Preferential Excimer Emission from Amphiphilic Alternating Copolymers of 2-Vinylnaphthalene and Maleic Acid in Aqueous Solution

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ABSTRACT: Water-soluble amphiphilic alternating copolymers of 2-vinylnaphthalene (2VN) and maleic acid (MAA), a-2VN(50)–MAA, were synthesized. The equimolar composition of these copolymers at widely varying ratios of the monomer concentrations suggested the 1:1 alternating structure. The fluorescence behavior of a-2VN(50)–MAA in aqueous solution was studied in comparison with that of a random copolymer of 2VN and acrylic acid (AA) with a 2VN loading of 44 mol % (r-2VN(44)–AA). The fluorescence spectra of this random copolymer showed a drastic change from a mixture of monomer and excimer emissions at basic pH to an almost pure but weak excimer emission at neutral and acidic pH ($\phi_F = 0.056$ at pH 6). In sharp contrast, the fluorescence of a-2VN(50)–MAA was dominated by a strong excimer emission independent of pH ($\phi_F = 0.26$ at pH 6). Reduced viscosity data suggested that a-2VN(50)–MAA retained a compact conformation even at basic pH, while r-2VN(44)–AA exhibited a sharp transition from an extended to a compact conformation on decreasing pH from 9 to 7. In contrast to the a-2VN(50)–MAA case the compact conformation of r-2VN(44)–AA led to considerable self-quenching. These striking differences between the alternating and random copolymers were qualitatively explained by speculating on the difference in the type of interaction between the naphthalene chromophores: an extensive aggregation with random orientation for r-2VN(44)–AA and a pairwise aggregation for a-2VN(50)–MAA. The former may result in a significant fraction of self-quenching sites as well as excimer-forming sites that compete with each other in trapping the migrating excitation. In contrast, the latter may exclusively result in excimer-forming sites with the rest of the chromophores well separated, such that only energy migration is allowed. The quenching of the excimer fluorescence by copper(II) ions was also studied. Both alternating and random copolymers showed very high quenching efficiency as a result of the ionic binding of the quencher ions by the copolymers.

Introduction

There is a considerable interest in functionalized polyelectrolytes.[1,2] In recent years a number of investigations have focused on the photophysics and photochemistry of water-soluble polymers with pendant aromatic groups as a chromophore.[3–8] An amphiphilic polyelectrolyte can be considered an organized assembly in the sense that (1) it "solubilizes" hydrophobic chromophores in water because of their covalent bonding to the polymer backbone and (2) the hydrophobic chromophores may aggregate to form an "organized structure" consisting of clusters of the hydrophobic moieties and charged interfaces.[9,10] A promising feature of functionalized polyelectrolytes is that a large variety of chemical modifications based on molecular design is possible as compared to the conventional organized assemblies such as surfactant micelles and vesicles.[10] Another potential advantage is that polymers per se can form a film, and they may possibly be assembled into a variety of devices and systems.

Earlier work with amphiphilic polyelectrolytes has shown that the photophysical and photochemical behavior of the hydrophobic chromophores is critically dependent on the nature of the microenvironments produced by the amphiphilic polyelectrolytes to which the chromophores are covalently attached.[3–14] Studies reported so far have mostly concentrated on random copolymers of various vinyl polycyclic aromatics and electrolyte monomers with different copolymer compositions.[3,9,11–14] In some cases the chromophore loadings on the copolymers have been limited to a low level to avoid chromophore–chromophore interactions that often lead to complexity in photophysical behavior including self-quenching.[11]

Clusters of hydrophobic chromophores in amphiphilic polyelectrolytes have a marked tendency to associate with amphiphilic quenchers in aqueous solutions, leading to an efficient static fluorescence quenching.[3,15] Electrostatic binding of ionic quenchers with a charge opposite to that of the polyelectrolyte also results in a similar phenomenon.[13,14] It has also been demonstrated that energy migration through clusters of the chromophores enhances the efficiency of fluorescence quenching but that the self-quenching process occurs via the singlet-ground-state interaction because the clusters are crowded with a random orientation of the chromophores.[3,15] This is especially true with the amphiphilic block copolymers.[15,16]

One of our primary interests is to understand how modification of the chemical structure of the polymer including sequence distribution such as random, block, alternating, etc. affects the microenvironmental features, which in turn would strongly affect the photophysicochemical behavior of the chromophores therein. In this context we have prepared water-soluble alternating copolymers of 2-vinylnaphthalene (2VN) and maleic acid (MAA), a-2VN(50)–MAA, and compared their photophysical behavior with that of a random copolymer of 2VN and acrylic acid (AA), r-2VN(44)–AA, with a roughly comparable mole fraction of 2VN. Contrary to our initial intuition, the alternating copolymer showed a striking preference of excimer fluorescence with a high quantum yield in an aqueous solution.

