it has been the general practice to interpret the spectra on the same basis as with thermally degraded polymers.[15,16] In this latter case although the evidence is somewhat conflicting[11,17] it is clear that the radical concentrations must be very much lower than with the γ irradiated specimens. However, Ohnishi, Nakajima, and Nitta,[4] citing unpublished calculations of Morokumo, have pointed out that the absorption bands of polyenyl radicals occur at significantly longer wavelengths than conventional conjugated polyenes of equal n value. For example, with $n = 6$ the values are 430–435 nm and about 365 nm, respectively. If this can be substantiated it will be necessary to accept lower n values than those previously suggested. The assignment of the n values from the resonance Raman measurements does not depend upon the relationship between the wavelengths of the absorption maxima and the conjugated sequence length. It is dependent upon the empirical relation established[5] between the precise frequency of ν_1 and ν_2 and the n value. However, in view of the effective increase in conjugation of the polyenyl radical of a given value it seems probable that the values of ν_1 and ν_2, for a given n, will be lower in the case of the polyene radical. Hence, equal doubt about the precise lengths of the conjugated polyene radicals may well exist in the case of the resonance Raman results. This uncertainty is of no consequence for the interpretation of the measurements reported above because we have been concerned with comparative rather than absolute n values.

Acknowledgments. The authors express their gratitude to Mr. P. J. Fydelor of the Department of Physics, Royal Military College of Science, Shrivenham, for undertaking the γ irradiation of the samples used in this study. They are also indebted to the School of Chemical and Physical Sciences, Kingston Polytechnic, for the time made available on the JEOL Raman spectrometer, to Dr. R. J. H. Clark, Department of Chemistry, University College, London, for the use of the Spex Ramalog Spectrometer, and to a referee for helpful comments on cross-linking reactions. Permission to publish this paper has been given by The British Petroleum Company Limited.

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Inter- and Intramolecular Interactions of Polymers as Studied by Fluorescence Spectroscopy. 6. Exciplex of Poly[oxy-2-(9-anthryl)methylpropyleneoxy-(4-*N*,*N*-dimethylaminobenzyl)malonyl]

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ABSTRACT: Poly[oxy-2-(9-anthryl)methylpropyleneoxy(4-*N*,*N*-dimethylaminobenzyl)malonyl] (PE(A-1D)) was prepared by polycondensation of the corresponding 1,3-propanediol with the corresponding diethyl malonate. Anthryl groups as electron acceptors and *N*,*N*-dimethylanilino groups as electron donors were alternatively arranged along a polyester main chain so that strong exciplex emission was observed. From the results of absorption, emission, and excitation spectra, inter- and intramolecular interactions of the polymer were discussed. Comparison of absorption spectra of PE(A-1D) with the monomer model compounds 1,3-diacetoxy-2-(9-anthryl)methylpropylene (II) and diethyl (4-*N*,*N*-dimethylaminobenzyl)malonate (I) indicated the presence of weak ground state interactions between chromophores. Solvent effects on intensity, lifetime, and/or peaking wavelength of the exciplex emission from PE(A-1D) were compared with those on the exciplex emission from 1-anthryl-3-(4-*N*,*N*-dimethylanilino)propane(III) and the anthracene–*N*,*N*-dialkylaniline system. It was concluded that the exciplex by PE(A-1D) was less susceptible to solvent polarity in comparison with the exciplex by III and the anthracene–dialkylaniline system due to hindered solvation and restricted mobility of chromophores in PE(A-1D). The transient absorption spectrum of the exciplex by PE(A-1D) in DMF agreed with that of anthracene anion radical indicating the ion-paired state is still emissive in the polymeric system. The ratio of exciplex emission (I_E) to that of monomer emission from anthryl groups (I_M) increased with concentration suggesting the interpolymer association in the concentration region of 10^{-4} M. The driving force of interpolymer association was attributed to the weak ground state interactions. It was also confirmed that excitation of either anthryl groups or *N*,*N*-dimethylanilino groups equally brought about the exciplex formation.

Studies on the excited state interactions of chromophores which are chemically bound to polymers provide various information relevant to the segment mobility, the local concentration of polymer bound functional groups, the inter- and intramolecular interactions, and the environment surrounding the chromophores in polymeric systems.

