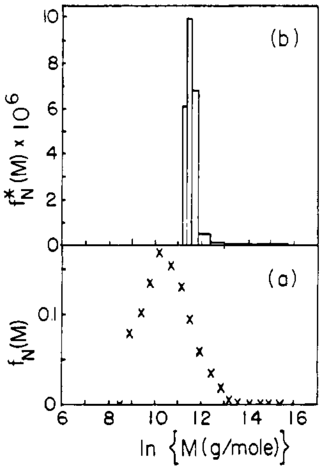

Figure 11. The number-average $f(M)$ for sample A (C = 0.4 wt %) is shown as derived from a histogram fit of light scattering data (θ = 120°) in panel b. The GPC results are given in (a).

offs, we suspect that the simple form of $G(\Gamma)$ may be useful and is adequate for qualitative analysis. For a broader distribution with a sharp cutoff, the histogram technique would be appropriate. However, for the unimodal polyacrylamide distribution in question, which is certainly not uncommon, the more time-consuming Pearson fit yields the best results.

A direct comparison of the GPC-derived $f(M)$ and $f(M)$ obtained from the transformation of $G(\Gamma)$ is made in Figure 11 for sample A. The obvious discrepancy is caused by the fact that the light scattering data are heavily biased by larger particles, which is easily appreciated when we realize that the scattering power increases as the sixth power of the radius of the molecule. On the other hand, the larger molecules tend to pass through the GPC column quickly, without being separated efficiently. The ratio of M_z/M_w indicates that from GPC, M_n:M_w:M_z = 1:2:4, while from the histogram and the Pearson fits, we obtain M_z/M_w = 1.6 and 2.5, respectively. We feel that when the higher molecular weight component is of interest, the light scattering $f(M)$ may be more relevant and useful.

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Photodegradation of 1-Naphthyl Methacrylate–Butyl Methacrylate Copolymers in Benzene Solution. 2. Effect of Intramolecular Excimer Formation

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ABSTRACT: Photostationary-state and transient fluorescence characteristics of copolymers of 1-naphthyl methacrylate (1NMA) with butyl methacrylate (BMA) have been investigated in deaerated benzene solution at room temperature. Dilute solutions of poly(1NMA-*co*-BMA) showed both monomer and excimer fluorescence emissions. The quantum yield for excimer emission (Φ_D) relative to that for monomer emission (Φ_M) increased with increasing 1NMA content. Φ_M was approximately equal to the quantum yield for main-chain scission (Φ_{cs}) whereas Φ_D varied in inverse proportion to Φ_{cs} throughout the entire range of 1NMA content. Time-resolved measurements of fluorescence decays in conjunction with the quantum yields enabled determination of a set of kinetic parameters for the photophysical and photochemical primary processes in poly(1NMA-*co*-BMA) in deaerated benzene solution. It is concluded that main-chain scission of poly(1NMA-*co*-BMA) occurs from the monomer fluorescence state of the side-chain 1-naphthyl chromophore, in competition with monomer emission, but hardly at all from the excimer fluorescence state.

Intramolecular excimer formation is a phenomenon observed commonly for a variety of polymers bearing fluorescent chromophores in the side chain.[1,2] A number of studies were accomplished by means of photostationary-state fluorometry to correlate intramolecular excimer formation with polymer structures,[3-8] properties of polymer solution,[9] micro-Brownian motion of a polymer chain in solution,[10,11] and energy migration along a polymer chain.[12-16] Recent time-resolved fluorometric studies have enabled characterization of the kinetics of intramolecular excimer formation and related photophysical processes in polymer systems.[17-22] Little attention has, however, been paid to the effect of intramolecular excimer formation on the photochemical reactions in a polymer chain.[23]

In the preceding paper in this series,[24] the photodegradation of copolymers of 1-naphthyl methacrylate (1NMA) with butyl methacrylate (BMA) in deaerated benzene solution was demonstrated to be affected markedly by the content of the 1NMA monomer unit. In this work, the photostationary-state and transient fluorescence characteristics of poly(1NMA-*co*-BMA) have been determined as a function of 1NMA content to clarify the relationship