Experimental Section

Materials. 2-Vinylnaphthalene (2VN) (Aldrich) was sublimed twice at 35 °C under a reduced pressure of ca. 10^{-5} Torr. Maleic anhydride (MAn) (Waco) was recrystallized twice from chloroform

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Table I
Characterization of the Copolymers of 2VN with MAn and with AA

run	comonomer	2VN mole fraction in monomer feed	yield, %	$\bar{M}_w$[a]	$\bar{M}_w/\bar{M}_n$	2VN mole fraction in copolymer NMR[b]	EA[c]	IR[d]
A-1	MAn	0.103	8.6	23 100	1.50	0.47	0.46	0.45
A-2	MAn	0.297	8.1	16 400	1.06	0.50	0.48	0.46
A-3[e]	MAn	0.500	8.5	27 400	1.27	0.50	0.49	0.51
A-4	MAn	0.651	10.0	21 300	1.60	0.49	0.50	0.50
A-5	MAn	0.851	8.5	37 200	2.05	0.50	0.57	0.51
R-1[f]	AA	0.039	33.7	82 900	2.09	0.05	0.03	
R-2	AA	0.080	12.1	50 100	1.23	0.25	0.23	
R-3[g]	AA	0.222	10.1	33 300	1.8	0.44	0.46	

[a] Polystyrene equivalent weight-average molecular weights determined by GPC for the methyl ester derivatives of the copolymers. [b] From the relative areas of the total aliphatic and total aromatic peaks in the ^{1}H NMR spectra for the methyl ester derivatives of the copolymers. [c] From the C/H ratio in the elementary analysis for the methyl ester derivatives of the copolymers. [d] From the D_{1165}/D_{750} ratio for the methyl ester derivatives of the copolymers. [e] Hydrolyzed polymer was designated a-2VN(50)–MAA. [f] Designated r-2VN(4)–AA. [g] Designated r-2VN(44)–AA.

and dried at room temperature over $CaCl_2$. Acrylic acid (AA) (Waco) was fractionally distilled under a reduced pressure of nitrogen and stored at low temperature for later use. Benzene used for polymerizations was dried over sodium wire and distilled. An ethereal solution of diazomethane was prepared according to the literature.[17] Water used for fluorescence measurements was deionized with an ion-exchange column and distilled twice. The pH of aqueous solutions was adjusted with aqueous sodium hydroxide and hydrochloric acid. Cupric sulfate (Waco) was extra-pure grade and used without further purification.

Alternating Copolymers. Copolymerizations of 2VN and MAn were performed as follows. A glass ampule containing 39 mmol of 2VN and MAn in a known ratio, 0.5 mol % (on the basis of total monomers) of 2,2′-azobis(isobutyronitrile) (AIBN), and 25 mL of benzene was outgassed on a vacuum line by five freeze–pump–thaw cycles and then sealed. The ampule was heated at 70 °C for 24 h: the polymers precipitated on formation. The resulting polymers were collected by centrifugation, purified by reprecipitating twice from tetrahydrofuran (THF) into a large excess of *n*-hexane and additionally twice from THF into ether, and then dried in vacuo. The copolymerizations were carried out with various mole fractions of 2VN in monomer feed (see Table I). Care was taken not to exceed 10% total conversion. For fear of spontaneous partial hydrolysis of the anhydride groups, which may occur during the purification of the copolymers, all characterizations of the copolymers were performed after complete hydrolysis followed by esterification.

Hydrolysis was carried out by treating the copolymer with aqueous sodium hydroxide. A mixture of the 2VN–MAn copolymer (0.2 g) in a 0.25 M aqueous NaOH (25 mL) was stirred at 50 °C for 10 min to effect dissolution of the copolymer and then allowed to stand overnight at room temperature. This mixture was diluted with 200 mL of water, dialyzed against pure water for 10 days, and finally lyophilized. In the IR spectra of the hydrolyzed copolymer the 1730-cm^{-1} band due to carboxylic acid appeared in place of the 1850- and 1775-cm^{-1} bands due to anhydride groups.

Esterification of the hydrolyzed copolymer was carried out as follows. An aqueous solution of the hydrolyzed copolymer was acidified to pH 2. White precipitates thus formed were washed with cold water and dried thoroughly under vacuum over $CaCl_2$. To a suspension of thus obtained copolymer (0.1 g) in 100 mL of benzene was added 40 mL of an ethereal solution of diazomethane. The reaction mixture was stirred at room temperature for 24 h to result in a clear solution. In order to secure the completion of the reaction another 20 mL of the ethereal diazomethane was added, and the stirring was continued for an additional 24 h. The mixture was then concentrated by evaporation of the solvents to about one-tenth its original volume. The copolymer was precipitated by an excess of ether and purified by reprecipitating from benzene into ether three times. Finally the benzene solution was lyophilized.

Random Copolymers. 2VN and AA were copolymerized in the presence of 0.5 mol % AIBN (on the basis of the total monomers) in *N*,*N*-dimethylformamide (DMF) at 60 °C for 24 h. The copolymerization was carried out in a sealed glass tube that had been outgassed by five freeze–pump–thaw cycles. The copolymers were twice purified by reprecipitation from a methanol solution into a large excess of ether followed by two more precipitations from methanol into *n*-hexane. An aqueous solution of the copolymer containing a small amount of NaOH was dialyzed against pure water for 10 days and then lyophilized.

