Effect of Monomer Sequence Distribution in 2-Vinylnaphthalene–Maleic Acid Copolymers on Energy Migration and Excimer Formation in Aqueous Solution

Yotaro Morishima,* Hak Sang Lim, and Shun-ichi Nozakura

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

John L. Sturtevant

Department of Chemistry and Center for Polymer Research, The University of Texas at Austin, Austin, Texas 78712. *Received June 6, 1988*

ABSTRACT: The copolymers of 2-vinylnaphthalene (2VN) and maleic anhydride (MAn) were demonstrated not to be "ideally" alternating copolymers and to include a small but significant fraction of both the 2VN–2VN and MAn–MAn diad sequences depending on the monomer feed ratio. The 2VN–dimethyl maleate (DMM) copolymers derived from the 2VN–MAn copolymers showed a weak excimer fluorescence in organic solution at room temperature. The excimer-to-monomer fluorescence intensity ratios are linearly related to the 2VN–2VN diad fraction. By comparison, a small difference in the 2VN–2VN diad fraction was strongly reflected in the fluorescence spectra of the corresponding 2VN–maleic acid (MAA) copolymers in aqueous solution; i.e., the excimer emissions are dominant over the monomer fluorescence for the copolymers prepared with an excess of 2VN in monomer feed. The steady-state and time-dependent fluorescence data combined with the characterization data on the monomer sequence distribution led to the conclusion that the excimer forming sites are mostly attributable to the 2VN–2VN diad sequences in the copolymers. The 2VN–MAA alternating sequences can also provide different types of excimers from which the blue-shifted fluorescence is emitted. Since the number of excimer-forming sites relative to the total number of the photon-absorbing naphthalene residues in a copolymer is extremely small, efficient energy migration through the 2VN–MAA alternating sequences is playing an important role in aqueous solution in concentrating the excitation energy at the excimer traps. The fluorescence spectroscopy was demonstrated to provide an extremely sensitive tool to detect "structural defects" in alternating copolymers.

Introduction

An increasing number of investigations have recently focused on the photophysics and photochemistry of amphiphilic polyelectrolytes covalently loaded with polycyclic aromatic chromophores.[1-6] This type of functionalized amphiphilic polyelectrolyte is particularly interesting in part becasue the photophysical behavior of the chromophores would provide useful information on the chain conformation, microphase structure, and chain dynamics of the polyelectrolytes and also because the photochemical reactivities of the attached functional groups can largely be modified as a result of macromolecular environmental effects. The chromophores are often viewed as a reporter in the former case and as a photochemical reaction center in the latter case.

Earlier work on amphiphilic polyelectrolytes has shown that the photophysical and photochemical behavior of the hydrophobic chromophores in aqueous solution is strongly dependent on the microenvironments created by the polymer chain where the chromophores exist.[1-6] The nature of these microenvironments is largely related to the conformational structures of the polymers in aqueous solution. We have been investigating how the polymer chain structure, particularly the monomer sequence distribution of hydrophobic and charged segments, such as block, random, and alternating sequences, affects the microenvironmental features with respect to the photophysical nature of the chromophores therein. Investigations reported so far have mostly concentrated on random copolymers of various vinyl polycyclic aromatics and electrolyte monomers with varying copolymer compositions. There are a few studies on the amphiphilic block[1c] and alternating[2b,f,7] copolymers.

In the preceding paper in this series, we reported on the comparison of alternating copolymers of 2-vinylnaphthalene (2VN) and maleic acid (MAA) in aqueous solution with a random copolymer of 2VN and acrylic acid (AA) with a comparable mole fraction of 2VN units in the copolymer.[7] The alternating copolymer studied previously had been prepared from the equimolar feed of 2VN and maleic anhydride (MAn). Striking differences in fluorescence and also in viscometric behavior between the 2VN–MAA and 2VN–AA copolymers strongly suggested that the sequence distribution is a critical factor on the microphase structure of the polymer coils in aqueous solution and, in turn, the extent and the mode of the interaction between the hydrophobic chromophores. During the course of the study on the 2VN–MAA copolymers, we have come across the fact that the fluorescence characteristics are strongly dependent on the monomer feed ratio of 2VN and MAn for the copolymerization of the parent 2VN–MAn copolymers.

The present paper focuses on the characterization of the sequence distribution in the 2VN–MAA copolymers prepared from varying monomer feed ratios and on how a small deviation of the sequence distribution from the alternation is reflected on the fluorescence behavior.

Experimental Section

Copolymers. Copolymerizations of 2VN and MAn were performed in the presence of 2,2′-azobis(isobutyronitrile) in benzene at 70 °C, as previously.[7]

Hydrolysis and subsequent esterification of the copolymers was also carried out as reported in our previous paper.[7]

The copolymer compositions were determined from the microanalysis for the methyl-esterified copolymers (the copolymers of 2VN and dimethyl maleate (DMM)).

For an estimation of molecular weight, GPC measurements were carried out for a THF solution of the 2VN–DMM copolymers with a Toyo Soda HLC-801A system. Monodisperse polystyrene samples were used as standards to calculate the molecular weight of the copolymers in the methyl ester form.

^{13}C NMR. ^{13}C NMR spectra were obtained on 10% w/v solutions of the 2VN–DMM copolymers in $CDCl_3$ at 60 °C using

0024-9297/89/2222-1148$01.50/0 © 1989 American Chemical Society

Table I
Composition and Sequence Data for the 2VN-MAn Copolymers

sample	u^a	$F_1{}^b$	F_{11}	F_{22}	$F_{12,21}$	$F_{11}/(F_{11} + F_{22})$	$L_{12,21}$	$\bar{M}_n{}^c$
2VN-MAn-1	0.111	0.44	0.004	0.132	0.864	0.025	8.26	9160
2VN-MAn-2	0.429	0.48	0.014	0.038	0.948	0.269	19.5	12200
2VN-MAn-3	1.00	0.50	0.033	0.016	0.951	0.673	20.3	15700
2VN-MAn-4	2.33	0.54	0.075	0.007	0.918	0.915	12.9	29500

[a] Mole ratio of 2VN/MAn in monomer feed. [b] 2VN mole fraction in the copolymers. [c] Polystyrene equivalent number-average molecular weights determined by GPC for the methyl esters of the copolymers.

