Inter- and Intramolecular Interactions of Polymers as Studied by Fluorescence Spectroscopy. I. Exciplex Formation of a Polyester with a Terephthalate Main Chain Having a Pendant ω-Carbazylbutyl Group

Shigeo Tazuke* and Yuziro Matsuyama

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo, Japan. *Received December 3, 1974*

ABSTRACT: Fluorescence spectra of poly{[2-(ω-carbazylbutyl)-2-methylpropane-1,3-diyl]oxy-terephthaloyloxy} (I) in THF and dioxane solution were studied. The relative intensity of the exciplex formed between the singlet excited state of the carbazyl group and the terephthalate group was taken as an index for inter- or intramolecular interaction. The inter- and intramolecular processes were separated from the concentration dependence of exciplex emission at around 490 nm. The results were compared with exciplex formation between dimethyl terephthalate and poly{[2-(ω-carbazylbutyl)-2-methylpropane-1,3-diyl]oxy-malonyloxy} (II) or 6-carbazyl-2,2-di(acetoxymethyl)hexane (III) as the monomer model compound. Intermolecular exciplex formation by I was shown to be more than a thousandfold more efficient that the combination of dimethyl terephthalate with II and III, indicating polymer association by I occurred at concentrations lower than 10^{-3} mol/dm^3. The lifetime of fluorescence and various solvent effects were also investigated.

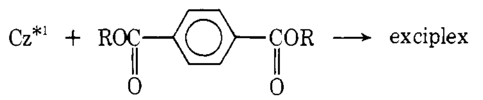
Fluorescence spectroscopy of polymers has been a potential approach to the investigation of inter- and intramolecular interactions and molecular motions. Apart from biopolymers, such studies of excimer formation have been limited almost entirely to olefinic polymers with aromatic or heterocyclic pendant groups such as polymers of styrene, vinylnaphthalene, acenaphthylene, vinylanthracene, *N*-vinylcarbazole, vinylpyrene, and their copolymers.[1-13] All of these studies were concerned with excimer formation in polymeric systems. But restrictions in the choice of structure in olefinic polymers prevented us from understanding molecular interactions as functions of environmental conditions surrounding the fluorophore. Flexibility of the skeletal structure of the polymer, the distance between fluorophores, the length and distribution of side chain, and many other factors could not be freely chosen by means of vinyl polymerization.

Polycondensation-type polymers are better than olefinic polymers for interpreting polymer effects on molecular interactions in relation to polymer structure since one can expect more latitude and less ambiguity on the design of polymer structure. The authors have synthesized polyamides[14] and polyesters[15] containing carbazole units and have studied charge transfer complex formation of the carbazole units with acceptors. Differences in the stability constants between monomeric model compounds and the polyesters are discussed for systems with more than one carbazole unit participating in formation of each complex.[15]

In the present study, exciplex formation between the carbazyl group and the terephthalate group was chosen as a measure of molecular interactions. Since exciplex formation is more specific and more sensitive to solvents than excimer formation, it is a better index for measuring molecular interactions.

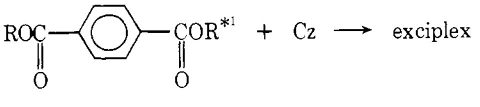
Results and Discussion

General Features of Fluorescence Spectra. Structures of samples (I, II, and III) and their fluorescence spectra are shown in Figure 1. It is clear that the fluorescence spectra of II and III are nearly identical whereas that of I displays a structureless broad emission around 490 nm characteristic of the exciplex formed between terephthalate and the singlet excited state of the carbazyl group.[16] Since the intensity of exciplex emission relative to monomer emission at 368 nm decreases with dilution, there is apparently participation of intermolecular exciplex formation even at a concentration as low as 10^{-4} mol/dm^3. The quantum yields of total fluorescence are about 0.3 for II and III, and much less than 0.1 for I as determined for a dilute solution ($\lesssim 10^{-5}$ mol/dm^3) in THF, indicating that the fluorescing state of the carbazyl group in I interacts with the terephthalate group to form an exciplex having a lower fluorescing probability or is deactivated without the formation of exciplex. In accordance with the difference in quantum yields, the fluorescence lifetime decreases from about 14 nsec for II and III to 8.1 nsec for the monomer emission (368 nm) of I,[17] indicating that the lowered intensity of fluorescence of the carbazyl group in I is a result of dynamic quenching by the terephthalate group.