Esterification of the copolymer was performed in the same manner as mentioned in the preceding subsection.

Characterization of Copolymers. In order to determine the copolymer composition ^{1}H NMR spectra for the copolymers (converted into their methyl ester forms) were measured in $CDCl_3$ at 70 °C by using a JEOL FX 90 spectrometer. The copolymer composition was calculated from the integrals of the total aromatic and aliphatic proton regions. The copolymer composition was also calculated from the C/H ratio for the methyl ester derivatives of the copolymers. For the copolymers of 2VN and dimethyl maleate the compositions were also determined from the relative peak intensities of the 1165-cm^{-1} (ester) and 750-cm^{-1} (naphthalene) bands in the IR spectra. The calibration curve, D_{1165}/D_{750} vs. the molar ratios of the ester/naphthalene groups, was obtained by using the esterified random copolymers of 2VN and acrylic acid (Table I). The values obtained by these methods are all in fairly good agreement as shown in Table I.

For an estimation of molecular weight GPC measurements were carried out for a THF solution of the methyl ester derivatives of the copolymers with a Toyo Soda HLC-801A system. Monodisperse polystyrene samples were used as standards to calculate molecular weights of the copolymers in the corresponding methyl ester form (Table I).

Fluorescence Spectroscopy. The steady-state fluorescence spectra were recorded at room temperature on a Shimazu RF-502A spectrofluorimeter or on a SPEX fluorimeter combined with the SPEX Datamate DM1A data aquisition system. Sample solutions were deaerated by bubbling with nitrogen for 30 min. Aqueous solutions with various pH had been allowed to stand overnight, and the pH was readjusted immediately before the fluorescence measurements. For the measurement of the fluorescence quantum yield (ϕ_F) for the copolymers the spectral response function was corrected by comparing with the spectra of quinine sulfate at each wavelength. 2-Methylnaphthalene in cyclohexane ($\phi_F = 0.27$)[18] was used as a standard by comparing the area under the fluorescence peak with that of a copolymer sample. Corrections for the inner filter absorption and for the change in refractive index were also made.[19]

Fluorescence decays were measured by using a correlated single-photon-counting system based on ORTEC electronic components, a PRA 510B air-filled (operated at ca. 350 Torr) flash lamp (full width at half-maximum (fwhm) is ca. 2.5 ns), and a RCA 8850 photomultiplier. Fluorescence decay curves were analyzed by reconvoluting a multiexponential decay function with the system response function and varying the parameters of the multiexponential fitting function until the best least-squares agreement with experiments was obtained.[4] Time-dependent fluorescences were also measured by using the picosecond laser system available at the Center for Fast Kinetic Research at The University of Texas at Austin, which includes a Nd:YAG laser

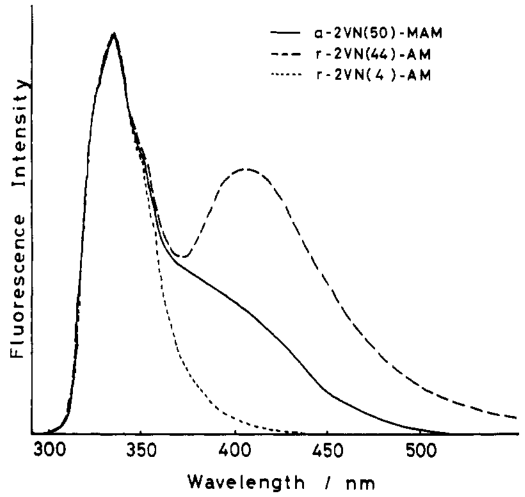

Figure 1. Steady-state fluorescence spectra of the ester type alternating and random copolymers measured in deaerated DMF solutions. The spectra were normalized at the emission maximum of the naphthalene monomer fluorescence: excitation, 290 nm.

with a 200-ps fwhm operated at the fourth harmonic (266 nm) combined with a Tektronix R7912 transient digitizer.

Results

Characterization of Alternating Copolymer. It is well-known that MAn copolymerizes with a variety of monomers to give alternating copolymers.[20] The compositions of the copolymers of 2VN and dimethyl maleate (MAM) derived from the parent copolymers of 2VN and MAn are summarized in Table I. The composition data obtained from NMR, C/H ratios, and IR are in good agreement. The copolymer compositions are practically equimolar over a wide range of the 2VN mole fraction in monomer feed, and hence the copolymerization has a tendency of alternating propagation. However, the copolymers deviate slightly from the equimolar composition if either monomer is in excess in the feed, indicating a small deviation of the reactivity ratios from zero. It seems reasonable, however, to consider that the copolymer obtained from the 1:1 monomer feed ratio is practically the same as the 1:1 alternating copolymer.

