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Fluorescence and Energy Transfer of Polypeptides Containing Naphthyl Groups in Their Side Chains

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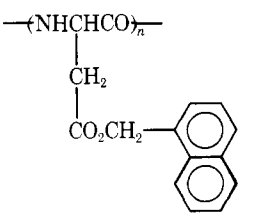
ABSTRACT: Energy transfer in the singlet state was studied in solution at 25 °C for poly(β-1-naphthylmethyl L-aspartate) and copolymers of β-1-naphthylmethyl L-aspartate and γ-benzyl L-glutamate. Transfer efficiencies, migration coefficients, migration lengths, and interaction radii were determined from the quenching studies using biacetyl as a quencher. The migration coefficient increases with increasing naphthyl groups in the copolymers. This means that singlet energy migrates among more naphthyl groups with increasing naphthyl groups in the polymer chain. Interaction radius for the fluorescence quenching by biacetyl was estimated to be in the range of 5.8 to 8.9 Å irrespective of whether energy donor is monomer or excimer. Moreover, it was shown that energy migration via excimer does not take place and energy of the excimer is localized.

Intramolecular energy transfer along the polymer chain has become a phenomenon of increasing interest and intensive study.[2-21] Functional groups situated at regular intervals along the backbone of a polymer may be compared in principle to a one-dimensional crystal and there is a possibility of energy migration from group to group along the polymer chain. Intermolecular energy transfer may also be affected by intramolecular energy transfer, since intuitively the migration of energy along the polymer chain increases the effective volume of the excited region or quenching sphere. Almost all the polymers used for such investigations are vinyl polymers. Polypeptides are well known to take some different conformations such as α-helix, β-structure and random-coil. Side chains of a helical polypeptide may be arranged along the rodlike helical main chain forming outer helix. Therefore, one can compare it to a better one-dimensional crystal than vinyl polymers because of its ordered structure and the absence of folding. One can further obtain some different arrangements of the side-chain chromophores corresponding to the difference in its secondary structure. We have been interested in studying how intra- and intermolecular energy transfer would be affected by conformational change of the polypeptides.[21,22] From this point of view, some polypeptides containing naphthyl groups in their side chain were prepared.[23-25] In the previous paper,[26] we showed evidence for singlet energy migration for poly(γ-1-naphthylmethyl L- and DL-glutamates) (PNLG and PNDLG) and copolymers of γ-1-naphthylmethyl L-glutamate and γ-benzyl L-glutamate.

We report here the results of quenching studies for poly(β-1-naphthylmethyl L-aspartate) (PNLA) and copolymers of β-1-naphthylmethyl L-aspartate and γ-benzyl L-glutamate. Their conformations have already been studied[24] and right-handed helices were assumed for all polymers except for pure PNLA only which may take a left-handed helix.



PNLA

Experimental Section

Syntheses of the polymers were described previously.[24] The degrees of polymerization of the samples were determined to be in the range of 30 to 65 by amino end-group titration. Dichloroethane (DCE) was "Dotite Spectrosol" grade. Hexafluoroisopropyl alcohol (HFIP) was Tokyo Kasei reagent grade. Naphthalene was Tokyo Kasei zone-refined grade. Biacetyl was freshly distilled before use. Solvents for fluorescence measurements are DCE and a mixed solvent of DCE and HFIP (1:1 by volume). PNLA is insolule in DCE but soluble in the mixed solvent. Therefore the mixed solvent had to be used for the polymer.

Fluorescence spectra at 290-nm excitation were measured at 25 °C with a Hitachi MPF-4 fluorescence spectrophotometer. The excitation was normal to the front surface of the cubical cell, and the fluorescence was observed through the side face at 90° to the incident light. The naphthyl molar concentration was 5×10^{-3} M for the quenching measurements. The intensities of monomer and excimer fluorescence were measured respectively at 332–333 nm (peak) and 400 nm. In the quenching experiments corrections were made for absorption of the exciting light by biacetyl. The lifetime measurements were conducted with the time-resolved attachment using the solutions 10^{-3} M in naphthyl groups. Pulsed light of the D_2 discharge lamp was triggered by the control unit. The half-value width of the sampling gate was a second or a third of the measuring lifetime. The decay curves at 320 and 400 nm were recorded on a chart-recorder. Because of the limitation of the apparatus for measurement of shorter lifetime, the lifetimes in the mixed solvent were estimated from intensity at 332 nm based on the lifetime of the copolymer containing 11% naphthyl