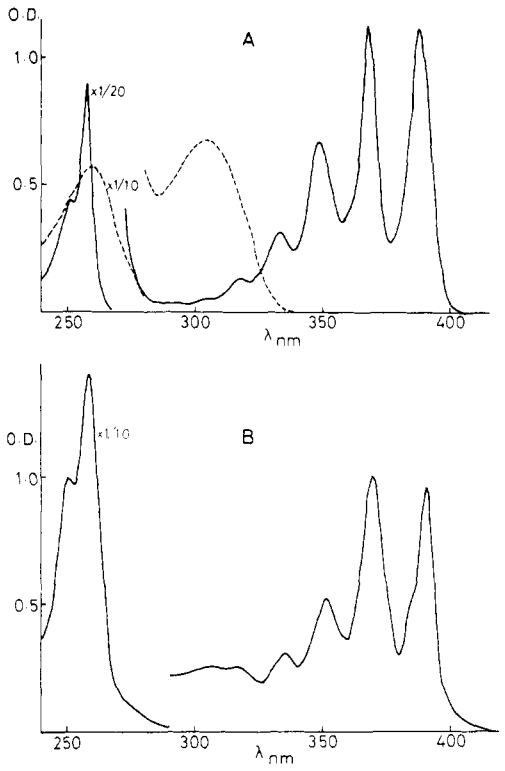


Figure 1. Absorption spectra of PE(A-1D) and its monomer model compounds in THF: A, (—) [II] = 1.04×10^{-4} M, (- - -) [I] = 2.26×10^{-4} M; B, [PE(A-1D)] = 9.17×10^{-5} M.

In previous articles, we discussed exciplex formation between carbazolyl side groups and terephthalate main chain[1] and excimer formation of polymer bound naphthyl[2] and anthryl[3] groups. The results are summarized as follows. (i) Excimer formation in polymer systems is much more efficient than that in the corresponding dimer model systems. (ii) Aggregate of polymer molecules has been suggested by the concentration dependence of the relative intensity of excimer or exciplex emission. (iii) The polymer bound exciplex is less susceptible to solvent effects. (iv) The structure of polymers reflects sensitively on the ease of excimer formation.

In view of comparing excimer and exciplex formation between polymer side groups, we are presenting the spectroscopic study on polymer bound exciplex formed between pendant anthryl groups and pendant *N,N*-dimethylanilino groups. This polymer is briefly reported in connection with the quenching study of exciplex systems.[4]

An advantage of dealing with the anthracene (A)–*N,N*-dialkylaniline (D) pair is the fact that the exciplex from the pair either freely separated[5] or linked by a polymethylene chain[6] has been already well studied so that comparison of the polymer bound exciplex with $D(-CH_2-)_nA$ and D + A is possible.

Experimental Section

Materials. Diethyl (4-*N,N*-Dimethylaminobenzyl)malonate(I). Diethyl (4-*N,N*-dimethylaminobenzylidene)malonate (30 g) prepared by base-catalyzed condensation of *p*-*N,N*-dimethylaminobenzaldehyde with diethyl malonate was hydrogenated in an autoclave under the hydrogen pressure of 15 kg/cm^2 at 70 °C using Pd on charcoal as a catalyst. The yield was 23 g (76%); bp 165–170 °C (4 mm); IR (neat) 1730 cm^{-1} (ester carbonyl); NMR ($CDCl_3$) δ 1.17 (6 H, t, J = 7 Hz, $CO_2CH_2CH_3$), 2.89 (6 H, s, $N(CH_3)_2$), 3.13 (2 H, d, J = 8 Hz, CH_2Ar), 3.65 (1 H, t, J = 8 Hz, >CH–), 4.20 (4 H, q, J = 7 Hz, $CO_2CH_2CH_3$), 6.94 (4 H, aromatic).