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Table I
Quantum Yields for Monomer Emission (Φ_M), Excimer Emission (Φ_D), and Main-Chain Scission (Φ_{cs}) of Poly(1NMA-*co*-BMA) in Deaerated Benzene Solution at Room Temperature[a]

					triad fraction of 1NMA[c]		
polymer	X_N[b]/mol %	Φ_M	Φ_D	Φ_{cs}	F_3[BNB]	F_3[NNB] = F_3[BNN]	F_3[NNN]
CP1NB-1	3.2	*d*	*d*	0.068	0.98	0.01	0.00
CP1NB-2	7.3	0.065	0.001	0.062	0.96	0.02	0.00
CP1NB-3	12.5	0.060	0.003	0.058	0.92	0.04	0.00
CP1NB-4	14.6	0.059	0.003	0.054	0.88	0.06	0.00
CP1NB-5	16.4	0.054	0.007	*d*	0.84	0.08	0.01
CP1NB-6	28.5	0.042	0.013	0.037	0.66	0.15	0.04
CP1NB-7	36.4	0.034	0.018	*d*	0.55	0.19	0.07
CP1NB-8	56.4	0.021	0.024	0.019	0.19	0.25	0.32
CP1NB-9	84.9	0.016	0.028	0.014	0.03	0.15	0.68
P1NMA	100	0.016	0.028	0.015	0.00	0.00	1.00

[a] On excitation at 285 nm. [b] 1NMA content in poly(1NMA-*co*-BMA). [c] Estimated from the terminal model[27] using monomer reactivity ratios $r_N = 0.54$ and $r_B = 0.76$. [d] Not determined.

between the intramolecular excimer formation and the main-chain carbon–carbon bond scission.

Experimental Section

Materials. 1NMA homopolymer and 1NMA copolymers with BMA prepared in the previous work[24] were used. A model compound for the 1NMA monomer unit in these polymers, 1-naphthyl isobutyrate (1NIB), was prepared as described previously.[24] Spectroscopic grade benzene was used as received.

Photostationary-State Fluorescence Spectra. Solutions of 1NMA-containing polymers in benzene having a UV absorbance of 0.83 at 285 nm were prepared. UV absorption spectra were measured on a Shimadzu UV-200S spectrophotometer. The equivalent concentration of 1-naphthyl chromophore under these conditions was estimated to be 1.2×10^{-4} mol dm^{-3}. The solutions thus prepared were deaerated by the method reported previously.[24] Fluorescence spectra were recorded on a Shimadzu RF-501 fluorescence spectrophotometer. The spectral response was corrected by a standard tungsten lamp. The quantum yields for monomer and excimer fluorescence emissions were determined by reference to a standard solution of quinine sulfate (5×10^{-3} mol dm^{-3}) in 0.5 mol dm^{-3} aqueous sulfuric acid.[22,25]

Time-Resolved Measurement of Fluorescence Decay. Fluorescence response functions were determined by a single-photon time coincidence method with an ORTEC 9200 nanosecond fluorometer and a Hitachi multichannel analyzer.[22,26] Pulsed light with a half-duration of ca. 2.5 ns was generated by a spark discharge in air across tungsten electrodes. The monomer fluorescence decay was observed through a Toshiba UV-D25 glass filter and a chrome alum solution filter (15 wt % in 0.5 mol dm^{-3} aqueous sulfuric acid, 1.5-cm path length). This combined filter had a maximum transmittance of 18.6% at 328 nm and 300–360-nm band-pass. The excimer fluorescence decay was observed through a Fuji SC-42 filter, which cut off wavelengths below 408 nm and has 50% transmittance at 429 nm.

Results and Discussion

Photostationary-State Fluorescence Characteristics of Poly(1NMA-*co*-BMA). A dilute solution of 1NIB (1×10^{-4} mol dm^{-3}) in benzene showed a fluorescence spectrum with vibrational structures at 330, 345, and 348 nm under deaerated conditions at room temperature. This fluorescence band can be assigned to the monomer emission from the 1-naphthyl chromophore. In concentrated benzene solution (1 mol dm^{-3}) the broad structureless emission band centered at 400 nm was simultaneously observed due to intermolecular excimer formation, but its intensity was extremely weak.

The UV spectrum arising from the 1-naphthyl chromophore of poly(1NMA-*co*-BMA) in dilute benzene solution at room temperature did not change with 1NMA content. It follows that intramolecular association between two 1-naphthyl chromophores in their electronic ground states is unlikely under these conditions.

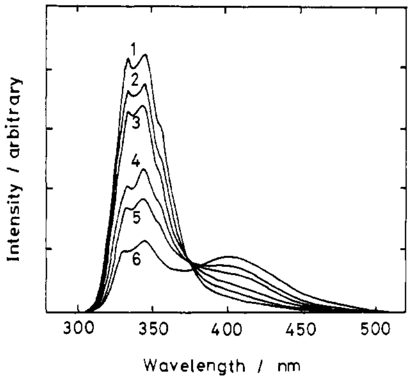

Figure 1. Fluorescence spectra of poly(1NMA-*co*-BMA) in deaerated benzene solution at room temperature on excitation of the 1-naphthyl chromophore (1.2×10^{-4} equiv mol dm^{-3}) at 285 nm: (1) CP1NB-2; (2) CP1NB-3; (3) CP1NB-5; (4) CP1NB-7; (5) CP1NB-8; (6) P1NMA.