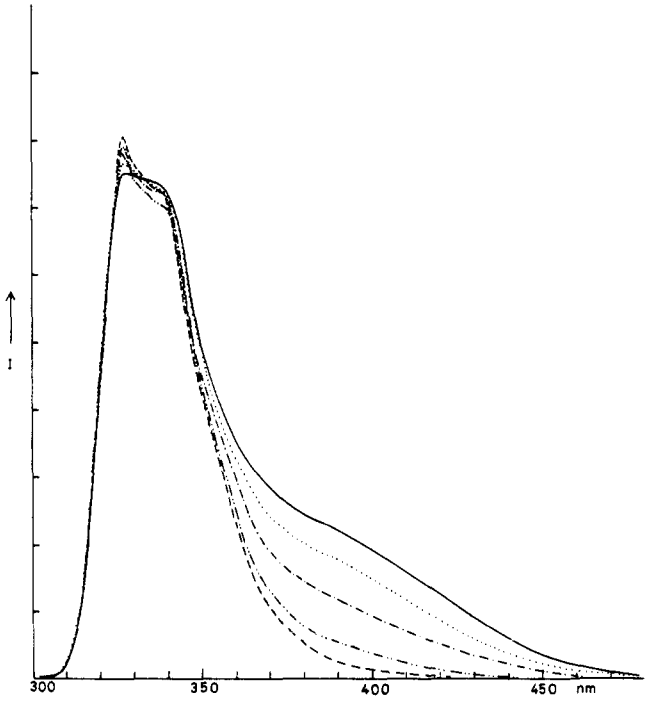


Figure 1. Fluorescence spectra of the copolymers in the mixed solvent of DCE and HFIP (1:1) at room temperature; 3×10^{-4} M in naphthyl units. Spectral intensities are not comparative for the different polymers. Naphthyl content: 100% (—); 74% (···); 54% (– · –); 34% (– · · –); 11% (- -).

groups only which was measured by the decay curve. All measurements were made on air-equilibrated solutions.

Results and Discussion

Fluorescence Spectra and Lifetimes. The fluorescence spectra of the copolymers in the mixed solvent at room temperature are shown in Figure 1. The structureless band appearing in the longer wavelength region can be attributed to the excimer emission since its intensity increases with increasing naphthyl content in the copolymers. The various photochemical processes occurring in the polymers and the related rate constants are given below. Two types of singlet excited species are formed: isolated excited naphthyl group (N*) and excimer (E*)

		Rate	
$N \xrightarrow{h\nu} N^*$		I	
$N^* \longrightarrow N + h\nu_f$		k_f	k_N
$\longrightarrow N$		k_{dN}	
$\longrightarrow {}^3N$			
$\xrightarrow{O_2} N$			
$\xrightarrow{N} E^*$		k_{EN}	
$E^* \longrightarrow N^* + N$		k_{NE}	k_E
$\longrightarrow N + N + h\nu_{ex}$		k_e	
$\longrightarrow N + N$		k_{dE}	
$\xrightarrow{O_2} N + N$			

in the presence of quencher (Q)

$$N^* + Q \rightarrow N + Q^* \qquad k_{qN}$$

$$E^* + Q \rightarrow N + N + Q^* \qquad k_{qE}$$

From this scheme, the time dependence of the fluorescence intensity of monomer, $I_N(t)$, and that of excimer, $I_E(t)$, are calculated as follows:[27]