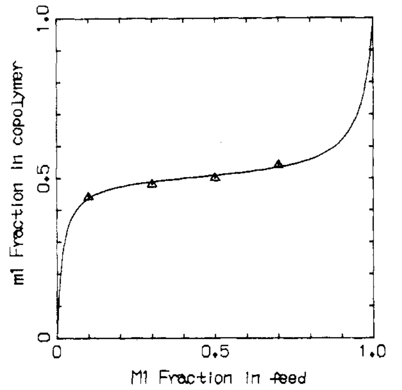

Figure 1. Relationship between the mole fraction of 2VN (M_1) in copolymer and that in monomer feed for the copolymerization of 2VN and MAn in benzene at 70 °C. Plots: experimental data. Solid line: the best fit curve for $r_1 = 0.07 \pm 0.018$ and $r_2 = 0.034 \pm 0.006$.

a JEOL JNM-GSX 400 spectrometer at 100 MHz.

Fluorescence Spectroscopy. The steady-state fluorescence spectra were recorded on a Shimadzu RF-502A spectrofluorimeter. Sample solutions were deaeriated by bubbling with nitrogen for 30 min. Aqueous solutions with various pH's were allowed to stand overnight, and the pH's were readjusted immediately before the fluorescence measurements. The pH's of the aqueous solutions were adjusted with aqueous sodium hydroxide and hydrochloric acid.

Fluorescence decays were measured by using the picosecond laser system available at the Center for Fast Kinetic Research at The University of Texas at Austin, which include a mode-locked Nd:YAG laser operated at the second harmonic to pump a cavity-dumped dye laser, giving an instrument response function of ca. 400-ps width. A 340-nm band-pass and 400-nm cut-off filters were used to collect emission of desired wavelengths. Data were input to a Tracor-Northern TN-7200 multichannel analyzer and later analyzed by conventional reconvolution techniques. The absorbances of all sample solutions were adjusted to ca. 0.4 at excitation wavelength (298 nm). The sample solutions were bubbled with nitrogen for at least 15 min before data collection.

Results

Characterization of the 2VN-DMM Copolymers. The copolymer composition data were presented in Figure 1. The copolymerization showed a tendency for alternation. However, the copolymers deviated slightly from the equimolar composition when either monomer was in excess in the feed. The monomer reactivity ratios were determined by computer fitting using the conventional copolymer composition equation as the fitting function and varying the parameters until the best least-squares agreement with experimental plots was obtained. The initial parameters for the computation were determined by the conventional Fineman-Ross plot. The curve depicted in Figure 1 is the best fit curve. The monomer reactivity ratios that yielded the best fit for 2VN (M_1) and MAn (M_2) were $r_1 = 0.07 \pm 0.018$ and $r_2 = 0.034 \pm 0.006$.

If only propagation steps are considered, the number fraction of the alternate diads, M_1M_2 and M_2M_1, is given by[8]

$$F_{12,21} = 2/(2 + r_1u + r_2/u) \quad (1)$$

where u is the molar ratio of the feed monomers ($u = [M_1]/[M_2]$). Similarly, the consecutive diad fractions for M_1M_1 and M_2M_2 are given respectively by[8]

$$F_{11} = r_1u/(2 + r_1u + r_2/u) \quad (2)$$

$$F_{22} = (r_2/u)/(2 + r_1u + r_2/u) \quad (3)$$

The average length of the alternate sequence can also be related to the monomer reactivity ratios:[8]

$$L_{12,21} = 2(1 + r_1r_2 + r_1u + r_2/u)/(2r_1r_2 + r_1u + r_2/u) \quad (4)$$

In Table I are listed the results of the calculations. Although the equimolar feed yields a copolymer with equimolar composition, 0.033 mole fraction of the 2VN-2VN diad and 0.016 mole fraction of the MAn-MAn diad are included in the resultant sequences. Note that the probability of finding the 2VN-2VN diad at a persisting alternate sequence end is simply given by $F_{11}/(F_{11} + F_{22})$.

For a more accurate analysis of the sequence distribution, the contribution of termination steps may also have to be taken into account. Considering the difference in the polarity between 2VN and MAn, one would assume that cross termination is highly favored. However, Tsuchida and Tomono have pointed out that the contribution of the termination between the propagating MAn radical ends at higher MAn mole fractions in feed cannot be neglected.[9] The former termination results in a 2VN-MAn diad, while the latter leads to a MAn-MAn diad sequence, in case the termination steps are exclusively by recombination. Therefore, there is a possibility that the F_{22} values for 2VN-MAn-1 and 2VN-MAn-2 in Table I are slightly underestimated.

Figure 2 compares the ^{13}C NMR spectra of the 2VN-DMM copolymers prepared from different monomer feed ratios of 2VN and MAn. All the resonance peaks were assigned on the basis of the relative intensities with reference to the assignments for the styrene-MAn alternating copolymers.[10] The intensities of all the spectra in Figure 2 are normalized by the most intensive peak at 127.5 ppm due to naphthalene ring carbons. It is noticeable that the peak intensities at 42.5, 51.5, and 170 ppm, due to methine, methyl, and carbonyl carbons on the DMM units, respectively, decrease as the 2VN/MAn feed ratio increases, indicating that the copolymer composition is slightly dependent on the monomer feed ratio in agreement with the results in Figure 1. The peaks centered at 137 ppm are assigned to C_1 carbon on the naphthalene ring, the carbon that is directly linked to the main chain. It is reasonable to consider that C_1 carbon would reflect a change in the sequence distribution more sensitively than would the other carbons in the naphthalene ring. In fact, the C_1 resonance peaks tend to be multiplet as the 2VN/MAn feed ratio increases, reflecting an increase in the 2VN-2VN diad fraction in the copolymer sequence. The small peaks at 140 and 141.5 ppm are noticeable for the copolymers prepared from higher 2VN/MAn feed ratios. We would attribute these peaks to C_1 carbons in the 2VN-2VN diad