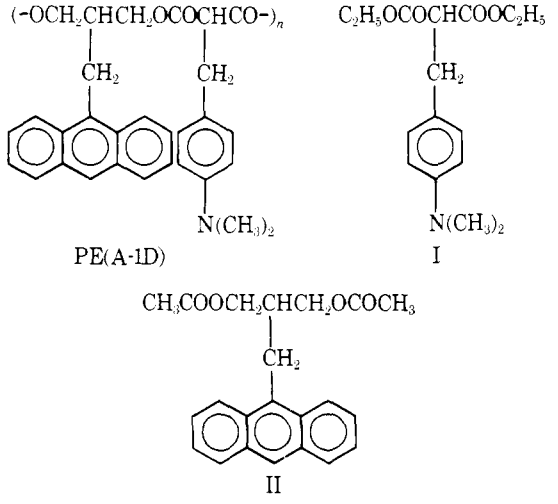
Poly[oxy-2-(9-anthryl)methylpropyleneoxy(4-*N,N*-dimethylaminobenzyl)malonyl] (PE(A-1D)). Equimolar amounts of I and 2-(9-anthryl)methyl-1,3-propanediol[3] were heated to allow polycondensation as described previously.[2] The molecular weight was estimated as 2000 ($\overline{DP}$ = 4–5) by gel permeation chromatography.

Solvents. Tetrahydrofuran was dried over $LiAlH_4$ and distilled. Other solvents were purified by accepted procedures.

Spectroscopy. Absorption and fluorescence spectra were measured by a Hitachi EPS-III spectrometer and a Hitachi MPF-4 spectrofluorometer, respectively. An attachment of the spectrofluorometer for time-resolved fluorescence spectroscopy was used to determine the fluorescence lifetime. Fluorescence spectroscopy was conducted under nitrogen atmosphene, and no correction was made on the fluorescence spectra.

Results and Discussion

Absorption Spectroscopy. Absorption spectra of PE(A-1D) and the monomer model compounds, I and II, are shown in Figure 1. The shape of the absorption spectrum of PE(A-1D) is identical with the sum of those of I and II, indicating



seemingly the absence of the ground state interactions. However, quantitative comparison of the broadness of spectra expressed arbitrarily by the ratio of the minimum absorbance at 359 and 379 nm to the peak absorbance at 390 nm suggests the presence of weak interactions between chromophores as presented in Table I. The absorption spectrum of the anthryl group in PE(A-1D) is slightly broader than that of the monomer model compound.

The ground-state interactions of exciplex-forming systems have been discussed for pyrene–DMA,[7] anthracene–DMA, DEA, 1,2,4,5-tetracyanobenzene–THF, and 1-(2 or 9-anthryl)-3-(*p*-*N,N*-dimethylaminophenyl)propane[8] either in low temperature matrices or in fluid solutions at room temperature. So far as anthracene–DMA system is concerned, there is obviously weak molecular association at room temperature. The temperature dependence of the UV absorption spectra of the relatively concentrated pyrene–DMA system was interpreted as the result of a weak CT complex formation at lower temperature and of contact CT complex formation at higher temperature.[8] Such weak but definite ground state interactions would influence the absorption spectra of PE(A-1D) as well. The minimum/maximum ratios of absorbance presented in Table I are, however, independent of concentration between 10^{-5} and 1×10^{-3} M within the accuracy of ±2%, indicating the interaction to be mostly intramolecular.

Table I
Broadness of Absorption Spectra of PE)a-1D) and II at the ^1L_a Band of Anthracene

	OD_{380}/OD_{390}	OD_{370}/OD_{390}	OD_{359}/OD_{390}
II	0.250	1.010	0.324
PE(A-1D)	0.308	1.043	0.374
Difference, %	+23.2	+3.3	+15.4

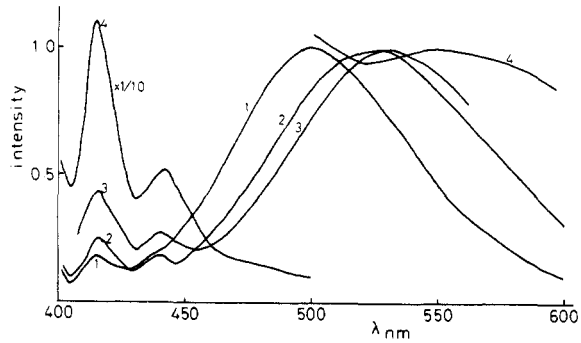


Figure 2. Emission spectra of PE(A-1D) in various solvents, [PE(A-1D)] = 1×10^{-4} M: 1, toluene; 2, THF; 3, methyl isobutyl ketone; 4, DMSO.