Steady-State Fluorescence. The fluorescence spectrum of the alternating copolymer of 2VN and dimethyl maleate (a-2VN(50)–MAM) derived from the equimolar feed of 2VN and MAn was compared with the spectra of random copolymers of 2VN and methyl acrylate in a dilute DMF solution (Figure 1). As expected the random copolymer with a 44 mol % 2VN loading (r-2VN(44)–AM) displayed both the normal fluorescence from monomeric naphthalene and excimer fluorescence. The random copolymer with a low napthhalene loading (4 mol %) (r-2VN(4)–AM) showed only monomer fluorescence. Excimer formation of pendant chromophores in a polymer is known to occur by interaction between the nearest or non-nearest neighbors in a dilute polymer solution.[21] Therefore, the observations in Figure 1 are reasonable given that some fractions of the naphthalene chromophores exist in these neighboring situations in r-2VN(44)–AM, while all the chromophores are essentially isolated in polymer sequences in r-2VN(4)–AM. The alternating copolymer, a-2VN(50)–MAM, exhibited both the monomer and excimer fluorescence in the DMF solution with the latter less noticeable than in the r-2VN(44)–AM case. It may be interesting to note here that, by contrast, the alternating copolymer of 2VN with methyl methacrylate shows essentially no excimer fluoresence in organic solvents.[22,28] No excimer emission was observed in alternating copolymers of vinylcarbazole with diethyl fumarate and fumaronitrile,[24] while excimer fluorescence was reported in alternating copolymers of maleic anhydride with stilbene and acenaphthylene.[25] These differences in fluorescence behavior suggest that the steric nature of the comonomer unit in alternating copolymers plays an important role in excimer formation.

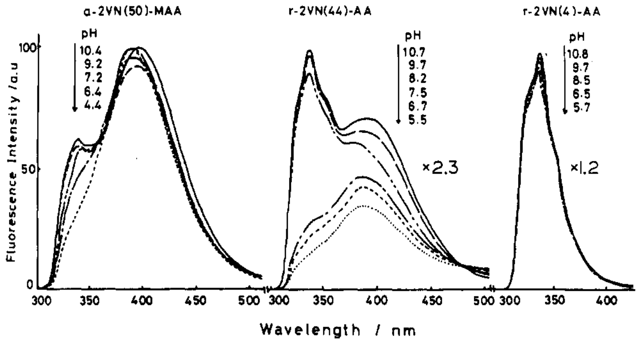

Figure 2. Steady-state fluorescence spectra of the aqueous solutions of the acid type alternating and random copolymers at various pHs: [naphthalene residue] = 0.3 mM; excitation, 290 nm.

The most striking observation in the present study was that the alternating copolymer of 2VN and MAA, a-2VN(50)–MAA, exhibited very prominent excimer fluorescence in aqueous solution with little or no monomer fluorescence. This is in sharp contrast to the fluorescence behavior of the methyl ester of this alternating copolymer in DMF solutions. Figure 2 compares the fluorescence spectra of a-2VN(50)–MAA in aqueous solutions at various pH with those of random copolymers of 2VN and acrylic acid (AA), r-2VN(4)–AA or r-2VN(44)–AA. A remarkable feature of the fluorescence of a-2VN(50)–MAA is that the excimer emission is very strong, and its intensity tends to remain unchanged over a wide range of pH while the monomer fluorescence, only noticeable as a small peak at higher pH, tends to decrease with decreasing pH and almost completely disappears at pH 4.4. In contrast, the fluorescence spectra of the random copolymer with 44 mol % naphthalene loading showed a considerable dependence on pH. Namely, r-2VN(44)–AA exhibited both monomer and excimer fluorescence at basic pH with the monomer fluorescence more prominent, and the total fluorescence intensity decreased markedly on lowering the pH from 10.7 to 5.5. It is noteworthy that a critical decrease of the monomer fluorescence intensity occurred in the narrow pH range of 8.2–7.5, suggesting a conformational transition. In an acidic medium r-2VN(44)–AA showed almost exclusively excimer emission. However, the intensity of this excimer emission was much lower than that of the alternating copolymer.

In Table II are listed the total fluorescence quantum yields calculated from the area under the steady-state fluorescence spectra. The quantum yield of the monomer fluorescence from the naphthalene moieties in the random copolymer with a low chromophore loading, r-2VN(4)–AA, is 0.12 at both pH 9 and 6, i.e., the pH has little or no effect on the intensity and the band shape of the monomer fluorescence that is the sole component for the emission of r-2VN(4)–AA. It is important to note that the total fluorescence quantum yields for a-2VN(50)–MAA are very high and little dependent on pH compared with those of r-2VN(44)–AA. The total quantum yield for the random copolymer is significantly lower than that of r-2VN(4)–AA at pH 6. These facts indicate that a considerable self-quenching process is occurring in r-2VN(44)–AA at lower pH in contrast to the alternating copolymer that efficiently

Table II
Fluorescence Quantum Yields and Decay Times for the Alternating and Random Copolymers in Aqueous Solutions

sample	pH	λ_{max},[a] nm	ϕ_F,[b]	fitting parameter[c] τ_i (ns)/a_i	$\bar{\tau}$,[d] ns
a-2VN(50)-MAA	9	277	0.28	5.6/0.751[e] 63.5/0.249[e]	51.3
a-2VN(50)-MAA	6	279	0.26	4.4/0.833[e] 65.9/0.167[e]	50.5
r-2VN(44)-AA	9	276	0.099	7.7/0.609[e] 57.0/0.391[e]	48.6
r-2VN(44)-AA	6	278	0.056	4.3/0.898[e] 55.6/0.102[e]	34.8
r-2VN(4)-AA	9	274	0.12	32.7/1.0[f]	
r-2VN(4)-AA	6	275	0.12	34.1/1.0[f]	

[a] Absorption maximum due to the ^1A–^1L_a transition of the naphthalene chromophore. [b] Total fluorescence quantum yield. [c] See eq 1 in the text for fitting function. [d] Average lifetime defined by eq 2. [e] For excimer emission. [f] The monomer fluorescence decay was approximately fit to the single-exponential function.