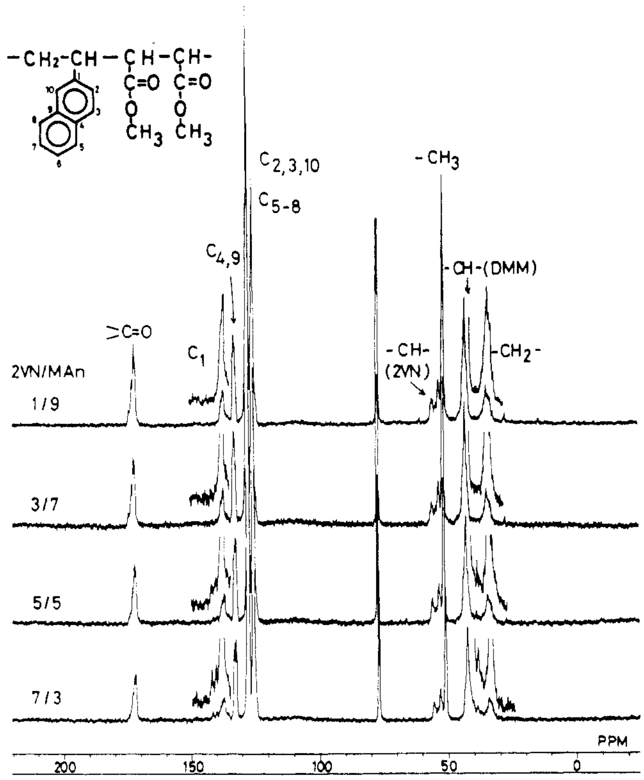

Figure 2. 100-MHz ^{13}C NMR spectra for the 2VN-DMM copolymers in $CDCl_3$ at 60 °C. The 2VN/MAn monomer feed ratios for the preparation of the precursor copolymers are indicated in the figure.

sequence. The multiplicity of the methylene carbon peaks tends to increase with an increase in the 2VN/MAn feed ratio. Peaks at 39 and 40.5 ppm may be ascribed to the methylene carbons in the 2VN–2VN diad sequence. Thus, a careful comparison of ^{13}C NMR spectra confirmed that the 2VN–DMM 1:1 copolymer, prepared from the equimolar feed, though it may practically be viewed as an alternating copolymer, contained a noticeable amount of 2VN–2VN diad sequence as suggested by the analysis of the monomer reactivity ratios. Unfortunately, however, the quantitative estimation of the 2VN–2VN diad fraction by the ^{13}C NMR spectra was not possible because of a considerable overlap of the related signals with other large resonance peaks due to the normal alternating sequences.

Viscosity Behavior of the 2VN–MAA Copolymers in Aqueous Solution. The effects of hydrophobic and electrostatic interactions on macromolecular structure and conformational transition in aqueous solution, if any, are well reflected in viscosity behavior.[1a] The reduced viscosities of the various 2VN–MAA copolymers in aqueous solution at a constant concentration of 0.2 g/dL are presented in Figure 3. All these copolymers exhibited extremely low values of the reduced viscosity at pH 4–6, indicating the highly compact structure in acidic solution. The viscosities showed a sharp increase at a pH between 6 and 7 due to the expansion of the polymer coils. These observations suggest that the naphthalene residues are highly aggregated owing to extensive hydrophobic interaction when the MAA residues are practically neutralized. As the carboxyl residues ionized, the conformational transition occurs from the compact to loose or extended forms, as is commonly known for amphiphilic poly(carboxylic acid).[11]

Consistent with interesting features known for maleic acid copolymers,[12] the viscosities showed a decrease with increasing pH in basic solution. There has been no concrete interpretation for the apparently peculiar behavior of maleic acid copolymers, except a few speculations such as an increase in the rotational freedom of the polymer main chain arising from the lack of hydrogen bonding at the complete dissociation,[12c] a "local salting out" effect at high charge densities,[12d] and a strong interaction between a polyion having a high local charge density and counterions around it.[12e] In most cases, the viscosity shows a maximum value at a 50% dissociation of the total carboxyl groups in the maleic acid copolymers.[12] It is interesting to note that the peak viscosity values at pH 8 for 2VN–MAA-1 (2VN/MAn = 1/9 in feed), 2VN–MAA-2 (2VN/MAn = 3/7), and 2VN–MAA-3 (2VN/MAn = 5/5) are in order of the molecular weight (see Table I), whereas the viscosity values are all similarly small, independent of the molecular weights, when the copolymers are in the compact form at acidic pH's. The peak for 2VN–MAA-4 (prepared from the highest 2VN/MAn feed ratio (7/3) in the present study) shifted toward basic pH by ca. 2 pH units and the peak viscosity value was significantly lower than that for 2VN–MAA-3, although the molecular weight of 2VN–MAA-4 is considerably higher. These facts suggest that a relatively small excess in the 2VN units and thus in the 2VN–2VN diad sequences in the copolymer has a significant effect on the structural expansion and contraction originating from the balance of hydrophobic and electrostatic interactions.

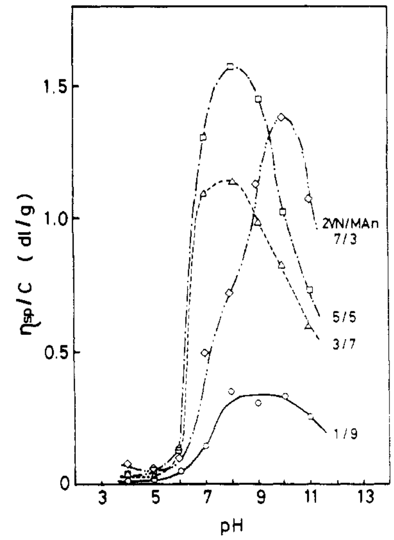

Figure 3. pH dependence of the reduced viscosity of the 2VN–MAA copolymers in aqueous solution: C = 0.2 g/dL at 30 °C. The 2VN/MAn monomer feed ratios for the preparation of the precursor copolymers are indicated in the figure.

