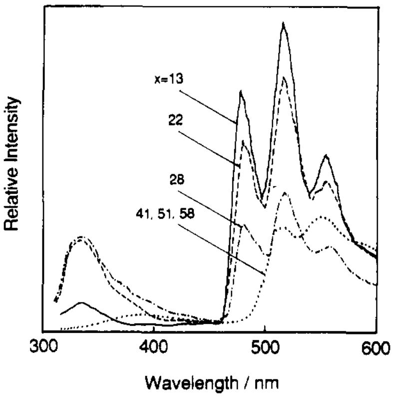

Figure 8. Phosphorescence and delayed fluorescence spectra for poly(A/Np(x)) with different Np contents in aqueous rigid solution at 77 K. Excitation wavelength, 290 nm.

anism, the time constant for a hopping (τ_h) between the Np groups is given by[18]

$$\tau_h = \tau(R/R_0)^6 \tag{1}$$

where τ is the unperturbed lifetime of the Np singlet-excited state, R is the distance between the Np groups, and R_0 is the Förster radius for self-transfer between the Np chromophores. We may use $R_0 = 0.83$ nm reported for 1-methylnaphthalene[19] and may assume $R = 0.35$ nm as the shortest possible distance for the chromophores without strong electronic interactions in the hydrophobic cluster. Then the value of τ_h can be calculated to be about 225 ps by using $\tau = 40$ ns, which is a fluorescence lifetime measured for poly(A/Np(13)) in aqueous solution at room temperature. This calculated hopping time, however, cannot explain the rapid energy transfer with a time constant of 29 ps observed for poly(A/Np(58)) in aqueous solution. Therefore, account must be taken of the role of energy delocalization due to other mechanisms such as the exchange mechanism and the exciton mechanism.[20]

The delayed emission spectra of the copolymers in aqueous rigid solution at 77 K are presented in Figure 8. All the copolymers exhibited both phosphorescence and delayed fluorescence at 77 K, although poly(A/Np(58)) showed extremely rapid migration and trapping of singlet excitations at room temperature. The copolymers of <28 mol % Np content showed normal phosphorescence and significant delayed fluorescence with an emission maximum of 330 nm attributable to the Np monomeric fluorescence. In contrast, poly(A/Np(x)) with >41 mol % Np content exhibited a phosphorescence emission red-shifted by ca. 38 nm from the normal phosphorescence band shown by the copolymers with a lower Np content. Furthermore, delayed fluorescence emitted by the copolymers with >41 mol % Np content is from the excimer at about 390 nm.

When triplet energy migration occurs among chromophores crowded in macromolecular environments, there is a chance for triplet–triplet (T–T) annihilation in which two migrating triplets give an excited singlet state and a thermally excited ground-state chromophore.[21] Thus, delayed fluorescence is an indication of the triplet migration in polymer systems.[21] It should be noted here that, even in the copolymer with the lowest Np content (poly(A/Np(13))), triplet energy migration and T–T annihilation occur. This implies that poly(A/Np(13)) assumes a sufficiently compact conformation to allow the triplets to migrate. As the Np content increases from 13 to 28 mol %, the copolymers showed a decrease in phosphorescence intensity and an increase in the delayed Np fluorescence.

The red-shifted phosphorescence observed for poly(A/Np(x)) with >41 mol % Np content indicates the presence of deep energy traps for the migrating triplets. The phosphorescence spectra for the copolymers with >41 mol % Np content shown in Figure 8 are very similar to the triplet-excimer phosphorescence spectra reported by Takemura et al.[22] Thus, we may conclude that, in an aqueous rigid solution at 77 K, very efficient triplet energy migration takes place within the Np aggregates of poly(A/Np(x)) with >41 mol % Np content and that the migrating triplets either are trapped by the triplet-excimer-forming sites or encounter them to undergo T–T annihilation to produce singlet excitations which are rapidly trapped by the preformed excimer-forming sites.

Red-shifted phosphorescence and delayed singlet-excimer fluorescence were reported for sulfonated poly(2-vinylnaphthalene) in aqueous rigid solution at 77 K by Guillet et al.,[3b] who proposed a hypercoiled conformation for the polymer in aqueous solution. More recently, Itoh et al.[23] studied the triplet energy migration of alternating and random copolymers of 9-vinylphenanthrene and MA in aqueous rigid solution at 77 K. They found that both the alternating and the random copolymers with 42 mol % phenanthrene units exhibited red-shifted phosphorescence by more than 20 nm as compared with a normal phosphorescence shown by the random copolymer with 3 mol % phenanthrene units. The preformed excimer-forming site for singlet excitations may also serve as a triplet-excimer-forming site in the present copolymer systems.

Conclusions

Random copolymers of 1-NpMAm and AMPS with high Np contents showed very strong excimer fluorescence in aqueous solution, whereas they showed a predominant monomer fluorescence in organic solution. The total fluorescence quantum yield in aqueous solution increased with increasing Np content, although the excimer component increased. For the copolymer with 58 mol % Np content, very rapid rise times (29 and 278 ps) were observed in excimer fluorescence, which were practically consistent with the decay times of the Np monomer fluorescence. These observations imply that, unlike conventional random copolymers with comparable Np contents, there exists little or no self-quenching site, despite the fact that Np residues are densely packed in the hydrophobic self-aggregate in aqueous solution, and that extremely rapid energy migration and transfer occur solely to preformed excimer sites existing in a small quantity in the copolymers. These photophysical characteristics of the present copolymers, as compared with conventional copolymers, suggest the importance of the role of the spacer bonds between the main chain and the pendent chromophore; i.e., the hindered rotation of the Np groups in the chromophore cluster in aqueous solution may disfavor self-quenching interactions as well as excimeric interactions, while photoexcited energy can delocalize over the Np cluster, owing to efficient energy migration.

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Registry No. 1-NaMAm, 137824-05-6; 1-NpMAm/AMPS (copolymer), 137824-06-7; 1-NpMNH$_2$, 118-31-0; $H_2C{=}C(Me)COCl$, 920-46-7.