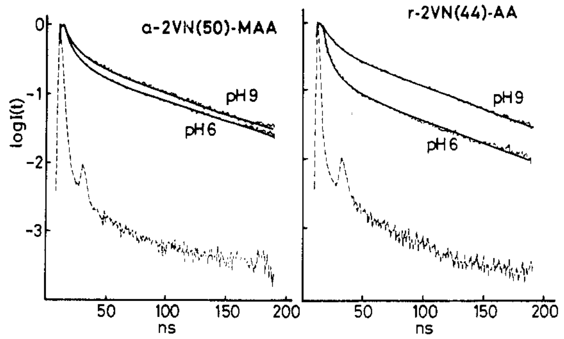

Figure 3. Excimer fluorescence decay curves for the alternating and random copolymers at pH 6 and 9: (solid line) best double-exponential fitting of the decay function; (dashed line) response function.

emits excimer fluorescence. Figure 3 compares the excimer fluorescence decay curves of the alternating and random copolymers. The excimer decay profiles for both a-2VN(50)-MAA and r-2VN(44)-AA are not single exponential. This is not surprising because the configurational constraints are likely to result in excimers with varying stability and hence varying lifetimes. Furthermore, the different macromolecular environments of the excimers may lead to photophysical complexity that is reflected in the lifetime. The excimer fluorescence decays displayed in Figure 3 were fitted to a double-exponential function described by

$$I(t) = \sum a_i \exp(-t/\tau_i) \tag{1}$$

The values of the preexponential factor a_i and the lifetime τ_i are listed in Table II together with the average lifetime defined by

$$\bar{\tau} = \sum a_i \tau_i^2 / \sum a_i \tau_i \tag{2}$$

There is a tendency that at lower pH the short-lived component increases and decays faster. The most notable difference between the alternating and random copolymers is that the latter shows much more decrease in the lifetime at a lower pH, suggesting a considerable self-quenching in the random copolymer in an acidic medium.

A significant difference in the fluorescence behavior between a-2VN(50)-MAA and r-2VN(44)-AA was also observed in the concentration dependency. Figure 4 compares fluorescence spectra (normalized at the monomer emission maximum) of the alternating and random copolymers at various concentrations at pH 10. In the case of r-2VN(44)-AA the concentration markedly affected the monomer-to-excimer fluorescence ratio, i.e., the intensity of excimer emission increased relative to the monomer fluorescence intensity with an increase in concentration of the polymer. At a concentration of 3 mM naphthalene residue excimer emission predominated over the monomer fluorescence. It should be noted here that the total

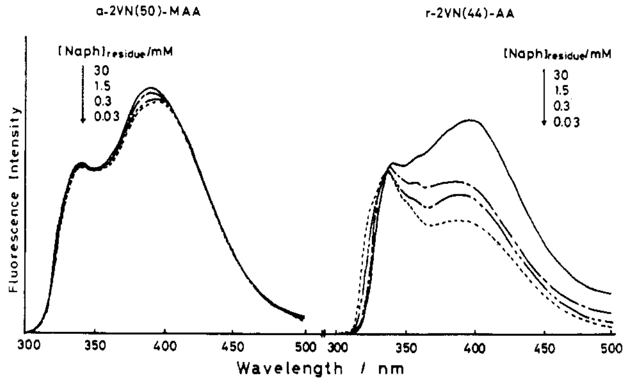

Figure 4. Comparison of the normalized fluorescence spectra of the alternating and random copolymers in aqueous solution (pH 10) at various concentrations: excitation, 290 nm.

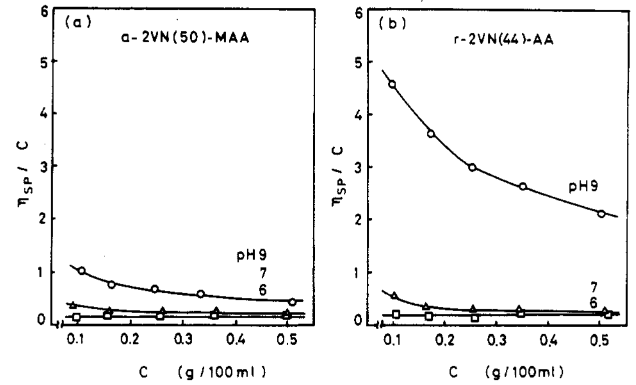

Figure 5. Reduced viscosity vs. concentration plots of the aqueous solutions of the alternating and random copolymers at various pH.

fluorescence quantum yield decreased with the increase of the excimer emission at higher concentrations. These observations are indicative of the intermolecular association of the random copolymer playing some role in excimer formation. By contrast, the alternating copolymer exhibited fluorescence spectra virtually independent of the concentration, which strongly suggests that excimer formation is an intramolecular process in a-2VN(50)-MAA.