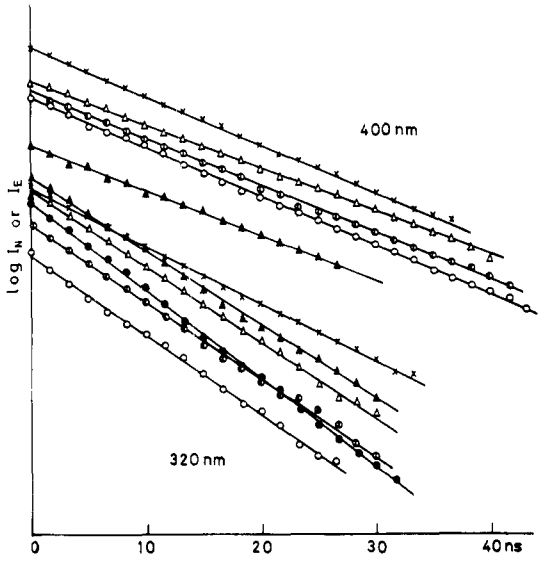


Figure 2. Semilogarithmic plots of the fluorescence decay curves; 10^{-3} M in naphthyl units in DCE. Naphthyl content: 74% (○); 54% (⊕); 34% (△); 11% (▲), PNLG (×), naphthalene (●).

$$I_N(t) = [k_f C_0/(\lambda_2 - \lambda_1)][(\lambda_2 - k_N)\exp(-\lambda_1 t) + (k_N - \lambda_1)\exp(-\lambda_2 t)]$$

$$I_E(t) = [k_e C_0 k_{EN}/(\lambda_2 - \lambda_1)][\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]$$

where

$$\begin{matrix}\lambda_1 \\ \lambda_2\end{matrix} = \tfrac{1}{2}[(k_N + k_E) \mp \{(k_E - k_N)^2 + 4k_{NE}k_{EN}\}^{1/2}] \qquad (1)$$

and C_0 is the concentration of N* at $t = 0$. Therefore, the decay curves must be double exponential both at the monomer and the excimer bands. However, the observed curves are single exponential (Figure 2), and the lifetime of the excimer (τ_E) is considerably longer than that of the monomer (τ_N). This result seems to indicate that the fluorescent excimers are not formed from the emitting monomers and that dissociation of the excimers to the emitting monomers is negligible.[8] Presumably, some specific (N N) pairs with appropriate geometrical configuration will make the excimers immediately at the time excitation,[8] but the other N groups will not make the excimers but will emit the monomer fluorescence.

Lifetimes of monomer and excimer fluorescence are shown in Tables I and II, respectively. In DCE, the lifetimes of monomer fluorescence for the copolymers are 13–14 ns which is close to the lifetime for naphthalene (11.6 ns). However, considerable decrease of lifetime is observed in the mixed solvent going from the copolymer with the least naphthyl groups to pure PNLA. This solvent effect is more significant such as the copolymer containing 74% naphthyl groups (13.1 → 3.5 ns) than for the isolated chromophores (11.6 → 9.5 and 13.9 → 11.9 ns for naphthalene and the copolymer with the least naphthyl groups, respectively). Increasing content of the naphthyl groups might cause somewhat of a change in the environment around each naphthyl chromophore in the mixed solvent. The lifetimes of excimer in DCE are almost independent of the naphthyl content in the copolymers (Table II) and are similar to those obtained for the PNLG series (20–24 ns).

Migration Coefficients. The plots of I_N^0/I_N against the concentration [Q] of biacetyl are shown in Figures 3 and 4 where I_N^0 and I_N are the intensities in the absence and presence of [Q], respectively. According to the reaction scheme, the following equation may be readily obtained.[8]

Table I
Fluorescence Quenching and Energy Migration

Donor	Naph %	Solvent[a]	τ_N, ns	$k_{qN}\tau_N$	$k_{qN} \times 10^{-9}$	p^b	$\Lambda \times 10^5$ [c]	L, Å
Copolymer	11	DCE	13.9	39	2.8	0.44	0.00	0
	34	DCE	13.5	48	3.6	0.57	0.54	37
	54	DCE	13.5	51	3.8	0.60	0.68	45
	74	DCE	13.1	56	4.3	0.68	1.02	52
PNLG	100	DCE	18.3	86	4.7	0.74	1.29	69
Naph[d]		DCE	11.6	114	9.8	0.77		
Copolymer	11	MS	11.9	51	4.3	0.43	0.0	0
	34	MS	7.4	45	6.1	0.61	1.3	44
	54	MS	5.0	42	8.4	0.84	2.9	54
	74	MS	3.5	35	10.0	1.00	4.0	53
PNLA	100	MS	3.5	27	7.7	0.77	2.4	41
PNLG	100	MS	3.1	27	8.7	0.87	3.1	44
Naph		MS	9.5	147	15.5	0.77		