We previously compared the solution viscosities of a 2VN–MAA copolymer (prepared from the equimolar feed) at various pH's with those of a random copolymer of 2VN and acrylic acid (AA) with roughly comparable 2VN mole fraction and molecular weight. We have concluded that the degree of chain expansion for the 2VN–MAA copolymer at basic pH's is much smaller than that of the 2VN–AA random copolymer which showed a considerably higher reduced viscosity at pH 9 following a much sharper conformational transition at a pH between 7 and 9.[7] Therefore, one may conclude that at a pH yielding a peak reduced viscosity in Figure 3 the copolymers are not highly expanded but are still in a loose compact form, in which the naphthalene moieties are closely situated so that hydrophobic interactions are still possible to occur to some extent.

Steady-State Fluorescence of the 2VN–DMM Copolymers in Organic Solution. The fluorescence spectra of the 2VN–DMM copolymers prepared from various

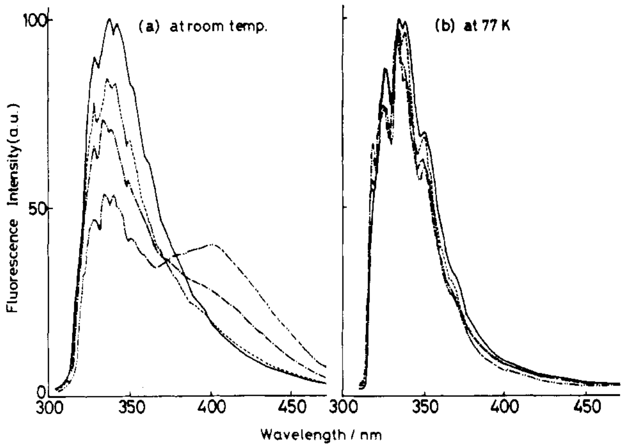

Figure 4. Steady-state fluorescence spectra of the 2VN-DMM copolymers in solution at room temperature (a) and in glass at 77 K (b). Solvent: tetrahydrofuran/diethyl ether (3/2 v/v) mixture (deaeriated). Excitation wavelength: 290 nm. The 2VN/MAn monomer feed ratios for the copolymerization of the precursors: (—) 1/9, (- - -) 3/7, (-·-) 5/5, and (-··-) 7/3.

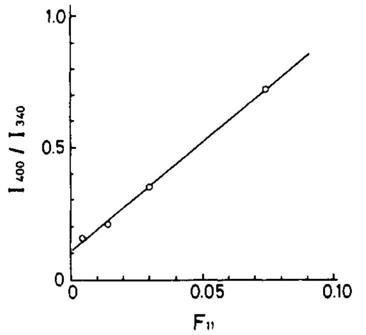

Figure 5. Relationship between the excimer-to-monomer fluorescence intensity ratio and the 2VN-2VN diad fraction in the 2VN-DMM copolymers observed in tetrahydrofuran/diethyl ether (3/2 v/v) at room temperature.

2VN/MAn feed ratios were compared at room temperature and at 77 K in a tetrahydrofuran/diethyl ether (3/2 v/v) mixed solvent (Figure 4). In solution at room temperature, a relatively weak excimer fluorescence was emitted, peaking at ca. 400 nm together with a normal fluorescence from monomeric naphthalene at 340 nm. The intensity of the excimer emission increased systematically with the increase in the 2VN/MAn feed ratio. In a glassy state at 77 K, on the other hand, excimer emissions are virtually absent. These facts are indicative of the excimer formation requiring a dynamic process; i.e., the segments should undergo a conformational change during the liftime of the singlet excited state to bring the two naphthalene rings into the necessary orientation for excimer formation.

The intensity ratios of excimer to monomer fluorescence, I_E/I_M, were plotted as a function of the 2VN-2VN diad fraction, F_{11}, in Figure 5. For the estimation of the I_E/I_M ratios, the contribution of each emission tail overlapping with the other peak was corrected respectively. The linear relationship between I_E/I_M and F_{11} in Figure 5 suggests that the density of excimer forming sites is proportionally related to the 2VN-2VN diad fraction. It should be noted here that the line does not pass through the origin; i.e., there exists a small fluorescence component at 400 nm even in the absence of any 2VN-2VN diad fractions in a polymer chain. The observations indicate that the excimer forming sites are predominantly located in the 2VN-2VN diad sequences where the nearest-neighbor chromophore interaction is possible, but that a slight contribution of excimers formed as a result of non-nearest-neighbor interaction in the normal alternating sequences may not be neglected. The I_{400}/I_{340} ratios are much higher than those simply expected from the direct excitation of the naphthalene moieties in the excimer forming sites in the polymer chain. Therefore, the role of the down chain energy migration should be considered to explain the results in Figures 4 and 5. The linear relationship in Figure 5 suggests that, since one excimer forming site is sufficiently separated from another along a polymer chain, an effective sphere over which an excited state can migrate to reach the excimer trap exists in isolation along the polymer chain without overlapping with another effective sphere. Namely, in organic solutions, where the 2VN-DMM copolymer chains are considered to be loosely coiled, the excited states cannot be delocalized over the entire polymer chain but they can only migrate within a limited range around the excimer trap.

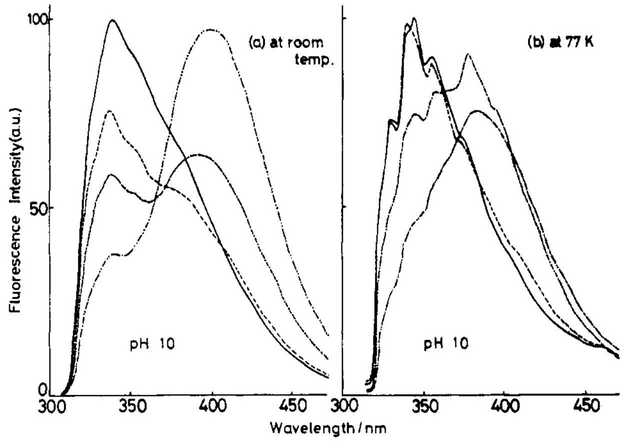

Figure 6. Steady-state fluorescence spectra of the 2VN-MAA copolymers in aqueous solution at room temperature (a) and in ice at 77 K (b) at pH 10. Excitation wavelength: 290 nm. The 2VN/MAn monomer feed ratios for the copolymerization of the precursors: (—) 1/9, (- - -) 3/7, (-·-) 5/5, and (-··-) 7/3.