On the contrary, the fluorescence spectrum of poly(1NMA-*co*-BMA) in deaerated benzene solution (1.2×10^{-4} equiv mol dm^{-3} 1-naphthyl chromophore) at room temperature is markedly dependent on 1NMA content as shown in Figure 1. Analogous to 1NIB in dilute solution, a low 1NMA content (7.3 mol %) copolymer CP1NB-2, gives essentially only a monomer emission band with vibrational structures at 330, 342, and 352 nm. In the case of 1NMA homopolymer (P1NMA), the characteristic excimer emission band centered at 400 nm is also observed even in dilute solution as has been reported by Guillet et al.[20,23] Furthermore, it is apparent in Figure 1 that the intensity of excimer emission increases whereas that of monomer emission decreases with increasing 1NMA content. These fluorescence characteristics indicate that intramolecular excimer formation occurs between 1-naphthyl chromophores concentrated locally within the domain of a poly(1NMA-*co*-BMA) chain.

Fluorescence Quantum Yields of Poly(1NMA-*co*-BMA). The fluorescence spectra shown in Figure 1 were resolved into their monomer and excimer emission components by spectral simulation. The profile of the monomer emission spectrum was obtained by reference to CP1NB-2. The quantum yields for monomer emission (Φ_M) and for excimer emission (Φ_D) were determined from the resolved spectra using a quinine sulfate standard. Numerical results are listed in Table I together with the quantum yield for main-chain scission (Φ_{cs}) evaluated previously.[24]

Following the so-called $n = 3$ rule, which states that efficient intramolecular excimer formation occurs between

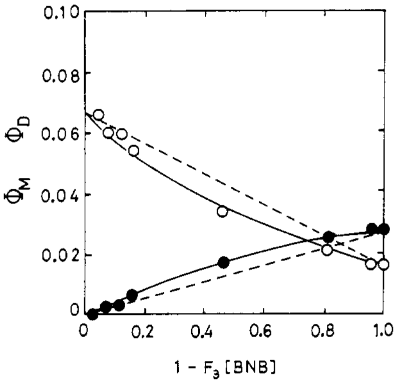

Figure 2. Variations of quantum yields for (○) monomer emission (Φ_M) and (●) excimer emission (Φ_D) of poly(1NMA-*co*-BMA) as a function of the total fraction of successive 1NMA sequences (1 - F_3[BNB]) on 285-nm excitation in deaerated benzene solution at room temperature.

two fluorescent chromophores separated by three carbon atoms along a polymer chain,[3] one expects that the isolated 1-naphthyl chromophore in a monomer sequence such as BMA-1NMA-BMA ([BNB]) should make only a minor contribution to the intramolecular excimer emission from the poly(1NMA-*co*-BMA). In copolymer systems, triad fractions are useful as a measure of the relative content of isolated chromophores in a copolymer chain.[22] The fractions of 1NMA monomer unit located in the center of the triads in a poly(1NMA-*co*-BMA) chain, F_3[BNB], F_3[NNB] (=F_3[BNN]), and F_3[NNN], were therefore estimated from the terminal model[27] using monomer reactivity ratios (Table I). The monomer reactivity ratios $r_N = 0.54$ for 1NMA and $r_B = 0.76$ for BMA were obtained by the Finemann–Ross method.[28] Figure 2 shows plots of Φ_M and Φ_D vs. the total fraction of successive 1NMA sequences, 1 - F_3[BNB] (=F_3[NNB] + F_3[NNN]).

Assuming that the isolated 1-naphthyl chromophore emits only monomer fluorescence and that the clustered 1-naphthyl chromophores can form excimer intramolecularly with an equal probability regardless of the monomer sequence, ϕ_M will increase linearly with F_3[BNB] (i.e., decrease linearly with 1 - F_3[BNB]) and ϕ_D with 1 - F_3[BNB]. This behavior can be represented by

$$\Phi_M = \phi_M{}^0 F_3[\mathrm{BNB}] + \phi_M(1 - F_3[\mathrm{BNB}]) \quad (1)$$