[a] MS = mixed solvent of DCE and HFIP (1:1 by volume). [b] Based on k_{diff} for naphthalene (1.27×10^{10}) and polymers (6.35×10^9) in DCE and for naphthalene (2.01×10^{10}) and polymers (1.00×10^{10}) in the mixed solvent. [c] Values calculated using D_Q in DCE (1.9×10^{-5} cm^2 s^{-1}) and in the mixed solvent (3.0×10^{-5} cm^2 s^{-1}). [d] Naphthalene.

Table II
Quenching of Excimer Fluorescence in DCE

Donor	Naph %	τ_E, ns	$k_{qE}\tau_E$[a]	$k_{qE}\tau_E$[b]	$k_{qE} \times 10^{-9}$ [a]	$k_{qE} \times 10^{-9}$ [b]	p^a	p^b
Copolymer	11	23.3	88	86	3.8	3.7	0.60	0.58
	34	23.8	100	97	4.2	4.1	0.66	0.65
	54	21.8	95	93	4.4	4.3	0.69	0.68
	74	20.7	92	87	4.4	4.2	0.69	0.66

[a] From eq 10. [b] From eq 11.

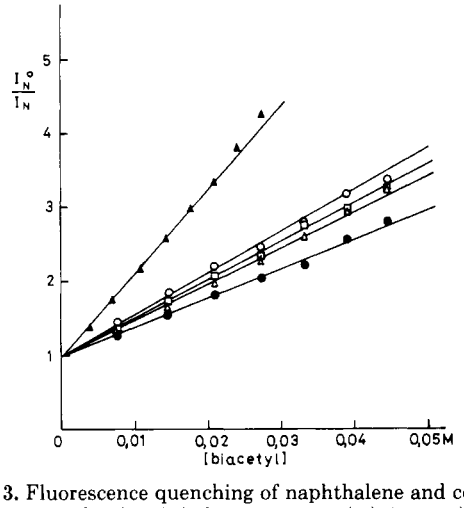


Figure 3. Fluorescence quenching of naphthalene and copolymers by biacetyl in DCE. Naphthyl content: 74% (○); 54% (□); 34% (△); 11% (●), naphthalene (▲).

$$\frac{I_N^0}{I_N} = \frac{k_E}{k_N k_E - k_{NE}k_{EN}}\left(k_N + k_{qN}[Q] - \frac{k_{NE}k_{EN}}{k_E + k_{qE}[Q]}\right) \quad (2)$$

If

$$k_N + k_{qN}[Q] \gg \frac{k_{NE}k_{EN}}{k_E + k_{qE}[Q]}$$

and $k_N k_E \gg k_{NE}k_{EN}$, eq 2 can be simplified to the Stern–Volmer form

$$I_N^0/I_N = 1 + k_{qN}\tau_N[Q] \quad (3)$$

which is almost in agreement with the experimental results although the effect of static quenching[28] or transient term[29] appears to be present for the higher slopes. The quenching rate parameters were obtained from the slopes and the measured lifetimes and tabulated in Table I.

The influence of diffusion on energy transfer has been treated theoretically by several authors. An approach developed by Voltz et al.[30] was used here. Omitting the transient term, the rate parameter for the diffusion-controlled quenching process is

$$k_{qN} = \frac{S_q N_0}{1000}(D_N + D_Q)PR \quad (4)$$

where N_0 represents Avogadro's number, D_N and D_Q are diffusion coefficients of the species N and Q, respectively, R is the interaction radius, S_q is the steric factor,[18,31] and P is the transfer probability. D_N is replaced by the migration coefficient Λ from the assumption that diffusion of polymer is negligible,[32] so that the rate parameter for the polymers can be expressed in the form