Steady-State Fluorescence of the 2VN-MAA Copolymers in Aqueous Solution. Figure 6 shows the fluorescence spectra of the maleic acid type copolymers in aqueous solution at pH 10. In contrast to the fluorescence behavior of the methyl ester type copolymers in organic solution, the aqueous solutions of the 2VN-MAA copolymers exhibited a marked tendency for emitting strong excimer fluorescence whose intensities were strongly dependent on the monomer feed ratio; i.e., the higher the 2VN/MAn feed ratio, the more dominant the excimer fluorescence over the monomer fluorescence. The emission peak tends to blue shift as the 2VN/MAn feed ratio decreases. It is noteworthy that the 2VN-MAA copolymers exhibited a considerable excimer emission at 77 K (Figure 6b). Those copolymers prepared from the feed ratios of 2VN/MAn = 5/5 and 7/3 showed particularly strong excimer fluorescence at 77 K peaking at ca. 380 nm, a "blue-shifted" excimer as compared to the room-temperature excimer. These facts suggest that the strong excimer emission is primarily due to "preformed" excimer sites which are populated by efficient energy migration. This is consistent with our previous conclusion.[7]

The tendency for the preferential excimer emission is more prominent in acidic media as shown in Figure 7. This is ascribable to the facts that the naphthalene moieties are more crowded in the copolymer in acidic solution. The excimer emission maximum tends to blue shift with decreasing 2VN/MAn feed ratio at both room temperature and 77 K.

Figure 8 compares the fluorescence spectra for 2VN-MAA-2 (2VN/MAn = 3/7 in feed) observed at various

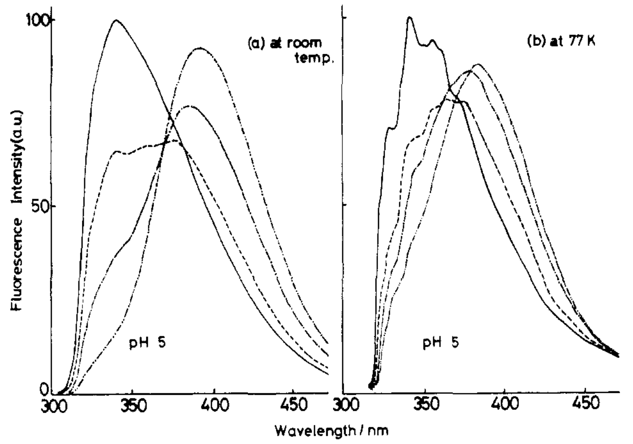

Figure 7. Steady-state fluorescence spectra of the 2VN–MAA copolymers in aqueous solution at room temperature (a) and in ice at 77 K (b) at pH 5. Excitation wavelength: 290 nm. The 2VN/MAn monomer feed ratios for the copolymerization of the precursors: (—) 1/9, (---) 3/7, (-·-) 5/5, and (-··-) 7/3.

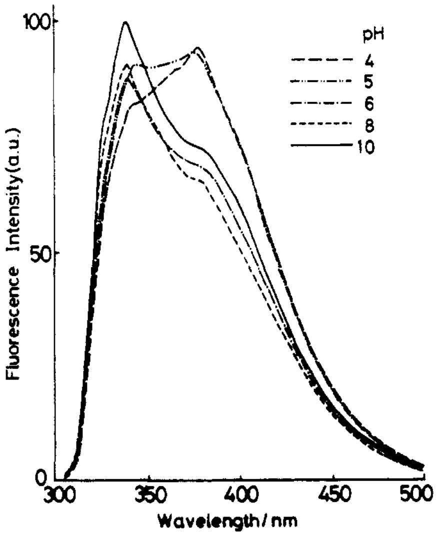

Figure 8. Steady-state fluorescence spectra of 2VN–MAA-2 (2VN/MAn = 3/7 in feed) in aqueous solution at various pH's. Excitation wavelength: 290 nm.

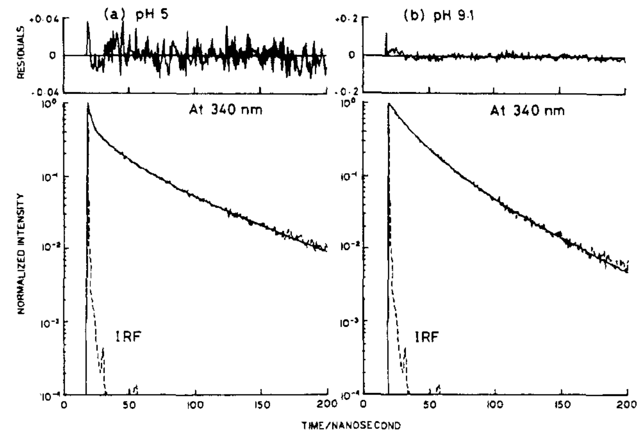

Figure 9. Fluorescence decay for 2VN–MAA-2 (2VN/MAn = 3/7 in feed) monitored at 340 nm at pH 5 (a) and pH 9.1 (b) at room temperature. Excitation wavelength: 298 nm. IRF: instrument response function.