$$\Phi_D = \phi_D(1 - F_3[\mathrm{BNB}]) \quad (2)$$

where $\phi_M{}^0$ is the quantum yield for monomer emission from the isolated 1-naphthyl chromophore and $\phi_M(<\phi_M{}^0)$ and ϕ_D are the quantum yields for monomer and excimer emissions from the clustered 1-naphthyl chromophores, respectively. In Figure 2 slight deviations from the linear relationships given by eq 1 and 2 (broken lines) are observed. It is possible to anticipate that intramolecular singlet–singlet energy migration occurs among the 1-naphthyl chromophores, leading to efficient excimer formation in poly(1NMA-*co*-BMA).[12–16,22a] The intramolecular excimer formation between non-nearest-neighbor 1-naphthyl chromophores[13] may also account for such deviations. It is nevertheless apparent in Figure 2 that the influence of energy migration or non-nearest-neighbor excimer formation is relatively minor under the conditions investigated.

In view of the above results, the following equations may be assumed to describe the fluorescence characteristics of poly(1NMA-*co*-BMA) in benzene solution:

$$\Phi_M = \phi_M{}^0\Theta + \phi_M(1 - \Theta) \quad (3)$$

$$\Phi_D = \phi_D(1 - \Theta) \quad (4)$$

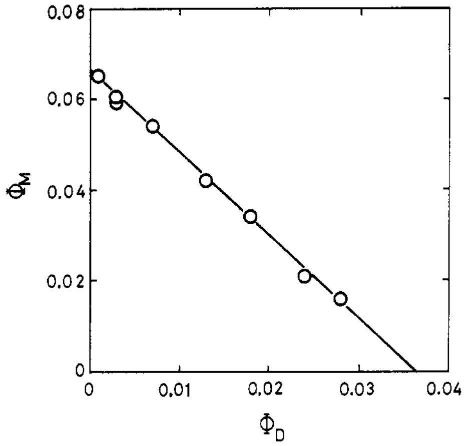

Figure 3. Linear relationship between quantum yields for monomer emission (Φ_M) and for excimer emission (Φ_D) of poly(1NMA-*co*-BMA) on 285-nm excitation in deaerated benzene solution at room temperature.

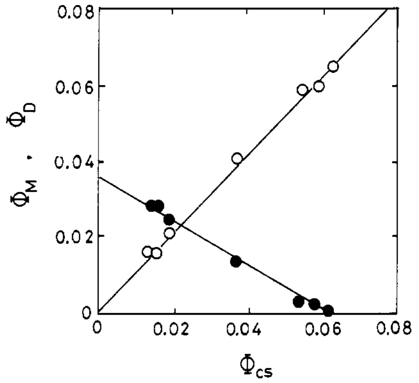

Figure 4. Linear relationships between quantum yields for fluorescence emissions [(○) monomer emission (Φ_M); (●) excimer emission (Φ_D)] and for main-chain scission (Φ_{cs}) of poly(1NMA-*co*-BMA) on 285-nm excitation in deaerated benzene solution at room temperature.

where F_3[BNB] in eq 1 and 2 is replaced by an effective fraction of the non-excimer-forming sites Θ located in a copolymer chain. Eliminating Θ from eq 3 and 4, we obtain the linear relationship between Φ_M and Φ_D as

$$\Phi_M = \phi_M{}^0 - \frac{\phi_M{}^0 - \phi_M}{\phi_D}\Phi_D \quad (5)$$

As plotted in Figure 3, eq 5 is seen to reproduce excellently the experimental data. This plot may verify the validity of the above assumption, i.e., 1-naphthyl chromophores in poly(1NMA-*co*-BMA) are classified into two groups depending on whether they are effective or ineffective for intramolecular excimer formation.

The intercept and the slope of the straight line in Figure 3 give values of $\phi_M{}^0 = 0.067$ and $(\phi_M{}^0 - \phi_M)/\phi_D = 1.9$, respectively.

Relationship between Fluorescence Emissions and Main-Chain Scission in Poly(1NMA-*co*-BMA). As reported in the preceding paper,[24] the main-chain scission of poly(1NMA-*co*-BMA) occurs via the electronically excited state of the 1-naphthyl chromophore. Analogous to the fluorescence emissions, the quantum yield for the main-chain scisson, Φ_{cs}, under 285-nm irradiation was demonstrated to be a function of 1NMA content.[24] Φ_M and Φ_D are plotted against Φ_{cs} in Figure 4 to determine the relationship between the photophysical and photochemical processes in the poly(1NMA-*co*-BMA) in deaerated

Table II
Fluorescence Relaxation Times of Poly(1NMA) in Deaerated Solution at Room Temperature

species	solvent	τ_1/ns	τ_2/ns	A_1/A_2	ref
monomer[a]	benzene	11.9	1.9	0.086	this work
	ethyl acetate	8.5	1.9	0.084	20
	CH_2Cl_2	7.3	1.4	0.031	20
	$CHCl_3$	9.3	1.0	0.003	20
	THF	7.9	1.9	0.13	23
excimer[b]	benzene	10.8	1.2		this work

[a] $I_M(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. [b] $I_D(t) = A_3\{\exp(-t/\tau_1) - \exp(-t/\tau_2)\}$.