$$k_{qN} = \frac{S_q N_0}{1000}(\Lambda + D_Q)PR \quad (5)$$

Taking $\Lambda = 0$ for the copolymer with the least naphthyl content from the viewpoint that the chromophores in this polymer may be considered to be almost isolated from each other, eq 5 reduces to

$$k_{qN}^0 = \frac{S_q N_0}{1000} D_Q PR \quad (6)$$

where k_{qN}^0 is the rate parameter for the polymer. From eq 5 and 6, the migration coefficient Λ is given by

$$\Lambda = D_Q\left(\frac{k_{qN}}{k_{qN}^0} - 1\right) \quad (7)$$

The results of these treatments are summarized in Table I.

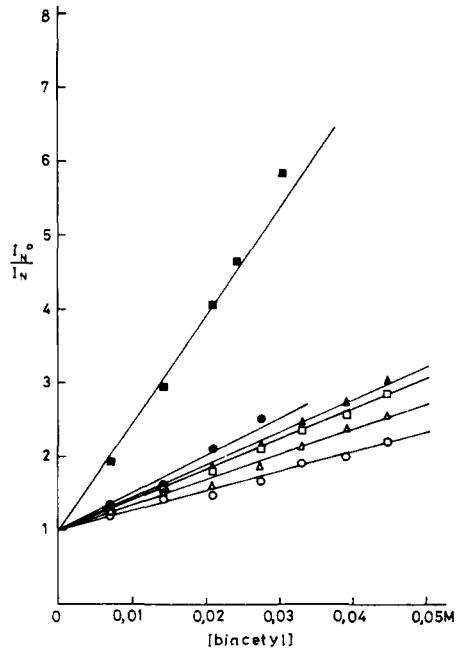


Figure 4. Fluorescence quenching of naphthalene, PNLA, and copolymers by biacetyl in the mixed solvent of DCE and HFIP (1:1). Naphthyl content: 100% (○); 74% (△); 54% (□); 34% (▲); 11% (●), naphthalene (■).

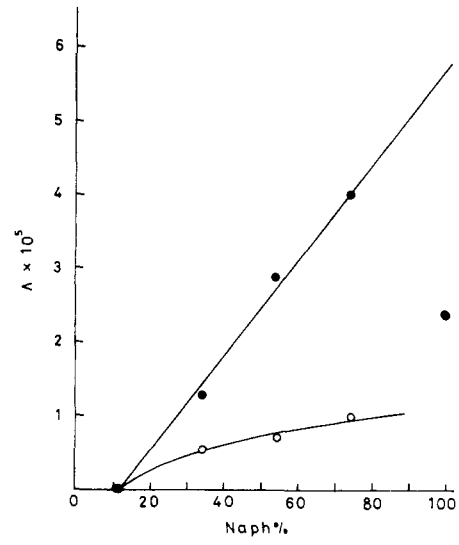


Figure 5. Dependence of migration coefficient on the naphthyl content in the copolymers. Solvent: DCE (○); mixed solvent of DCE and HFIP (1:1) (●).

The diffusion coefficient of biacetyl D_Q is 1.9×10^{-5} cm^2 s^{-1} in DCE[18] and 3.0×10^{-5} cm^2 s^{-1} in the mixed solvent. The latter value was estimated assuming that the ratio of k_{qN} and D_Q is the same in both solvents for naphthalene.

Figure 5 shows that Λ increases gradually in DCE and linearly in the mixed solvent with increasing naphthyl content for the right-handed helices. The results confirm that when the sequences of naphthyl units are interrupted by inactive comonomer units, the effective singlet migration coefficients are decreased. Such an effect of inactive comonomer units was observed by us[26] for PNLG series and North and Treadaway[39] for *N*-vinylcarbazole–methylacrylate copolymers. The migration coefficient for PNLA only which may take a different conformation from others[24] is smaller than that obtained by extrapolating the linear Λ vs. naph % plot of the right-handed helices to pure PNLA. The assumed Λ for the "right-handed PNLA" ($\Lambda = 5.9 \times 10^{-5}$ cm^2 s^{-1}) is also greater than that for PNLG.