Solution Properties. For an understanding of the striking contrast in fluorescence behavior of a-2VN(50)-MAA and r-2VN(44)-AA, the viscosity behavior of these copolymers in aqueous solutions was compared.

It is well established that reduced viscosities of fully ionized polyelectrolytes show a sharp increase on dilution, plots of the reduced viscosity against the concentration of the polymer being strongly negatively sloped.[26] This is actually the case for r-2VN(44)-AA at pH 9, where the polymer retains an extended chain conformation (Figure 5b). In this random copolymer two competitive effects are exerted on the conformational equilibrium, i.e., an

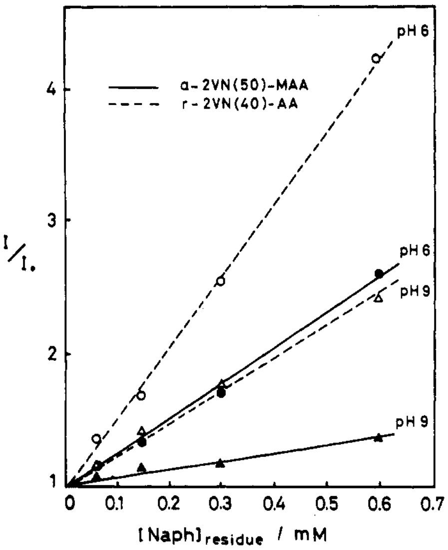

Figure 6. Enhancement of the fluorescence intensity of ANS in aqueous solution as a function of the concentration of the naphthalene residues of the alternating and random copolymers.

attractive hydrophobic interaction among the naphthalene groups and a repulsive Coulombic effect among the charged segments. At pH 7 or lower, however, the reduced viscosities of the random copolymer drastically dropped with a marked decrease in the negative slope of the viscosity plot as displayed in Figure 5b. As the pH is lowered from 9 to 7, the degree of ionization of the carboxyl groups decreases. This would strongly favor hydrophobic interactions among the naphthalene residues, which can prevail over Coulombic repulsions among the partially protonated carboxylate segments.[3] Thus, the random copolymer would form a microheterogeneous structure with hydrophobic aggregates of naphthalene moieties at pH 7 or lower. From these facts it is clear that r-2VN(44)–AA undergoes a sharp conformational transition at a pH between 9 and 7. This is reflected in the sharp decrease of the monomer fluorescence intensity observed in the pH range 8.2–7.5 (Figure 2b).

In striking contrast, the alternating copolymer shows no such viscosity behavior that is typical of an extended conformation of fully ionized polyelectrolytes at basic pH and hence no indication of the conformational transition upon pH change. The molecular weights and molecular weight distributions of the alternating and random copolymers are similar, as is evident from the GPC data of their methyl ester derivatives (Table I). This rules out the possibility that the difference in the reduced-viscosity plots of the alternating and random copolymers may be attributed to the difference in molecular weight.

In an attempt to answer a question as to why the alternating copolymer retains a compact structure at basic pH, we examined the hydrophobic association of sodium 8-anilino-7-naphthalenesulfonate (ANS), a hydrophobic fluorescence probe, with the copolymers. Figure 6 compares the enhancements of the fluorescence intensity of ANS in the presence of a-2VN(50)–MAA and r-2VN(44)–AA. The random copolymer strongly enhanced the ANS fluorescence. This is particularly true at pH 6.2. By contrast, the alternating copolymer exhibited a much smaller enhancement of ANS fluorescence; i.e., even at an acidic pH the enhancement is comparable to that resulting from r-2VN(44)–AA at a basic pH where the random copolymer is in the extended conformation. These data can be explained in terms of the presence of naphthalene aggregates in the random copolymer with which ANS tends to be preferentially associated.

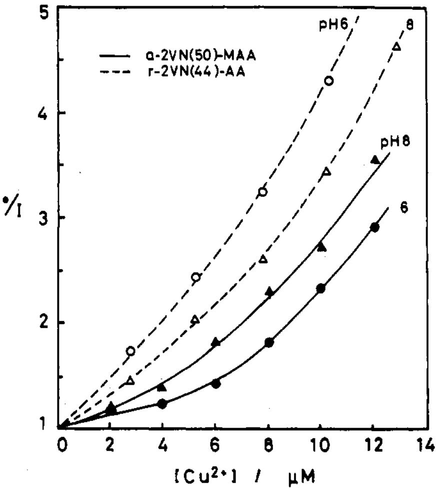

Figure 7. Stern–Volmer fluorescence quenching plot for the excimer of the alternating and random copolymers in the presence of Cu^{2+} ions.