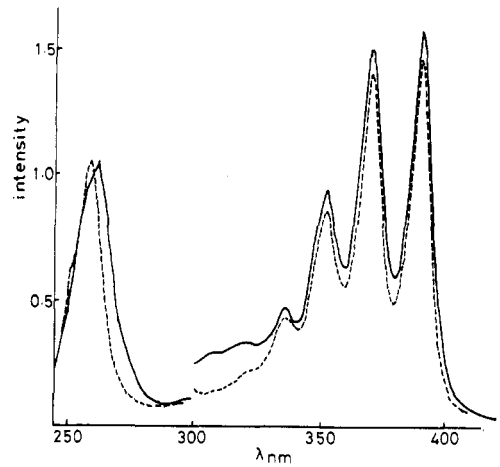


Figure 3. Excitation spectra of PE(A-1D) in THF: (- - -) monitoring at 415 nm (monomer emission); (—) monitoring at 515 nm (exciplex emission).

Emission and Excitation Spectra. Emission spectra of PE(A-1D) brought about by exciting the ^1L_a band of anthryl groups in various solvents are shown in Figure 2. The relative intensity of exciplex emission, I_E/I_M, is very much higher than that of anthracene–DMA system of comparable concentration, where I_E and I_M are the intensities of exciplex and monomeric emission, respectively. To obtain the equivalent value of I_E/I_M in the anthracene–DMA system, the DMA concentration has to be in the order of 10^{-1} M. Consequently, the apparent concentration of DMA in the polymer system shown in Figure 2 may be assumed to be 10^3 times higher than the bulk concentration of PE(A-1D) on the assumption that the rate constants of the photophysical processes in the polymer system are identical with those of the anthracene–DMA system. To forward the discussion on polymer effects on exciplex formation, dynamics of exciplex formation in the polymer system have to be analyzed.

An advantage of studying the polymer bound exciplex is the fact that the concentrations of both donor and acceptor are identical and can be kept low, which enables the measurement of excitation spectra over the whole region of absorption. The excitation spectra in Figure 3 and the absorption spectra in Figure 1 indicate the presence of two exciplex-forming processes, (1) and (2).

$$A^* + D \rightarrow (AD)^* \quad (1)$$

$$A + D^* \rightarrow (AD)^* \quad (2)$$

It was confirmed that excitation of either A or D brought about identical exciplex emission. The endothermic process (eq 3) was not detected by scanning the monitoring wavelength between 300 and 380 nm, the peak absorption of the anthryl group at 390 nm being excited.

$$A^* + D \rightarrow (AD)^* \rightarrow A + D^* \quad (3)$$

The ground-state interactions discussed in the previous section seem to participate in the exciplex formation. The shapes of excitation spectra are analyzed by calculating the intensity ratios as tabulated in Table II. The broadness of the excitation spectra depends slightly on the monitoring wavelength. The higher intensities of excitation spectra at 380 and 359 nm when the exciplex emission is monitored, relative to those determined by monitoring the monomer emission, would be the reflection of D–A interactions in the ground state (eq 4).

$$D + A \rightleftarrows DA \xrightarrow{h\nu} (DA)^* \quad (4)$$

Although the presence of various exciplexes has been proposed for the anthracene–DMA system in cyclohexane matrix,[8] the shape of the exciplex emission from PE(A-1D) is independent of the wavelength of excitation suggesting the presence of only one exciplex species.

Table II
Dependence of Excitation Spectra of PE(A-1D) on the Monitoring Wavelength

Monitoring wavelength, nm	I_{380}/I_{390}	I_{370}/I_{390}	I_{359}/I_{390}	I_{305}/I_{390}
414	0.331	0.964	0.377	0.088
515	0.362	0.954	0.388	0.164
Difference, %	+9.4	−1.0	+2.9	+86.4

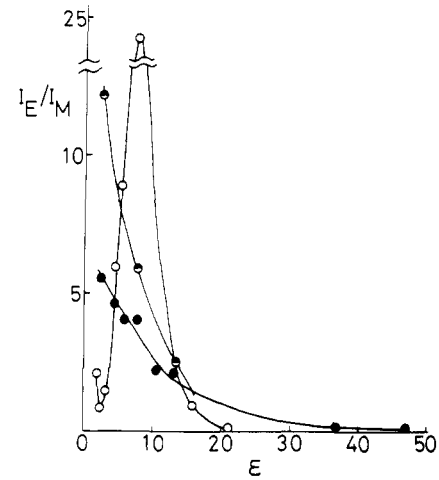


Figure 4. Relative intensity of exciplex emission as a function of solvent polarity: (●) PE(A-1D) (I_E/I_M), (○) III (ϕ_E/ϕ_M);[6a] (◓) anthracene-*N*,*N*-dimethylaniline (I_E/I_M).