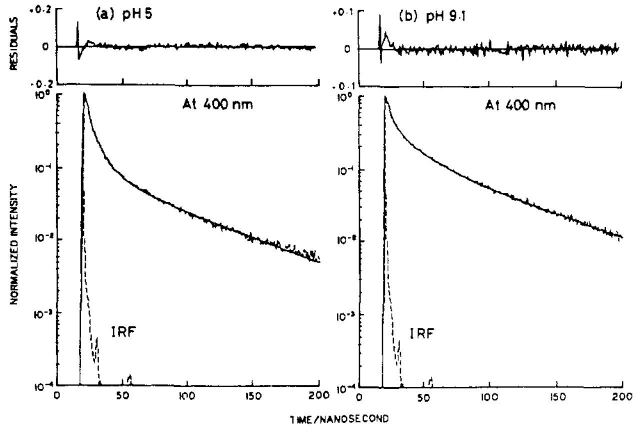

Figure 10. Excimer fluorescence decay for 2VN–MAA-2 (2VN/MAn = 3/7 in feed) monitored at 400 nm at pH 5 (a) and pH 9.1 (b) at room temperature. Excitation wavelength: 298 nm. IRF: instrument response function.

pH's. At pH 4, excimer emission at ca. 380 nm was dominant over the monomer fluorescence. The relative intensity of excimer to monomer fluorescence remarkably decreased between pH 5 and 6. However, the fluorescence spectra showed little change over the pH range 6–11, normal fluorescence from monomeric chromophores being dominant.

Excitation spectra monitored at 340 and 395 nm for 2VN–MAA-2 were found to be practically identical (data not shown), leading to the following conclusions. The light absorbing sites are the same for the monomer, and excimer fluorescence and the excimer emissions predominantly occur via energy migration from these chromophores to the preformed excimer sites which exist in a very small number within the polymer chain. If there is a significant contribution of the direct excitation of the preformed dimer sites to the observed excimer emission, then the electronic perturbation due to the ground-state pairwise interactions of the naphthalene moieties may be reflected in the excitation spectra monitored at 395 nm.

Time-Dependent Fluorescence of the 2VN–MAA Copolymers in Aqueous Solution. Figures 9 and 10 compare the fluorescence decay profiles for 2VN–MAA-2 at pH's 5 and 9 at which the steady-state fluorescence spectra exhibited a considerable difference, as shown in Figure 8. The fluorescence decays were monitored at 340 nm (Figure 9) and at 400 nm (Figure 10). There is a significant overlap of the excimer emission at 340 nm especially at acidic pH's, whereas the contribution of the monomer fluorescence at 400 nm is very small (see Figure 8).

All the decay curves observed were nonexponential and analyzed with a sum of three exponential function of the following form:

$$I(t) = \sum a_i \exp(-t/\tau_i) \tag{5}$$

The values of the relative weight of the preexponential factors a_i and the lifetimes τ_i are listed in Table II. Although the multiexponential function in eq 5 is a convenient mathematical form for fitting the experimental data, the physical interpretation of the individual lifetimes is not necessarily possible. The decay data measured at 340 nm showed that at pH 5 there was a significant shortening of the lifetime for the fastest decay component of the naphthalene monomer fluorescence. Since the copolymer is practically neutralized at pH 5 and assumes a compact form which is crowded with the naphthalene moieties, energy migration and subsequent energy transfer to the excimer sites and also to the self-quenching sites are facilitated,[7] and therefore, the short-lived component of the naphthalene monomer emission decays faster. It is noteworthy that the excimer time-dependent fluorescence monitored at 400 nm does not contain a rise component (Figure 10), which is consistent with extremely

Table II
Fluorescence Decay Times for 2VN-MAA Copolymers in Aqueous Solution

sample	2VN/MAn[a]	λ_{em},[b] nm	pH	fitting parameters,[c] τ_i/a_i		
2VN-MAA-1	1/9	400	9.1	1.8/0.645	10.2/0.266	40.8/0.089
2VN-MAA-2	3/7	340	5	2.3/0.551	18.2/0.269	59.1/0.180
2VN-MAA-2	3/7	340	9.1	7.8/0.341	21.1/0.475	47.9/0.184
2VN-MAA-2	3/7	400	5	4.0/0.651	10.9/0.271	63.5/0.078
2VN-MAA-2	3/7	400	9.1	4.8/0.647	26.5/0.244	77.2/0.109
2VN-MAA-3	5/5	400	9.1	2.0/0.662	19.6/0.230	78.6/0.108

[a] Mole ratios in monomer feed for the copolymerization of the parent copolymer. [b] Wavelength at which the fluorescence decays were monitored. [c] See eq 5 in the text for the fitting function.

rapid or static excimer formation. The decay data shown in Figure 10 suggest that there are excimers with a range of stabilities, reflecting configurational constraints imposed on the pair of naphthalene residues and a variety of microenvironments for the excimer sites. A large fraction of the excimer emission decays even faster than does monomer fluorescence, although there is a small fraction of long-lived components in the excimer decays.

Figure 11 compares the excimer decay profiles at pH 9.1 for the 2VN-MAA copolymers prepared from different 2VN/MAn feed ratios. It should be noted that the excimer emission of 2VN-MAA-1 (2VN/MAn = 1/9 in feed) decayed extremely fast and showed no long-lived components as compared with 2VN-MAA-2 and 2VN-MAA-3 which contain ca. 11% of a long-lived (77-79 ns) component in their excimer decays (Table II). These observations will be discussed in some detail in the following section.

Discussion

From the number-average molecular weight and the copolymer composition data, we can roughly estimate the number of constituent monomer units in a polymer chain. For example, a 2VN-MAA-1 chain consists of ca. 27 2VN and ca. 34 MAA units. A calculation using the diad fraction data given in Table I leads to the fact that in this copolymer there exists ca. 52 alternating diads and ca. 0.24 2VN-2VN diad in a chain; 1 2VN-2VN diad is present only every 4 polymer chains. Therefore, in the case of 2VN-MAA-1, the 2VN-2VN diad sequence cannot be a candidate for the preformed excimer sites. Similar calculation revealed that 2VN-MAA-2 and 2VN-MAA-3 have ca. 1.1 and ca. 3.5 2VN-2VN diad sequences in a polymer molecule, respectively. This suggests that the 2VN-2VN diad sequence in these copolymers may provide excimer sites responsible for the long-lived decay component (Figure 11).