Scheme I

process		rate
absorption	$^1M + h\nu \rightarrow {}^1M^*$	I_{abs}
monomer fluorescence	$^1M^* \rightarrow {}^1M + h\nu_M$	$k_{FM}[^1M^*]$
internal quenching	$^1M^* \rightarrow {}^1M$	$k_{IM}[^1M^*]$
main-chain scission	$^1M^* \rightarrow$ products	$k_{SM}[^1M^*]$

benzene solution. Within experimental error both plots give straight lines represented by

$$\Phi_M = 1.06\Phi_{cs} + 0.0001 \qquad (6)$$

$$\Phi_D = 0.0354 - 0.557\Phi_{cs} \qquad (7)$$

Since the lowest excited singlet state $^1(\pi,\pi^*)$ of the 1-naphthyl chromophore should be involved as a primary intermediate electronic state in the main-chain scission of poly(1NMA-*co*-BMA) under 285-nm irradiation, it is reasonable to predict that the local quantum yield for main-chain scission $\phi_{cs}{}^0$ in the non-excimer-forming sites differs from that (ϕ_{cs}) in the excimer-forming sites. Thus the apparent quantum yield Φ_{cs} may be given by

$$\Phi_{cs} = \phi_{cs}{}^0\Theta + \phi_{cs}(1 - \Theta) \qquad (8)$$

Substitution of Θ derived from eq 8 in eq 3 and 4 gives the linear relationships

$$\Phi_M = \frac{\phi_M{}^0 - \phi_M}{\phi_{cs}{}^0 - \phi_{cs}}\Phi_{cs} + \frac{\phi_M{}^0\phi_{cs} - \phi_M\phi_{cs}{}^0}{\phi_{cs}{}^0 - \phi_{cs}} \qquad (9)$$

$$\Phi_D = \frac{\phi_D\phi_{cs}{}^0}{\phi_{cs}{}^0 - \phi_{cs}} - \frac{\phi_D}{\phi_{cs}{}^0 - \phi_{cs}}\Phi_{cs} \qquad (10)$$

where all the ϕ values are constant and independent of 1NMA content. Equations 9 and 10 agree with the experimental eq 6 and 7, respectively. Comparison of the coefficients in eq 10 with those in eq 7 enables evaluation of $\phi_{cs}{}^0$ as 0.0636 scissions per quantum absorbed by the 1-naphthyl chromophore in the nonexcimer sites.

Transient Fluorescence Characteristics of Isolated 1-Naphthyl Chromophore. The low 1NMA content (3.2 mol %) copolymer CP1NB-1 shows single-exponential decay of the transient fluorescence emission with a lifetime τ_0 = 9.2 ns in deaerated benzene solution at room temperature, as shown in Figure 5. Since the 1-naphthyl chromophores in CP1NB-1 are distributed virtually in an isolated condition (Table I), the fluorescence decay shown in Figure 5 refers to the behavior of the lowest excited singlet state of the 1-naphthyl chromophore ($^1M^*$) in the nonexcimer sites. It follows that the general kinetic processes associated with the relaxation of $^1M^*$ in the nonexcimer sites can be given as in Scheme I.

In Scheme I the main-chain scission is assumed to occur in competition with the fluorescence emission from the lowest excited singlet state of the 1-naphthyl chromophore. Recently, from the photochemical behavior of 1NMA–vinyl ketone copolymers Guillet et al. suggested that the quantum yield for main-chain scission from the triplet state of the 1-naphthyl chromophore is close to zero.[23] This provides a rationale for the above assumption.

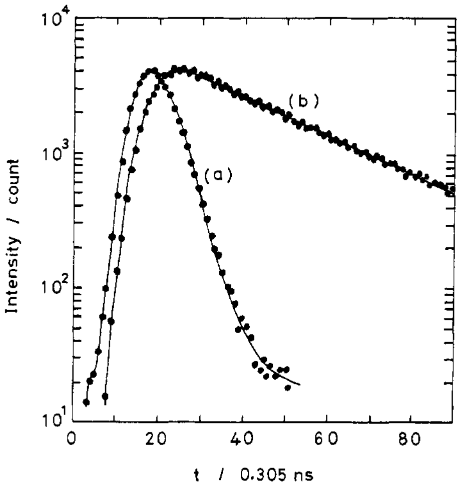

Figure 5. Transient fluorescence emission of CP1NB-1 in deaerated benzene solution at room temperature: (a) profile of pulsed light; (b) monomer fluorescence decay.