Solvent Effects on Wavelength, Intensity, and Lifetime of Exciplex Emission. The general effects of increasing solvent polarity upon intermolecular exciplex formed between small molecules are to shift the peaking wavelength to a longer wavelength region and to decrease both the intensity and the lifetime of exciplex emission. These general trends are observed for both the anthracene (A)–*N*,*N*-dialkylaniline (D) system and PE(A-1D). However, the emission behavior of PE(A-1D) shown in Figure 2 is much less susceptible to solvent polarity. It is noteworthy that the exciplex emission from PE(A-1D) can still be detected in extremely polar solvents, DMF (ε 36.7) and DMSO (ε 46.7), whereas the exciplex emission of the A–D system is not detected in acetonitrile (ε 37.0).[9] As shown in Figure 4, the smaller dependence of I_E/I_M on

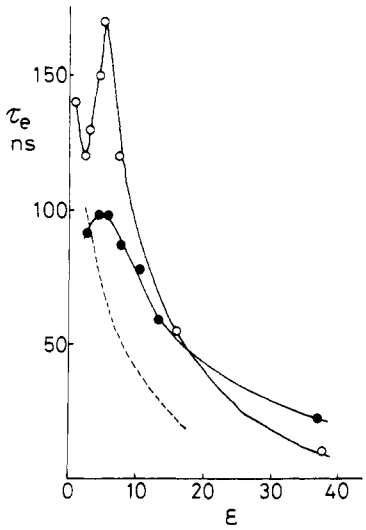


Figure 5. Lifetime of exciplex as a function of solvent polarity: (●) PE(A-1D); (○) III;[6a] (- - -) anthracene–*N,N*-diethylaniline.[5d]

PE(A-1D), where I_E and I_M are the intensities of exciplex and the locally excited state of the anthryl group, respectively, on solvent polarity in comparison with 1-(9-anthryl)-3-(4-dimethylaminophenyl)propane (II) and the A–D system, would be a characteristic of polymer effect. From the statistical viewpoint, III should have higher probability of exciplex formation than PE(A-1D) on the assumption that neighboring groups alone participate in exciplex formation by PE(A-1D). Since the classical work by Hirayama[10] presenting the $n = 3$ rule for the excimer formation between chemically bound chromopores, various intramolecular excimer and exciplex systems have been investigated.[11–13] Although the original proposal of the $n = 3$ rule should be revised according to the recent results, it is now widely accepted that the separation between chromophores by three methylene groups is the most favorable condition to bring two chromophores together in a face-to-face orientation. The ease of intermolecular excimer formation by a pair of a given separation seems to be a function of the lifetime of the locally excited state as well as the strictness of the orientational requirement. For example, α,ω-diphenylalkane forms excimer only when phenyl groups are spaced by a propylene group whereas the intramolecular excimer of α,ω-dipyrenylalkane is observed for a wide range of the spacing polymethylene chain.[14] The excimer emission is the weakest when the spacing methylene groups are between 4 and 8. At this region of separation, the peaking energy of excimer emission is higher than that of normal intermolecular excimer emission of pyrenyl groups indicating the distorted structures of the intramolecular excimers. Although the parallel orientation of donor and acceptor is a favorable condition also for exciplex formation, the steric requirement is not as strict as in the case of excimer formation. The exciplexes of $D(-CH_2-)_nA$ are observed for $n = 3,2$, and 1 when A is 9-anthryl or 1-pyrenyl, D being *N,N*-dimethylanilino group.[6a,12] The exciplex quantum yield decreases with decreasing n and the unstable exciplexes ($n = 2$ and 1) require additional stabilization by solvation to be emissive.