The excimer fluorescence spectra of the copolymers are viewed as a superposition of excimer emissions from different conformational sites and thus different stabilities. In fact, the steady-state fluorescence spectra imply that there are more than two different types of excimers: the one giving the emission maximum at 400 nm as is generally observed for naphthalene excimer, and the other at shorter wavelengths. It may be reasonable to consider that the blue-shifted excimer emissions with shorter lifetimes are attributed to excimers with a range of configurational constraints leading to different overlaps between the two naphthalene rings. On the basis of the fact that in aqueous solution the 2VN-MAA copolymers with lower 2VN-2VN diad fractions show relatively weak blue-shifted excimer emissions at both acidic and basic pH's, while the ones with higher 2VN-2VN diad fraction show much stronger excimer emissions at 400 nm at basic pH's, one would speculate that blue-shifted excimers can be formed within the alternating sequences in a small quantity, while the "normal" 400-nm excimers are predominantly formed in the 2VN-2VN diad sequences.

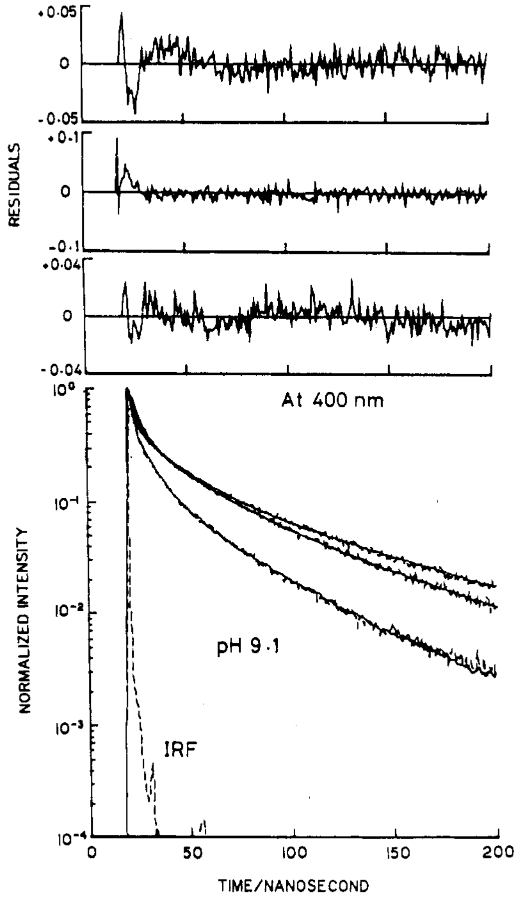

Figure 11. Excimer fluorescence decay for 2VN-MAA-3 (2VN/MAn = 5/5 in feed), 2VN-MAA-2 (2VN/MAn = 3/7), and 2VN-MAA-1 (2VN/MAn = 1/9) (from upper to lower trace) observed at 400 nm at pH 9.1. Excitation wavelength: 298 nm.

Extensive energy migration through the alternating sequences is an important process in highly populating the excimer in aqueous solution. This is in contrast to the fluorescence behavior of the 2VN-DMM copolymers in organic solution. It is noteworthy that even at basic pH's the conformation of the 2VN-MAA copolymers is not highly extended and is crowded with the naphthalene residues in a relatively loose form such that geometrical requirements for the Förster-type energy migration are satisfied in the clusters of the naphthalene moieties.

The present study demonstrated the high sensitivity of the photophysics to small changes in the copolymer composition. These findings suggest that the fluorescence spectroscopy may generally provide an extremely sensitive tool to characterize the sequence distribution in "alternating" copolymers consisting of chromophore monomer units.

Further detailed photophysical studies on the peculiar pH dependence of reduced viscosity in the basic pH region (Figure 3) are now in progress in our laboratory.

Conclusions

The "alternating" copolymers of 2VN and MAn contain a small but significant fraction of the 2VN–2VN and MAn–MAn diad sequences regardless of the monomer feed ratio. The 2VN–2VN diad sequence provides excimer forming sites, and a small difference in this diad fraction is dominantly reflected in the fluorescence spectra of the 2VN–MAA copolymers in aqueous solution. Alternating sequences that result in crowded naphthalene residues in a compact polymer structure in aqueous solution (particularly at acidic pH's) would provide blue-shifted excimers with a range of stabilities. Since the number of the excimer forming sites in a polymer chain are extremely small as compared to the total number of the naphthalene residues, the efficient down chain energy migration through the alternating 2VN–MAA sequences plays an important role in concentrating the excitation energy onto the excimer traps.

Acknowledgment. This work was pursued in part at the Department of Chemistry, The University of Texas at Austin. The authors would like to thank Prof. S. E. Webber for his help and extremely useful suggestions and discussions during the course of this work. We acknowledge the use of the facilities of the Center for Fast Kinetics Research, The University of Texas at Austin. Y. M. also thanks Dr. Y. Itoh of the Webber group at The University of Texas at Austin for useful discussions.

Registry No. (2VN)(MAn) (copolymer), 106821-90-3; (2VN)(DMM) (copolymer), 117652-10-5; 2VN, 827-54-3; MAn, 108-31-6.

References and Notes

(1) (a) Morishima, Y.; Itoh, Y.; Nozakura, S. *Makromol. Chem.* **1981**, *182*, 3135. (b) Itoh, Y.; Morishima, Y.; Nozakura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 467. (c) Morishima, Y.; Itoh, Y.; Hashimoto, T.; Nozakura, S. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2007. (d) Morishima, Y.; Tanaka, T.; Itoh, Y.; Nozakura, S. *Polym. J.* **1982**, *14*, 861. (e) Itoh, Y.; Morishima, Y.; Nozakura, S. *Photochem. Photobiol.* **1984**, *39*, 603. (f) Morishima, Y.; Itoh, Y.; Nozakura, S.; Ohno, T.; Kato, S. *Macromolecules* **1984**, *17*, 2264. (g) Morishima, Y.; Kobayashi, T.; Nozakura, S. *J. Phys. Chem.* **1985**, *89*, 4081. (h) Morishima, Y.; Kitani, T.; Kobayashi, T.; Saeki, Y.; Nozakura, S.; Ohno, T.; Kato, S. *Photochem. Photobiol.* **1985**, *42*, 457. (i) Morishima, Y.; Nozakura, S. *J. Polym. Sci., Polymer Symp.* **1986**, *74*, 1. (j) Morishima, Y.; Kobayashi, T.; Furui, T.; Nozakura, S. *Macromolecules* **1987**, *20*, 1707.