Table III
Kinetic Parameters Involved in the Photophysical and Photochemical Processes for Poly(1NMA-*co*-BMA) in Deaerated Benzene Solution at Room Temperature

		monomer process	rate const/ 10^7 s^{-1}			excimer process	rate const/ 10^7 s^{-1}
X	k_M	k_{FM}	0.73	Y	k_D	k_{FD}	0.29
		k_{IM}	9.6			k_{ID}	7.9
		k_{SM}	0.69			k_{SD}	0.0008
		k_{DM}	38			k_{MD}	3.7

Following Scheme I, the fluorescence response function is of a single-exponential form

$$I_M{}^0(t) = k_{FM} \exp(-t/\tau_0) \qquad (11)$$

where the lifetime τ_0 is given by

$$1/\tau_0 = k_{FM} + k_{IM} + k_{SM} = k_M \qquad (12)$$

The quantum yields for fluorescence emission and main-chain scission are

$$\phi_M{}^0 = k_{FM}\int_0^\infty \exp(-t/\tau_0)\, dt = k_{FM}\tau_0 \qquad (13)$$

$$\phi_{cs}{}^0 = k_{SM}\int_0^\infty \exp(-t/\tau_0)\, dt = k_{SM}\tau_0 \qquad (14)$$

The rate constants k_{FM} and k_{SM} can be evaluated from eq 13 and 14, respectively, using the experimental data $\phi_M{}^0$ = 0.067, $\phi_{cs}{}^0$ = 0.0636, and τ_0 = 9.2 ns. The rate constant k_{IM} is also obtained by substituting the k_{FM}, k_{SM}, and τ_0 values in eq 12. Numerical results are listed in Table III.

Transient Fluorescence Characteristics of Clustered 1-Naphthyl Chromophores. In contrast to the behavior of CP1NB-1, the monomer fluorescence decay of

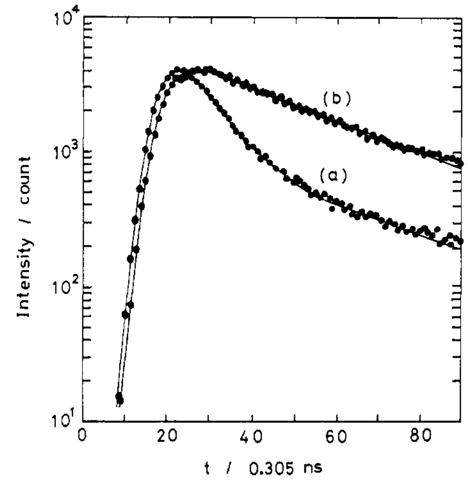

Figure 6. Transient fluorescence emission of P1NMA in deaerated benzene solution at room temperature: (a) monomer fluorescence decay; (b) excimer fluorescence decay.

Scheme II

process		rate
absorption	$^1M + h\nu \rightarrow {}^1M^*$	I_{abs}
monomer fluorescence	$^1M^* \rightarrow {}^1M + h\nu_M$	$k_{FM}[^1M^*]$
internal quenching	$^1M^* \rightarrow {}^1M$	$k_{IM}[^1M^*]$
main-chain scission	$^1M^* \rightarrow$ products	$k_{SM}[^1M^*]$
excimer formation	$^1M^* + {}^1M \rightarrow {}^1D^*$	$k_{DM}[^1M^*]$
excimer fluorescence	$^1D^* \rightarrow {}^1M + {}^1M + h\nu_D$	$k_{FD}[^1D^*]$
internal quenching	$^1D^* \rightarrow {}^1M + {}^1M$	$k_{ID}[^1D^*]$
main-chain scission	$^1D^* \rightarrow$ products	$k_{SD}[^1D^*]$
excimer dissociation	$^1D^* \rightarrow {}^1M^* + {}^1M$	$k_{MD}[^1D^*]$