Construction of a molecular model of PE(A-1D), however, shows that the structure favorable for exciplex formation is easily attainable by locating the C_2 axis of D parallel to the long axis of A, the spacing between D and A being about 3 Å. The neighboring groups seem to reinforce the exciplex structure by restricting the mobility of D and A. The participation of nonneighboring groups in exciplex formation is also to be considered. The molecular weight dependence of the intensity of the polymer-bound exciplex between carbazolyl

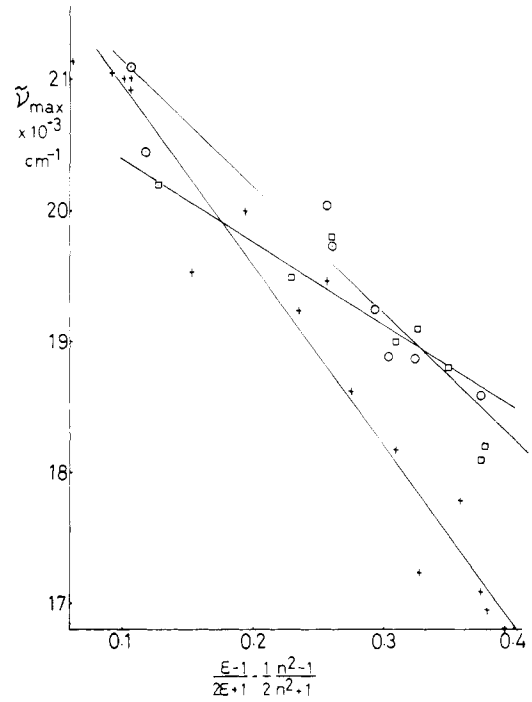


Figure 6. The Lippert–Mataga plots: (□) PE(A-1D); (+) III;[6c] (⊙) anthracene–*N,N*-diethylaniline.[5c]

and terephthalate groups[1b] would be the manifestation of D and A to be in the aggregate state whose local concentration is a function of the size of polymer. Participation of energy migration along the polymer chain in exciplex formation by PE(A-1D) is highly unlikely, since anthryl groups are separated by D and the process $A^* + D \rightarrow D^* + A$ is not feasible as already mentioned.

The emission behaviors of PE(A-1D) and III are distinctively different in nonpolar solvents. The relative exciplex emission by PE(A-1D) and the A–*N,N*-diethylaniline system in nonpolar solvent is strong whereas that of III is weak. A certain degree of stabilization by solvation was explained to be necessary for the exciplex by III. For PE(A-1D), large freedom would be afforded to the relative orientations of chromophores and therefore PE(A-1D) behaves like a pair of monomeric A and D whose exciplex emission is the strongest in *n*-hexane.

The lifetime of exciplex by PE(A-1D) is also insensitive to solvent polarity relative to that of III or the A–D system as shown in Figure 5. The lifetime of exciplex by PE(A-1D) in DMF is as long as 22 ns whereas that of III is ~5 ns. The increase in solvent polarity brings about the decrease in exciplex lifetime as well as the exciplex intensity, the later being more pronounced. This has been interpreted as due to the decreased emission probability of exciplex. On the contrary, the nonradiative decay process is facilitated by solvation. Further increase in solvent polarity eventually induces ionic dissociation of the exciplex. However, ionic dissociation of both PE(A1-D) and III is not possible. Anthryl and *N,N*-dimethylanilino groups would therefore be present as an ion pair or a zwitter ion in the excited state. To confirm the relative degree of solvation, the Lippert–Mataga plots are shown in Figure 6. As expected from the results shown in Figures 1 and 2, solvent effect on the peaking wavelength of exciplex emission is smaller for PE(A-1D) than for III or the D–A pair. The reduced solvation of PE(A-1D) would account for the difference, the structure of chromophores being the same.