(1)

Although the fluorescence state of I is greatly different from either II or III, absorption spectra of these three samples are identical in the wavelength region longer than 270 nm in which the carbazyl group is an exclusive photoabsorbing species as shown in Figure 2. Excitation spectra of this wavelength region agreed with the relevant absorption spectra. At the wavelength below 270 nm, the participation of the terephthalate group in photoabsorption led to a considerable difference in the absorption spectra of I. Since the absorption of the solvent increases and the output of the exciting light source decreases below 250 nm, the excitation spectra do not reflect the shape of absorption spectra very well. However, compared with the excitation spectra of I when the monomer emission and the exciplex emission are independently monitored (Figure 2B, a and b), the emission intensity of the exciplex is higher relative to that of monomer emission for irradiation below 250 nm where the absorption by the terephthalate group participates strongly. This observation indicates the participation of the following process. Such a duality of exciplex formation can be expected since diethylaniline forms exciplexes with both anthracene and diphenyl. Anthracene in the former case and *N*,*N*-diethylaniline in the latter case are the excit-



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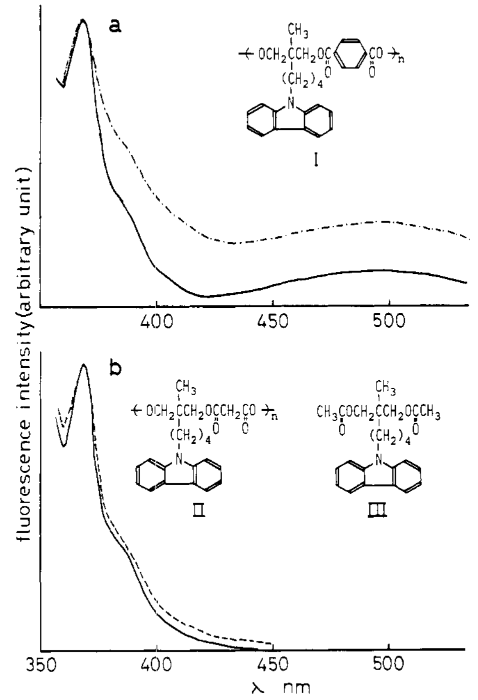

Figure 1. Fluorescence spectra of polyesters with pendant carbazyl groups in THF: (a) [I] = 1×10^{-2} mol/dm^3 (-·-) and 4×10^{-4} mol/dm^3 (—); (b) [II] = 1×10^{-4} mol/dm^3 (- - -) and [III] = 1×10^{-4} mol/dm^3 (—).

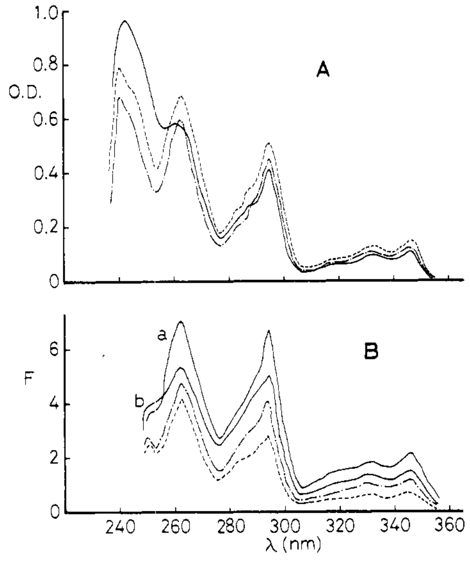

Figure 2. Absorption (A) and excitation (B) spectra with solute concentration 10^{-4} mol/dm^3 in dioxane: (—) I, in B, monomer emission (a) and exciplex emission (b) were independently monitored; (-·-) II; (- - -) III.

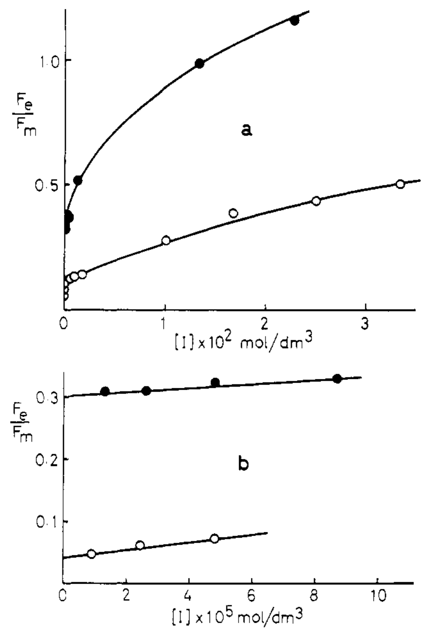

Figure 3. Exciplex emission of I as a function of concentration. F_e maximum at 470–495 nm, F_m maximum at 368 nm solvent (THF (○) and dioxane (●)): (a) concentrated system, (b) diluted system.