Transfer Efficiencies. In the above treatment, P is a measure of the efficiency of transfer on encounter of donor–acceptor pairs and was assumed to be the same for all polymers. Several authors[14,32] adopted another approach to energy migration by using the parameter p defined as the ratio of quenching rate parameter k_q obtained from the Stern–Volmer equation to the diffusion constant k_{diff}. If energy migration occurs, the p value tends to increase corresponding to the increased k_q. The increase in the p value, for the polymer series, means the increased probability of an encounter with a quencher molecule as the result of delocalization of singlet energy along the chain. Only for the copolymers with a small amount of chromophores in their chains could the p value be equated to P since the chromophores are separated from each other and thus energy migration is unlikely. As an index for energy migration we also obtained the p values of the PNLA series using eq 8 of Osborne and Porter[33] to calculate the diffusion constant from the solvent viscosity η.

$$k_{diff} = 8RT/2000\eta \quad (8)$$

Equation 8 has proved to be more consistent with experimental results and is more reasonable theoretically than the traditional Debye equation.[34] Dubois et al.[35] have shown that naphthalene fluorescence quenching by biacetyl is viscosity dependent, and Heskins and Guillet[32] have estimated the p values for quenching of naphthalene fluorescence by symmetric ketones and also by ethylene–carbon monoxide copolymers assuming that transfer was limited only by the diffusion constant. They found that if one assumes that the polymers do not diffuse at all, the p values obtained for quenching of naphthalene fluorescence by ethylene–carbon monoxide copolymers and 6-undecanone were identical. Somersall and Guillet[14] found that the p value is about four times greater for polymeric ketones than for small ketones in the quenching of ketone fluorescence by biacetyl assuming negligible polymer diffusion and concluded that the excitation energy on the polymer chain is delocalized along the chain to facilitate transfer from the macromolecule by effectively increasing the probability of an encounter with a quencher molecule.

Figure 6 shows the variation of the p value as a function of naphthyl content. Contrast to the gradual increase in DCE, the p value in the mixed solvent increases linearly with increasing naphthyl content and reaches 1.0 at 74% naphthyl content. The difference in the p value between the two solvents also increases with increasing naphthyl content. The insensitivity to the solvent change of the polymer with the least naphthyl content may be attributable to the behavior of its naphthyl side chains as their monomeric counterparts being well isolated from each other. The p values of the polymer containing 74% naphthyl groups are 1.5 and 2.3 times greater in DCE and in the mixed solvent respectively than the corresponding values for the above polymer. The p value for PNLA is smaller than that obtained by extrapolating the linear p vs. naph % plot of the right-handed copolymers in the mixed solvent. If PNLA took a right-handed helix, the p value for the polymer would become 1.24 which is implicative of $k_{qN} > k_{diff}$. The reason for the solvent effect is not clear. One possible explanation is that the orientation of the side-chain naphthyl chromophores is perturbed by the solvent change with the result of suppressed excimer formation in the mixed solvent. In fact, fluorescence spectra showed that excimer formation is considerably suppressed in the mixed solvent. This suppression must have some effect on energy migration since once energy is trapped in the excimer-forming sites it is localized.[26] To evaluate this effect, we are now investigating

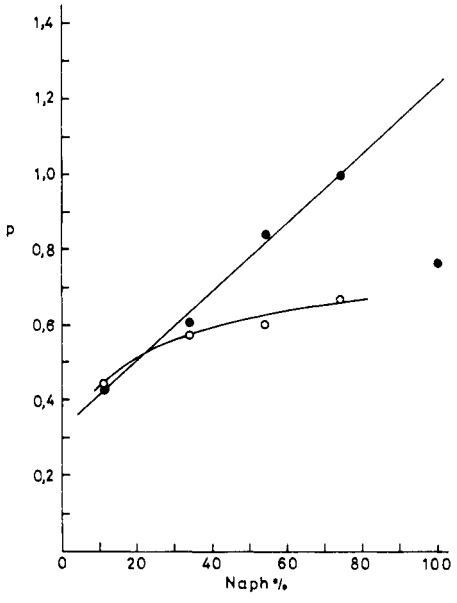


Figure 6. Dependence of transfer efficiency on the naphthyl content in the copolymers. Solvent: DCE (○); mixed solvent of DCE and HFIP (1:1) (●).