P1NMA is nonexponential as shown in Figure 6a. The observed response function of monomer emission, $I_M(t)$, is represented approximately by the sum of two exponentials

$$I_M(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \tag{15}$$

where τ_1 and τ_2 denote the relaxation times corresponding to the longer and shorter decay components, respectively. On the other hand, the excimer response function $I_D(t)$ in Figure 6b can be approximated by the difference of the same exponential terms

$$I_D(t) = A_3\{\exp(-t/\tau_1) - \exp(-t/\tau_2)\} \tag{16}$$

The relaxation times τ_1 and τ_2 evaluated from Figure 6 are listed in Table II together with the literature values.[20,23]

Analogous response functions composed of double exponentials have also been reported for other fluorescent polymers, e.g., poly(*N*-vinylcarbazole),[17] poly(1-vinylnaphthalene),[19] poly(naphthyl acrylate),[20] and poly[(1-naphthyl)alkyl methacrylate].[21]

The kinetic scheme with respect to the intermolecular excimer formation of small molecules in fluid solution has been established by Birks et al.[29] In the Birks mechanism the fluorescence response functions of monomer and excimer emissions are known to have forms identical with eq 15 and 16, respectively. It is therefore reasonable to describe the kinetics of intramolecular excimer formation for P1NMA in dilute solution based on a modified Birks scheme (Scheme II). As an extension, the behavior of the fluorescence state of the 1-naphthyl chromophores in the excimer sites may also be described for any poly(1NMA-*co*-BMA) in terms of Scheme II.

It should be noted that the intramolecular excimer formation in Scheme II is assumed to be of pseudo first order ($k_{DM}[^1M^*]$), because it does not occur randomly but is a prescribed process depending on polymer configuration and conformational change. This is in striking contrast to the homogeneous intermolecular excimer formation via a second-order reaction process ($k_{DM}[^1M^*][^1M]$) in fluid solution.[29]

In a conventional manner,[29] Scheme II leads to the monomer and excimer fluorescence response functions

$$I_M(t) = \frac{k_{FM}}{\lambda_2 - \lambda_1}\{(\lambda_2 - X)\exp(-\lambda_1 t) + (X - \lambda_1)\exp(-\lambda_2 t)\} \tag{17}$$

$$I_D(t) = \frac{k_{FD}k_{DM}}{\lambda_2 - \lambda_1}\{\exp(-\lambda_1 t) - \exp(-\lambda_2 t)\} \tag{18}$$

where

$$\lambda_{1,2} = 1/\tau_{1,2} = \tfrac{1}{2}[(X + Y) \mp \{(Y - X)^2 + 4k_{DM}k_{MD}\}^{1/2}] \tag{19}$$

$$X = k_{FM} + k_{IM} + k_{SM} + k_{DM} = k_M + k_{DM} \tag{20}$$

$$Y = k_{FD} + k_{ID} + k_{SD} + k_{MD} = k_D + k_{MD} \tag{21}$$

The quantum yields for monomer and excimer emissions are the forms

$$\phi_M = \int_0^\infty I_M(t)\,dt = \frac{k_{FM}(k_D + k_{MD})}{k_M(k_D + k_{MD}) + k_{DM}k_D} \tag{22}$$

$$\phi_D = \int_0^\infty I_D(t)\,dt = \frac{k_{FD}k_{DM}}{k_M(k_D + k_{MD}) + k_{DM}k_D} \tag{23}$$

Similarly, the quantum yield for main-chain scission is given by

$$\phi_{cs} = \int_0^\infty \left\{\frac{k_{SM}}{k_{FM}}I_M(t) + \frac{k_{SD}}{k_{FD}}I_D(t)\right\} dt = \frac{k_{SM}(k_D + k_{MD}) + k_{SD}k_D}{k_M(k_D + k_{MD}) + k_{DM}k_D} \tag{24}$$

Main-chain scissions from both $^1M^*$ and $^1D^*$ are involved in eq 24.

Comparing eq 15 with eq 17, we obtain

$$A_1/A_2 = (1/\tau_2 - X)/(X - 1/\tau_1) \tag{25}$$

Using this relationship and the measurement of the monomer fluorescence decay (Table II) enables determination of X ($=k_M + k_{DM}$) as 4.9×10^8 s^{-1}. Furthermore, substitution of X and k_M ($=1/\tau_0$) in eq 20 gives the rate constant for intramolecular excimer formation k_{DM} as listed in Table III.

Equation 19 shows that the following relationships between relaxation times τ_1 and τ_2 are fulfilled:

$$1/\tau_1 + 1/\tau_2 = X + Y \tag{26}$$

$$1/\tau_1\tau_2 = XY - k_{DM}k_{MD} \tag{27}$$

Using a set of known kinetic parameters, we evaluate Y ($=k_D + k_{MD}$) from eq 26 as 1.2×10^8 s^{-1}. Consequently, we obtain the rate constant for excimer dissociation (k_{MD}) (Table III) and then $k_D = 8.2 \times 10^7$ s^{-1} by substituting Y and k_{MD} in eq 21.