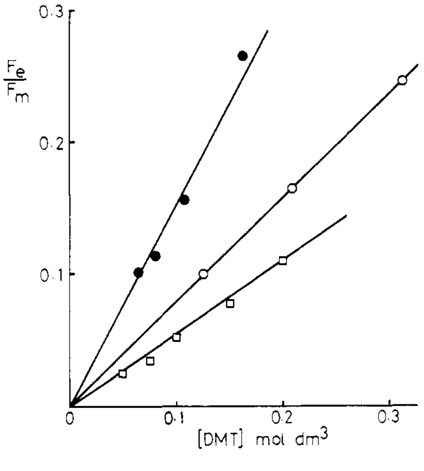

Figure 4. Exciplex emission of DMT–II and DMT–III systems at variable DMT concentrations ([II], [III] = 10^{-4} mol/dm^3): (□) II–DMT in THF, (○) III–DMT in THF, (●) III–DMT in dioxane.

ed species.[18] In the study of exciplex formation between small molecules, the concentration of ground state component is much greater than that of the photoabsorbing species so that it is generally impossible to maintain a low absorbance over a wide range of wavelength in determining excitation spectra.

Concentration Dependence of Exciplex Formation. The broad emission of the exciplex of I is well separated from the sharp monomer emission as shown in Figure 1. The exciplex emission is therefore independent of the monomer emission whereas the intensity of monomer emission at 368 nm may be an apparent value due to overlap with the exciplex emission which extends considerably toward the shorter wavelength region. The ratios of exciplex and apparent monomer emission intensities are plotted as a function of the concentration of I in Figure 3. The intercept of F_e/F_m at zero concentration and the slope of the plots represent the probabilities of intra- and intermolecular exciplex emission relative to the apparent monomer emission, respectively. As reference systems, the F_e/F_m values for the exciplex formed between II or III and DMT are plotted as a function of [DMT] in Figure 4.

A kinetic expression of exciplex formation between the singlet excited state of the carbazyl group and the terephthalate unit is given as follows, where Cz, TP, and E denote carbazyl, terephthalate, and exciplex.

$$\begin{array}{llr}
\mathrm{Cz} \xrightarrow{h\nu} \mathrm{Cz}^{*1} & I_{\mathrm{abs}} & (3) \\
\mathrm{Cz}^{*1} \longrightarrow \mathrm{Cz} + h\nu_{f\mathrm{m}} & k_{f\mathrm{m}}[\mathrm{Cz}^{*1}] & (4) \\
\mathrm{Cz}^{*1} \longrightarrow \mathrm{Cz} & k_{\mathrm{dm}}[\mathrm{Cz}^{*1}] & (5) \\
\mathrm{Cz}^{*1} + \mathrm{TP} \longrightarrow \mathrm{E} & k_{\mathrm{e}}[\mathrm{Cz}^{*1}][\mathrm{TP}] & (6) \\
\mathrm{E} \longrightarrow \mathrm{Cz}^{*1} + \mathrm{TP} & k_{\mathrm{e}'}[\mathrm{E}] & (7) \\
\mathrm{E} \longrightarrow \mathrm{Cz} + \mathrm{TP} + h\nu_{f\mathrm{e}} & k_{f\mathrm{e}}[\mathrm{E}] & (8) \\
\mathrm{E} \longrightarrow \mathrm{Cz} + \mathrm{TP} & k_{\mathrm{de}}[\mathrm{E}] & (9)
\end{array}$$

Table I
Spectroscopic Data of I, II, and III in THF

Sample	Mol wt[a]	λ_{max}, nm Absorption spectra	 Fluorescence spectra	ϕ_f	τ_f
I	9600	346, 331	352, 368, 490[b]	0.1[c]	8.1[d]
II	4800	345, 331	352, 368	0.26	14.0
III		345, 331	351, 368	0.28	14.6

[a] Determined by GPC. Reduced value using polystyrene as standard. [b] Exciplex emission. [c] The shape of the spectrum depends on concentration. [d] Value for monomer emission. [I] = 10^{-4} mol/dm^3.