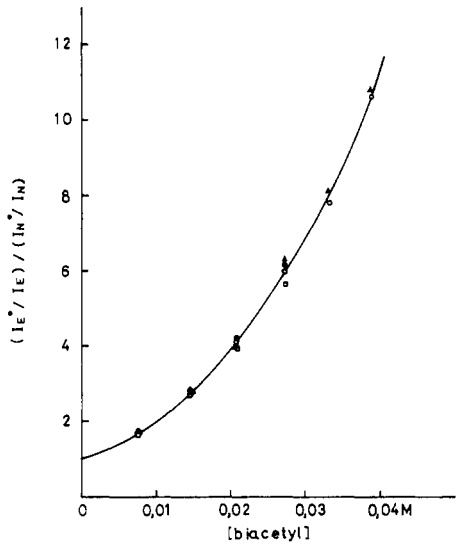


Figure 7. Dependence of $(I_E^0/I_E)/(I_N^0/I_N)$ on the concentration of biacetyl in DCE. Naphthyl content: 74% (○); 54% (△); 34% (●); 11% (□).

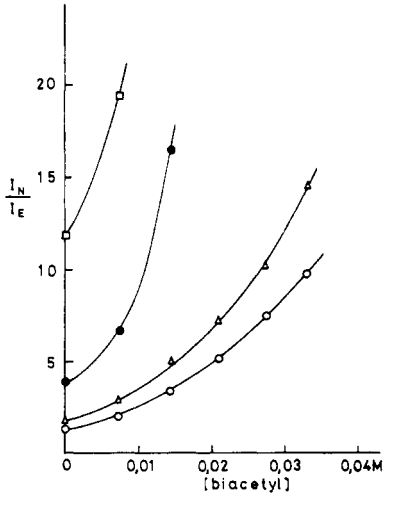


Figure 8. Dependence of I_N/I_E on the concentration of biacetyl in DCE. Naphthyl content: 74% (○); 54% (△); 34% (●); 11% (□).

the energy transfer of poly-L- and DL-naphthylalanines which do not show excimer emission.[25]

Migration Lengths. If energy migration occurs preferentially along an array of naphthyl chromophores, it may be treated as a one-dimensional random walk, and

$$L = \sqrt{2\Lambda\tau_N} \tag{9}$$

is the rms displacement in a time τ_N.[36] In spite of great differences in the migration coefficient, migration lengths are almost the same in both solvents (Table I). Though the migration coefficient in the mixed solvent reaches 4.0×10^{-5} cm^2 s^{-1} for the polymer with 74% naphthyl groups, increased migration length cannot be attained by its lifetime which is shortened unfortunately.

Excimer Quenching. To obtain the rate parameter for excimer quenching one may use either of the following equations[8,15]

$$(I_E^0/I_E)/(I_N^0/I_N) = 1 + k_{qE}\tau_E[Q] \tag{10}$$

or

$$\frac{I_N}{I_E} = \frac{g}{\tau_E} + gk_{qE}[Q] \tag{11}$$

$$(g = k_f/k_e k_{EN})$$

where I_E^0 and I_E are the intensities in the absence and presence of [Q], respectively. Figures 7 and 8 show the variations of $(I_E^0/I_E)/(I_N^0/I_N)$ and I_N/I_E as a function of biacetyl concentration at 25 °C in DCE. In both cases, departure from linearity was observed when biacetyl concentration increased. It might be caused by reabsorption of only excimer fluorescence by biacetyl. Detailed insight of this phenomenon is beyond the scope of the present paper. Here the results of using the initial slope are shown in Table II. Excellent agreement between the quenching rate parameters determined from (10) and (11) is remarkable. The rate parameter for excimer quenching seems to be independent of the naphthyl content in the copolymers and the same as that reported for the PNLG series. These results demonstrate that energy migration via excimer does not occur and the energy of excimer is localized. Thus the validity of the assumption that excimer migration is impossible since excimers have no ground states can be justified.