Table III
Parameters for the Excimer Fluorescence Quenching by Copper(II) Ions

sample	pH	K_{SV},[a] M^{-1}	$\bar{\tau}$,[b] ns	k_q,[c] M^{-1} s^{-1}
a-2VN(50)–MAA	8	9.4×10^4	52.5	1.8×10^{12}
a-2VN(50)–MAA	6	6.4×10^4	50.5	1.3×10^{12}
r-2VN(44)–AA	8	1.7×10^5	46.7	3.6×10^{12}
r-2VN(44)–AA	6	2.8×10^5	34.8	8.0×10^{12}

[a] Apparent Stern–Volmer constant determined from the initial slope of the Stern–Volmer type plot of the steady-state fluorescence quenching. [b] Average lifetime determined by single-photon counting techniques. [c] Aparent second-order rate constant for the fluorescence quenching.

Fluorescence Quenching with Copper(II) Ions. Excimer fluorescence quenching by Cu^{2+} ions was investigated at an acidic and a basic pH. The basic condition was limited to pH 8 for fear of the formation of cupric hydroxide gels. In Figure 7 the ratios of the excimer fluorescence intensities in the absence and the presence of copper(II) ions, I_0/I, were plotted as a function of the quencher concentration. The quenching for both a-2VN(50)–MAA and r-2VN(44)–AA showed a high efficiency and a marked curve upward with increasing quencher concentration. Being a cationic species, copper(II) ions are bound to the negatively charged polymers, leading to a close proximity of the chromophores and the quencher, thereby giving rise to an increased rate of quenching. Hence, the steady-state quenching data do not fit simple Stern–Volmer kinetics. However, the use of an apparent Stern–Volmer constant (K_{SV}) estimated from the initial slope of the plots of I_0/I vs. quencher concentration allows a semiquantitative comparison of the quenching efficiency. These values are shown in Table III. From K_{SV} and the average lifetime the apparent second-order rate constant of the quenching (k_q) was calculated. The excimer quenching of r-2VN(44)–AA was more efficient than that of the alternating copolymer.

The addition of copper(II) ions caused a shortening of the average fluorescence decay time. An example of the fluorescence decay curve of the alternating copolymer in the presence of a 12.9 μM cupric sulfate at pH 6 was compared with the decay curve in the absence of the quencher (Figure 8). The decay curve in the presence of quencher ions could be satisfactorily fitted by a three-exponential function, which includes a very short lifetime component (τ_i = 0.3 ns, a_i = 0.714). The ratio of the average lifetime in the absence and presence of quencher

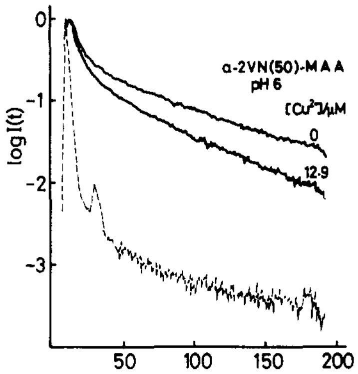

Figure 8. Fluorescence decay traces for the aqueous solution of the alternating copolymer at pH 6 in the presence of Cu^{2+} ions. The decay curve was best fitted to the three-exponential function with the decay parameters (τ_i/a_i) 0.3/0.774, 7.7/0.169, and 51.3/0.057. The decay curve in the absence of the quencer is also presented for comparison.

was $\bar{\tau}_0/\bar{\tau} = 1.39$, much smaller than the I_0/I ratio in the steady-state quenching. These facts indicate that the quenching is static in nature.

Discussion

The absorption bands due to the naphthalene $^1A-^1L_a$ transition for both a-2VN(50)-MAA and r-2VN(44)-AA showed a slight red shift (see Table II) with a slight tailing on the longer wavelength side as compared to the same absorption band of r-2VN(4)-AA. This is presumably the result of the electronic perturbation between nearby naphthalene chromophores. In spite of this sign of the chromophore interaction for both copolymers the alternating copolymer behaved differently from the random copolymer r-2VN(44)-AA in the reduced viscosity and the ANS probe experiments: a-2VN(50)-MAA showed neither conformational transition nor formation of hydrophobic aggregates (see Figure 5a and Figure 6). Even at basic pH the conformation of the alternating copolymer seems to be compact and not extended. Nevertheless, the alternating copolymer exhibited a strong excimer band with a high quantum yield. From these striking features one may speculate that naphthalene moieties in the alternating copolymer tend to interact in a pairwise fashion and the chromophore pairs may exist without further clustering. We assume that the driving force for this pairwise interaction may be hydrophobic because no such chromophore interaction appears to exist in a DMF solution of the alternating copolymer.