I_{abs} is the rate of absorbing photon by carbazyl group, k_{fm}, k_{dm}, and k_e are rate constants for the fluorescing process, radiationless deactivation, and exciplex formation relevant to the singlet excited state of carbazyl group, and k_e, k_{fe}, and k_{de} are rate constants for dissociation, the fluorescing process, and radiationless deactivation of exciplex, respectively. Applying the usual assumption of stationary concentrations for $[Cz^{*1}]$ and [E], F_e/F_m is expressed by (10).

$$F_e/F_m = k_{fe}[E]/k_{fm}[Cz^{*1}] = k_{fe}k_e[TP]/k_{fm}(k_{e'} + k_{fe} + k_{de}) \quad (10)$$

Since intramolecular exciplex formation is considered as concentration independent, the initial slope of the plots, F_e/F_m vs. [TP], provides a measure of the probability of exciplex emission relative to monomer fluorescence. The initial slopes of the plots, F_e/F_m vs. [I] or [DMT], in THF depicted in Figures 3b or 4 respectively are 910 for I, 0.55 for the DMT–II system, and 0.78 for the DMT–III system. The difference in these initial slopes can be discussed in terms of six rate constants for elementary processes 4–9.

For both polymer and its monomeric model compound, k_{fm} and k_{dm} are thought to be identical. Values of both ϕ_f and τ_f determined for II and III (Table I) indicate that k_{fm} and k_{dm} are not affected if the carbazyl group is either isolated or built into a polymer. Consequently, the assumption that k_{fm} and k_{dm} of I are also the same as those of II or III is reasonable. The dissipation rate constant of the exciplex ($k_{e'} + k_{fe} + k_{de}$) is assumed to be not much different for I and the combination of II or III with DMT. The τ_f measured for exciplex emission of I in dioxane is 31 nsec at [I] = 5 × 10^{-4} mol/dm^3, which is reasonable for a lifetime of an exciplex in a solvent of low dielectric constant in accordance with the above assumption. As a consequence, the major part of the difference in the initial slopes of Figures 3 and 4 should be ascribed to the difference in k_e, namely the probability of exciplex formation.

The prominent polymer effect resulting in intermolecular exciplex formation of I, that is over 10^3 times more efficient than in the systems in which at least one component is monomeric, can be explained by two ways. The first considers the difference in the rate of molecular association assuming no preliminary molecular aggregation of nonexcited species. The second takes into account the molecular aggregation of polymers prior to photoexcitation since the high local concentration of the terephthalate group around the excited carbazyl group enhances the probability of the exciplex formation. Although uniform distribution of all species in the ground state is a generally accepted principle for analyzing exciplex or excimer formation in dilute solutions, this concept can hardly account for the present findings. To explain the results, a higher probability of encounters between polymers has to be assumed whereas the diffusion constant of a polymer molecule is known to be less than that of a small molecule. Indeed, the probability of exciplex formation is smaller for the DMT–II system than for the DMT–III systems as shown by the slope of the F_e/F_m vs. [DMT] plots in Figure 4. The encounter probability between polymers is expected to be even smaller. The results mentioned above strongly indicate the importance of molecular association of macromolecules even in solutions so dilute that all solutes have been hitherto assumed to be independent. It is surprising that there are virtually no functional groups in polymer I which bring about intermolecular forces such as coulombic, charge transfer, or hydrophobic forces. One possibility is the very weak charge transfer interactions between carbazyl and terephthalate groups in the ground state, which cannot be detected by absorption spectroscopy. Recent findings concerning stereospecific ground state interactions between benzene and very weak electron donating or electron accepting ethylenes detected

Table II
Dependence of F_e/F_m on Solvent Compositions

	Relative value of F_e/F_m in mixed solvents (F_e/F_m in THF = 1.00) n-hexane/THF = 28 (v/v)	 Ethanol/THF = 28 (v/v)
III + DMT (0.18 mol/dm^3)	1.54	0.09
I (5 × 10^{-4} mol/dm^3)	1.22	0.13

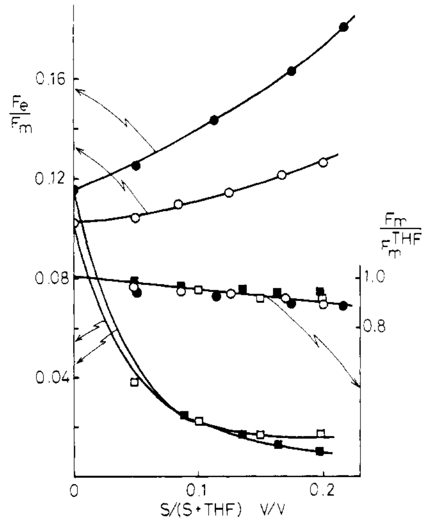

Figure 5. Effects of mixed solvent on exciplex emission: (○) [I] = 5 × 10^{-4} mol/dm^3, S = n-hexane; (●) [III] = 1.2 × 10^{-4} mol/dm^3, [DMT] = 0.18 mol/dm^3, S = n-hexane; (□) [I] = 5 × 10^{-4} mol/dm^3, S = ethanol; (■) [III] = 1.2 × 10^{-4} mol/dm^3, [DMT] = 0.18 mol/dm^3, S = ethanol.

by NMR spectroscopy but not by absorption spectroscopy[19] may warrant the concept of a ground state interaction in the present system. Even if the binding force of a unit pair is weak, association of polymer chains in polymeric systems would be enhanced by "zippering". Another factor contributing to polymer association is the configuration of the polymer. One can see from a molecular model of I that the space between two side chains is adequate to accomodate the carbazyl group. When a carbazyl group approaches to the polymer molecule, the model in which the approaching carbazyl group is located above the terephthalate unit in the main chain will be a favorable conformation.