Photophysical and Photochemical Processes in Poly(1NMA-*co*-BMA). The fluorescence emissions and main-chain scission of poly(1NMA-*co*-BMA) under photostationary-state conditions can be interpreted in terms of linear combinations between the local behavior in the nonexcimer sites and that in the excimer sites (eq 3, 4, and 8). It is apparent from the transient fluorescence measurements that CP1NB-1 and P1NMA provide two extremes of such local behavior. The overall kinetic scheme for the photophysical and photochemical processes in the poly(1NMA-*co*-BMA) may therefore be represented by a combination of Schemes I and II.

Assuming that all quantum yields derived from Schemes I and II refer to the local terms in any poly(1NMA-*co*-BMA), we rewrite eq 9 and 10 as

$$\Phi_{\mathrm{M}} = \frac{k_{\mathrm{FM}}k_{\mathrm{D}}}{k_{\mathrm{SM}}k_{\mathrm{D}} - k_{\mathrm{M}}k_{\mathrm{SD}}}\left(\Phi_{\mathrm{cs}} + \frac{k_{\mathrm{SD}}}{k_{\mathrm{D}}}\right) \qquad (9')$$

$$\Phi_{\mathrm{D}} = \frac{k_{\mathrm{M}}k_{\mathrm{FD}}}{k_{\mathrm{SM}}k_{\mathrm{D}}}\left(\frac{k_{\mathrm{SM}}}{k_{\mathrm{M}}} - \Phi_{\mathrm{cs}}\right) \qquad (10')$$

Kinetic parameters in eq 9′ and 10′ are known except for k_{FD} and k_{SD}. The rate constants for excimer fluorescence (k_{FD}) and for main-chain scission from the excimer singlet state (k_{SD}) can be obtained by comparing eq 9′ and 10′ with the experimental eq 6 and 7. The rate constant for excimer internal quenching (k_{ID}) can be determined finally from the definition $k_{\mathrm{D}} = k_{\mathrm{FD}} + k_{\mathrm{ID}} + k_{\mathrm{SD}}$ (eq 21).

Table III summarizes a set of kinetic parameters for poly(1NMA-*co*-BMA) in deaerated benzene solution. From Table III a conclusion concerning the effect of intramolecular excimer formation on the photodegradation can be drawn as follows: The main-chain scission from the excited singlet state of the 1-naphthyl chromophore ($k_{\mathrm{SM}} = 6.9 \times 10^6\ \mathrm{s}^{-1}$) is comparable to the monomer fluorescence emission ($k_{\mathrm{FM}} = 7.3 \times 10^6\ \mathrm{s}^{-1}$). Since the rate constant for intramolecular excimer formation ($k_{\mathrm{DM}} = 3.8 \times 10^8\ \mathrm{s}^{-1}$) is approximately 4 times that for monomer internal quenching ($k_{\mathrm{IM}} = 0.96 \times 10^8\ \mathrm{s}^{-1}$), the quenching of the fluorescence state of the 1-naphthyl chromophore in the excimer sites is highly efficient compared with the case in the nonexcimer sites. The lower rate constant for excimer dissociation ($k_{\mathrm{MD}} = 3.7 \times 10^7\ \mathrm{s}^{-1}$), which is 1 order of magnitude below k_{DM}, shows that the excimer dissociation to regenerate the monomer fluorescence state is negligible relative to the association into the excimer fluorescence state. It is particularly noteworthy that main-chain scission from the excimer fluorescence state makes little contribution to the photodegradation of poly(1NMA-*co*-BMA) because of its extremely small rate constant ($k_{\mathrm{SD}} = 8 \times 10^3\ \mathrm{s}^{-1}$). Thus the intramolecular excimer formation is responsible for the photostabilization of poly(1NMA-*co*-BMA).

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Determination of Molecular Weight Distribution of Synthetic Flexible-Chain Polyelectrolytes by Polyacrylamide Gel Electrophoresis[1]

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ABSTRACT: Polyacrylamide gel electrophoresis was found to yield high resolution in the determination of chain length distributions of synthetic polyelectrolytes. Data are reported for poly(styrenesulfonate) obtained from polystyrene with narrow molecular weight distributions and for unfractionated poly(acrylic acid).

Although gel permeation chromatography (GPC) has proved to be a powerful method for the determination of the molecular weight distribution (MWD) of high polymers, its application to water-soluble polymers has en-

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