Preliminary results on ns flash photolysis of PE(A-1D) in DMF[15] indicate that the exciplex is indeed an ion pair. The $S_n \leftarrow S_1$ absorption shows the maximum at ~14 000 cm^{-1},

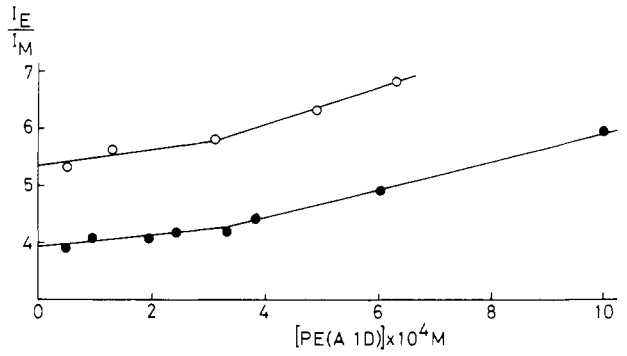


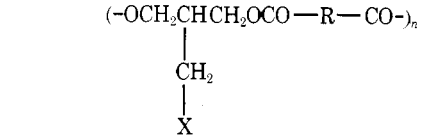
Figure 7. Concentration dependence of I_E/I_M of PE(A-1D): (○) in toluene; (●) in THF.

which agrees with the reported spectra of anthracene anion radical produced by radiation-induced one-electron transfer in 2-methyltetrahydrofuran at 77 K.[16] Furthermore, the lifetime of the absorption (~20 ns) is identical with that of exciplex emission.

There are accumulating results that both viscosity and polarity of solvent do not affect polymer-bound excimer and exciplex much in comparison with small molecular reference systems.[2a,17] The relatively weak solvent effects on the exciplex by PE(A-1D) may be interpreted as follows. The polymer-bound exciplex is protected by the polymer chain so that solvent molecules are not allowed to enter in the vicinity of exciplex and entire relaxation to nonradiative structures is not achieved even in very polar solvents. In addition, the polyester main chain may act as a moderately polar solvent which stabilizes exciplex. Such self-solvated exciplex would be insensitive to solvent effect. If the unrelaxed ion pair state is metastable due to restricted solvation, there should be a rapid equilibrium as below. This picture explains the identical lifetime of $A^{-}\cdot$ and $(AD)^*$ as well as the shorter wavelength of exciplex emission by PE(A-1D) than that by III or the D–A pair in polar solvents.

$$(DA)^* \rightleftarrows (D^+A^-)_{\text{nonrelaxed}} \rightarrow \text{reaction or back-electron transfer} \quad (5)$$

Concentration Dependence of Exciplex Emission. The concentration dependence of I_E/I_M depicted in Figure 7 proves the intermolecular interactions of PE(A-1D) in the concentration region of 10^{-4} M. A similar result was obtained in the case of poly[oxy-2-(9-carbazolyl)butylpropyleneoxyterephthaloyl][1a,b] also in the concentration region of 10^{-4} M. On the other hand, the concentration dependence of I_E/I_M of excimer emission is much weaker as shown by fluorescence spectroscopy of naphthyl,[2] anthryl,[3,18] and pyrenyl[17] groups chemically bound to polyesters having comparable main-chain structures to PE(A-1D) as shown below.[19] The I_E/I_M values of these polymer bound excimers are independent of concentration below 10^{-3} M, although the concentration dependence of I_E/I_M was observed at higher concentration. Since the I_E/I_M–concentration relation depends on the degree of polymerization[1b] and all polymers studied are not of identical degree of polymerization, detailed discussion is not possible. Nevertheless, the exciplex-forming polymers are more prone to interpolymer interactions than the excimer-forming polymers. The sequence of the degree of polymerization of polymers is as follows: the pyrenyl polymers > the carbazolyl terephthalate polymer > PE(A-1D), the anthryl polymers, the naphthyl polymers. Whereas the ease of interpolymer interactions is in the following order: PE(A-1D), the carbazolyl terephthalate polymer > the pyrenyl polymers, the anthryl polymers, the naphthyl polymers. This result seems reasonable since the intermolecular forces operating between a weak D–A pair must be stronger than between like molecules. Small intermolecular forces could be multiplied as a result of the "zipping" process in polymer systems.



X = 1-naphthyl, 9-anthryl, 1-pyrenyl
R = >CHCH$_2$–X, $(-CH_2-)_2$, $(-CH_2-)_4$, $(-CH_2-)_6$, $(-CH_2-)_8$, $(-CH_2-)_{10}$, $-C_6H_4-$

Acknowledgment. The authors are greatly indebted to Professor N. Mataga and Dr. H. Masuhara, Faculty of Engineering Science, Osaka University, for ns flash photolysis and stimulating discussions on the dynamic properties of exciplex.

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