The change in the intercept of F_e/F_m at infinite dilution is over sevenfold as shown in Figure 3b whereas τ_f increases only by a factor of 4 when the solvent is changed from THF to dioxane. The τ_f for I is 7.6 and 31 nsec in THF and in dioxane, respectively. In addition to the effects of dielectric constant,[18,20] the prominent solvent effect in intramolecular exciplex emission would arise from a change in dimension of a polymer molecule as a function of solvent. A more expanded conformation of a polymer is expected in THF than in dioxane as manifested by the fact that η_{sp}/c in THF is 0.15, whereas that in dioxane is 0.13 for 1% solution. Stronger intramolecular interaction should be favored in poorer solvents as has been suggested for polystyrene.[3]

Exciplex Emission in Mixed Solvent Systems. Further results of the solvent effects on the F_e/F_m of I are shown in Figure 5. As expected, the values of F_e/F_m of both monomer and polymer systems increase and decrease on addition of nonpolar solvent (*n*-hexane) and polar solvent (ethanol), respectively. The effect is mostly on F_e, since F_m is not affected much by solvent as shown by the plots of F_m/F_m^{THF} in Figure 5. The enhancement of F_e/F_m by addition of 20% *n*-hexane by volume corresponds to the increase in τ_f of exciplex emission. Under the same conditions as in Figure 5, the τ_f of exciplex formed by I in THF is 7.6 nsec whereas that in *n*-hexane–THF = 2:8 is 9.2 nsec. Both positive and negative solvent effects in F_e/F_m are less pronounced for the polymer system as shown in Table II. These results seem to indicate that the macroscopic solvent composition is different from the microscopic one in the vicinity of macromolecules where exciplex formation takes place. Since THF is a better solvent for I than *n*-hexane or ethanol, it is likely that a specific solvation sphere is formed in which the content of THF is richer than that expected from the bulk composition of mixed solvents.

Experimental Section

Materials. Preparation of polyesters (I and II) and the monomer model compound (III) has already been reported.[15] Dimethyl terephthalate (DMT) (Yoneyama Chemical Industry, Ltd.) was recrystallized once from toluene. Anthracene (Tokyo Kasei Kogyo, Ltd.) was column chromatographed and then recrystallized twice from ethanol. Dioxane, THF, *n*-hexane, and ethanol used for spectroscopy were purified by accepted procedures.

Fluorescence Spectroscopy. A Hitachi MPF-4 fluorescence spectrometer was used for recording emission and excitation spectra at room temperature. For the study of concentration dependence of F_e/F_m, fluorescence spectra of concentrated solutions required corrections at the wavelength region of monomer emission due to reabsorption of emitted light by the solute. This spectrometer has a light path of 0.5 cm for emitted light when the slit for exciting light is narrow enough. Then, the monomer fluorescence (F_m) to be employed for calculation of F_e/F_m is given by (1) neglecting the effect of secondary emission, where F_m is the observed intensity of monomer emission, c is the concentration of solute, and ϵ is the molar extinction coefficient of the solute at the wavelength of monitoring fluorescence. The correction factor is less

$$\log F_m/F_m' = 0.5\epsilon c \qquad (11)$$

than 5% for I at 368 nm at a concentration of 1×10^{-2} mol/dm^3. For II and III, the correction factors are much smaller.

Quantum Yield of Fluorescence (ϕ_f). The ϕ_f values were determined for dilute solutions in the concentration region in which a linear relation between the integrated fluorescence intensity and the absorbance of the sample solution at the wavelength of excitation was sustained. Such a condition was satisfied for the solutions having an absorbance of less than 0.05. All measurements were conducted under a nitrogen atmosphere and a $\phi_f = 0.28$ for anthracene in ethanol solution[21] was adopted as standard.

Lifetime of Fluorescence (τ_f). The τ_f values were determined by means of phase shift method using a FL-10 phase fluorometer, Japan Spectroscopic Co. Ltd. A desired emission wavelength was selected by inserting appropriate filters.[22]

References and Notes

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