(2) (a) Delaire, J. A.; Rodgers, M. A. J.; Webber, S. E. *J. Phys. Chem.* **1984**, *88*, 6219. (b) Bai, F.; Chang, C. H.; Webber, S. E. *Macromolecules* **1986**, *19*, 588, 2484, 2798. (c) Webber, S. E. *Macromolecules* **1986**, *19*, 1658. (d) Delaire, J. A.; Rodgers, M. A. J.; Webber, S. E. *Eur. Polym. J.* **1986**, *22*, 189. (e) Delaire, J. A.; Sanquer-Barrie, M.; Webber, S. E. *J. Phys. Chem.* **1988**, *92*, 1252. (f) Bai, F.; Webber, S. E. *Macromolecules* **1988**, *21*, 628.

(3) (a) Guillet, J. E.; Rendall, W. A. *Macromolecules* **1986**, *19*, 224. (b) Guillet, J. E.; Takahashi, Y.; McIntosh, A. R.; Bolton, J. R. *Macromolecules* **1985**, *18*, 1788. (c) Guillet, J. E.; Wang, J.; Gu, L. *Macromolecules* **1986**, *19*, 2793.

(4) (a) Chu, D.-Y.; Thomas, J. K. *Macromolecules* **1984**, *17*, 2142. (b) Harrop, R.; Williams, P. A.; Thomas, J. K. *J. Chem. Soc., Chem. Commun.* **1985**, 280.

(5) (a) Turro, N. J.; Arora, K. S. *Polymer* **1986**, *27*, 783. (b) Arora, K. S.; Hwang, K.-C.; Turro, N. J. *Macromolecules* **1986**, *19*, 2806. (c) Arora, K. S.; Turro, N. J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 243. (d) Arora, K. S.; Turro, N. J. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 259.

(6) Herkstroeter, W. G.; Martic, P. A.; Hartman, S. E.; Williams, J. L. R.; Farid, S. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2473.

(7) Morishima, Y.; Kobayashi, T.; Nozakura, S.; Webber, S. E. *Macromolecules* **1987**, *20*, 807.

(8) Tada, K.; Fueno, T.; Furukawa, J. *J. Polym. Sci., A-1* **1966**, *4*, 2981.

(9) Tsuchida, E.; Tomono, T. *Makromol. Chem.* **1971**, *141*, 265.

(10) (a) Johnson, L. F.; Heatly, F.; Bovey, F. A. *Macromolecules* **1970**, *3*, 175. (b) Inoue, Y.; Nishioka, A.; Chujo, R. *Makromol. Chem.* **1972**, *156*, 207. (c) Buchak, B. E.; Ramey, K. C. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 401. (d) Roth, H.; Arnold, M.; Raetzsch, M. *Acta Polym.* **1981**, *32*, 277. (e) Barron, P. F.; Hill, D. J. T.; O'Donnell, J. H.; O'Sullivan, P. W. *Macromolecules* **1984**, *17*, 1967.

(11) (a) Mandel, M.; Leyte, J. C.; Stadhouder, M. G. *J. Phys. Chem.* **1967**, *71*, 603. (b) Joyce, D. E.; Kurucsev, T. *Polymer* **1981**, *22*, 415. (c) Morcellet-Sauvage, J.; Morcellet, M.; Loucheux, C. *Makromol. Chem.* **1981**, *182*, 949.

(12) (a) Dubin, P. L.; Strauss, U. P. *J. Phys. Chem.* **1970**, *74*, 2842. (b) Sakurada, I.; Sakaguchi, Y.; Uehara, H. *Kobunshi Kagaku* **1970**, *27*, 82. (c) Ohno, N.; Nitta, K.; Sugai, S. *Kobunshi Kagaku* **1971**, *28*, 671. (d) Kitano, T.; Kawaguchi, S.; Ito, K.; Minakata, A. *Macromolecules* **1987**, *20*, 1598. (e) Kitano, T.; Kawaguchi, S.; Anazawa, N.; Minakata, A. *Macromolecules* **1987**, *20*, 2498.

Photocross-Linking of EPDM Elastomers. Reactions with Model Compounds Studied by Electron Spin Resonance

J. Hilborn* and B. Rånby

Department of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden.

Received May 8, 1987; Revised Manuscript Received July 12, 1988

ABSTRACT: The initial radical reaction to occur in photocross-linking of EPDM elastomers was studied by ESR on model compounds (ethylidenenorbornane, dihydrodicyclopentadiene, *trans*-2-heptene, and *cis*-2-heptene). After cleavage of 1-hydroxycyclohexyl phenyl ketone to benzoyl and hydroxycyclohexyl radicals, the benzoyl radical abstracts the most labile hydrogens on the model compounds to form allylic radicals. These radicals were trapped using pentamethylnitrosobenzene as a spin-trapping agent. When *trans*-2-heptene was used, the benzoyl radical added to the unsaturation to some extent to form a rather stable radical. This would explain the measured lower reactivity in cross-linking of its EPDM than with the other diene elastomers.

Introduction

By copolymerization of ethylene, propylene, and a diene, elastomeric products (EPDM) can be produced, which unlike polydiene rubbers contain a saturated backbone. This is an advantage with respect to oxidative and photolytic aging which in polydienes leads to cleavage of the main chain. The unsaturation is pendant on the main chain and incorporated by copolymerization with either hexadiene, ethylidenenorbornene, or dicyclopentadiene.

It is possible to cross-link the EPDM rubbers by using ultraviolet light and radical-producing photoinitiators.[1] The advantage of photocross-linking is primarily the saving of energy. In conventional systems with thermal initiation, the energy is applied to both the rubber and the initiator. In photocross-linking, the energy can be transferred selectively to the photoinitiator. A secondary advantage is

0024-9297/89/2222-1154$01.50/0 © 1989 American Chemical Society