Interaction Radii. From eq 6, the interaction radius can be expressed in the form

$$R = 1000k_{qN}^0/N_0 D_Q P S_q \tag{12}$$

The value P can be equated to the p value for the polymer containing the least naphthyl groups because of its behavior in energy transfer as isolated donor. Leroy et al.[18] proposed the following steric factor for helical polypeptides.

$$2\pi < S_q < 3\pi$$

Using the value we calculated the interaction range for the quenching of naphthyl fluorescence by biacetyl. The results are shown in Table III. The values are almost the same irrespective of the differences in solvent and polymer used and are smaller than $R = 11$ Å proposed by Birks et al.[37] for the interaction radius for the quenching of naphthalene fluorescence by biacetyl, but a little greater than $R_c = 5.8$ Å, the sum of the molecular radii of naphthalene (3.1 Å) and biacetyl (2.7 Å) calculated by Gorrell and Dubois.[38] The interaction radius calculated for the quenching of excimer fluorescence is also the same range though it might apparently be expected to be

Table III
Interaction Radii

Polymer series	Solvent	Interaction radius
PNLA	DCE	$5.9\ Å < R < 8.9\ Å$
PNLA	MS[a]	$5.9\ Å < R < 8.9\ Å$
PNLG	DCE	$5.8\ Å < R < 8.8\ Å$
PNLA	DCE	$5.8\ Å < R < 8.8\ Å$[b]

[a] MS = mixed solvent of DCE and HFIP (1:1 by volume). [b] Interaction range for excimer quenching. The range was obtained by using the mean p value 0.66 of the values from eq 10.

greater than for an isolated excited chromophore. The localization of the π orbitals in the excimer might be the reason for this observation.

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On the Kinetics of Polymer Degradation in Solution. 5.[1,2] Pulse Radiolysis of PMMA Using the Light Scattering Detection Method

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ABSTRACT: The time dependence of the change of the light scattering intensity (LSI) of PMMA solutions after irradiation with a 2-μs pulse of 15-MeV electrons was monitored. Evidence for the existence of two intermediates causing main chain scission was obtained. The LSI decays in two modes: (1) a fast decay with a lifetime of ca. 20 μs probably corresponding to the diffusion of fragments which are generated by main chain ruptures occurring via electronically excited or ionic intermediates; (2) a slow decay with a lifetime τ (slow) $\approx$ 6 ms ($k_2 = 170\ s^{-1}$) corresponding presumably to a lateral macroradical. τ(slow) decreases with increasing concentrations of O_2 and C_2H_5SH. The degree of degradation also decreases with increasing concentration of these two additives. The following rate constants for the reaction of O_2 and C_2H_5SH with the transient causing the slow main chain ruptures were determined in acetone (at room temperature): $k_{O_2} = 1 \times 10^7\ M^{-1}\ s^{-1}$ and $k_{C_2H_5SH} = 2.5 \times 10^4\ M^{-1}\ s^{-1}$. Solvents used were acetone, n-hexanone-2, and acetonitrile.

Preliminary experiments[3] led to the conclusion that the radiation-induced main-chain degradation of poly(methyl methacrylate) (PMMA) in solution proceeds via two different intermediates. Evidence for these was obtained by monitoring the time dependence of decrease of light scattering intensity (LSI) after the irradiation of a dilute solution of PMMA with a 2-μs pulse of 15-MeV electrons. Immediately after the pulse the LSI decreased rapidly with a lifetime of less than 150μs. Subsequently a slow decrease with a lifetime of about 6 ms ($k = 170\ s^{-1}$) was observed. It was suggested that the rapid decay is due to main chain scissions caused by an electronically excited or an ionic transient. The slow decay, on the other hand, was thought to be due to main chain ruptures caused by free radicals.

In order to substantiate these suggestions experiments were carried out with acetone solutions containing oxygen or ethanethiol. In additional experiments acetonitrile and n-hexanone-2 were used as solvents instead of acetone. The results of these experiments are described in this paper. They affirm the suggestion that the slow LSI decay is correlated to the