The formation of excimers requires that two aromatic rings be parallel to each other at a distance of about 3 Å. From CPK models it seems plausible that the nearest-neighbor naphthalene residues in a-2VN(50)-MAA can easily retain such an orientation if the adjoining chromophores are not perfectly face-to-face, as is often assumed to be required for excimer formation. Since it seems to be impossible for all the naphthalene chromophores to be perfectly oriented for excimer formation along the polymer backbone, one must take into account the contribution of down-chain energy migration to the excimer fluorescence. In case the lifetime of the singlet excited state is long enough compared with the time required for segmental motion (of the order of 2-4 ns[27]), the excimer is also likely to be formed between the chromophores that are initially distant from each other. If a dynamic process is involved, we should observe a rising component in the time-dependent excimer fluorescence. We have carefully checked this point in the fluorescence decay data acquired by a single-photon-counting system as well as by a picosecond laser system. However, we found no indication of the rise process of the excimer emissions for both a-2VN(50)-MAA and r-2VN(44)-AA. Since the excimer interaction between a singlet-excited-state chromophore and a ground-state chromophore in a proper orientation takes place extremely rapidly on excitation of the chromophore, all excimer emissions in the present system are considered to come from preformed excimer sites. Furthermore, we speculate that excitation can migrate until the preformed excimer sites are reached to achieve highly preferential excimer emissions.

Even though the naphthalene groups are situated close enough in a compact conformation, they cannot necessarily retain a proper orientation for excimer owing to configurational constraints exerted by the polymer chains. Therefore, it is reasonable to consider that singlet-ground-state interactions in orientations not suitable to form excimer are the dominant route of the self-quenching. These self-quenching sites would compete with the preformed excimer sites for the migrating excited states, and the outcome of the competition would determine the total fluorescence quantum yield.

The geometrical requirements for the Förster type energy migration are much less restrictive than those for the excimer formation. Given that the Förster distance for naphthalene is 7 Å,[28] the down-chain energy migration seems to be possible in a-2VN(50)-MAA, although the 2VN units are separated by a pair of adjacent carboxyl groups along the polymer main chain. Therefore, in the alternating copolymer the chain conformation may be such that the naphthalene moieties would either interact to result in excimer-forming sites or stay at a distance at which only energy migration can occur. The fraction of self-quenching sites in the alternating copolymer may be very small. On the contrary, in the hydrophobic aggregates of r-2VN(44)-AA the naphthalene groups are so closely packed to one another that a large fraction of the chromophores may exist in orientations that are not suitable to form excimer but act as self-quenching sites.

The excimer emission was highly efficiently quenched by copper(II) ions. For a-2VN(50)-MAA the k_q value at pH 8 was slightly larger than that at pH 6, presumably reflecting the degree of ionization of the carboxyl groups. In contrast, for r-2VN(44)-AA the value of k_q at a weakly basic pH was smaller than that at a weakly acidic pH. This is explicable in terms of the effective concentration of the quencher ions in the macromolecular environments. At pH 6 the random copolymer assumes a compact conformation, although a significant fraction of the carboxyl groups are still ionized and the quencher cations are effectively bound. Therefore, the effective concentration of the bound copper(II) ions can be higher than it is at pH 8 where the free volume of the polymer is much larger. A comparison of the quenching efficiency of alternating and random copolymers reveals that quenching of the excimer emission of the alternating copolymer is less effective. The interpretation of this interesting phenomenon remains for our future study.

Conclusions

The fluorescence spectra of the water-soluble 1:1 alternating copolymer of 2-vinylnaphthalene and maleic acid were dominated by a strong excimer emission in both acidic and basic aqueous solutions with the total quantum yields of 0.26 and 0.28 at pH 6 and 9, respectively. The viscosity behavior implied that the pH has little or no effect on the chain conformation; the alternating copolymer retains a compact conformation even at basic pH where the carboxyl groups are fully ionized. These observations were markedly different from those for a random copolymer of 2-vinylnaphthalene and acrylic acid (44 mol % naphthalene loading). The random copolymer exhibited a drastic conformational transition from an extended to a compact form on decreasing pH from 9 to 7. This was clearly reflected in the fluorescence behavior; i.e., the former conformation resulted in a mixture of monomer and excimer emissions, while the latter resulted primarily in excimer emission with considerable self-quenching ($\phi_F = 0.056$ at pH 6).

These differences between the alternating and random copolymers were explained by speculating on (1) the difference in the type of interaction between the naphthalene chromophores, an extensive aggregation of the naphthalene chromophores with a random orientation for the random copolymer and a pairwise aggregation for the alternating copolymer, and (2) a situation where preformed excimer sites are competing with self-quenching sites for migrating excitation. The pairwise interaction in the alternating copolymer seems to be geometrically favorable for the excimer interaction. Furthermore, the rest of the naphthalene moieties that failed to interact with each other in the alternating sequences may not be close enough to form either excimer or self-quenching sites but may be close enough for Förster energy migration.

Acknowledgment. This work was pursued in part as a Japan–U.S. Cooperative Research Project "Cooperative Photoconversion and Photosynthesis Research". A part of this study was also supported by Grant-in-Aid for Scientific Research No. 59430019 from the Ministry of Education, Science, and Culture, Japan. We acknowledge the use of the facilities of the Center for Fast Kinetics Research, The University of Texas at Austin, and helpful discussions with Dr. M. A. J. Rodgers. Y.M. also thanks Drs. Edward Gaffney and Donald Nealon for discussions and help with the fluorescence lifetime measurements.

Registry No. Cu, 7440-50-8; (2VN)(AA(methylester)) (copolymer), 106821-91-4.

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