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(13) (a) Yuan, H. L.; Tazuke, S. Symposium on Photochemistry, Sapporo, Sept 1981, Preprints, p 223. (b) Yuan, H. L.; Tazuke, S. The 30th Polymer Symposium, Tokyo, Oct 1981. *Polym. Prepr., Jpn.* **1981**, *30* (6), 1048. (c) Yuan, H. L.; Tazuke, S. The 45th CSJ Annual Meeting, Okayama, Oct 1981, Preprints.
(14) This does not mean that monomer emission alone is observed at 77 K. Instead of exciplex emission, new emission appears around 430 nm, which is tentatively attributed to the emission from the excited EDA complex formed in the ground state.
(15) Although the rate constant of chain transfer to 4 will be independent of DP, a growing radical occluded in the high molecular weight polymer domain would have more chance for chain transfer to the polymer before being bimolecularly terminated. Radical polymerization of methacrylates is susceptible to the gel effect, and the termination rate constant is a function of segment diffusion rather than diffusion of whole polymer molecules (North, A. M.; Reed, G. A. *Trans. Faraday Soc.* **1961**, *57*, 859. *J. Polym. Sci., Part A-1* **1963**, *1*, 1311). The present methacrylate, bearing bulky side groups, is likely to fall in this category. With increasing DP, the distance of segment diffusion for bimolecular termination increases and consequently, the possibility of polymer chain transfer will increase.

Inter- and Intramolecular Interactions of Polymers As Studied by Fluorescence Spectroscopy. 10. Excimer Formation by Polyesters Bearing Pyrenylmethyl Groups and Their Dimer Model Compounds

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ABSTRACT: Thermodynamic parameters for excimer formation by polyesters bearing pyrenylmethyl groups and their dimer model compounds were studied. The polymer samples were prepared by polycondensation of 2-[(1-pyrenyl)methyl]-1,3-propanediol with thiophenyl esters of succinic acid (PE(Py-2)), adipic acid (PE(Py-4)), sebacic acid (PE(Py-8)), and decanoic acid (PE(Py-10)). Corresponding dimer models were prepared from the monoacetate of the diol and the diacyl chloride of dibasic acids (DE(Py-2), DE(Py-4), DE(Py-8), and DE(Py-10)). The peak wavelength of excimer emission was 475 nm. The relative intensity of excimer emission (F_d) to that of monomer emission (F_m) was taken as an index of interactions between chromophores. Different from polymer-bound exciplex systems, these PE and DE polyesters did not exhibit interpolymer association. Intrapolymer excimer formation required good segment mobility, and evidence for preformed excimer sites was not obtained. Excimer formation by the polymers was 5–10 times more efficient than that by corresponding dimer models whereas the monomer model compound (the diacetate of the diol) did not form excimer at all at a concentration of 10^{-5} M. Thermodynamic parameters for intramolecular excimer formation indicated that excimer formation by the polymers was favored both enthalpically and entropically over the relevant dimer models. The restricted segment mobility in the polymers brought about a higher activation enthalpy of both formation and dissociation of intrapolymer excimer in comparison with the dimer models, the dissociation process being more strongly retarded by the polymer chain. High local chromophore concentration in the polymers could not explain the difference in the temperature-independent part of thermodynamic parameters. The low entropy state of polymer-bound chromophores seemed to facilitate the entropy-losing process of excimer formation. The role of energy migration was also discussed. Based on these results the origin of polymer effects on segment interactions was analyzed.

Excited-state interactions in polymeric systems have been of interest from the standpoints of both fundamental and applied research.[1] Besides the purpose of studying the photophysics of excimer in polymer, excimer formation can serve as a useful label to study molecular interactions in polymers. Among the variety of fluorescent probes detecting hydrophobicity, segment mobility, and so on, excimer-forming chromophores provide information on molecular interactions.[2]

We have been interested in various kinds of molecular interactions as a basis of functionalized polymers.[1a] As indices of molecular interactions we chose excited-state interactions such as exciplex,[3] excimer,[4] and fluorescence quenching[5] as well as ground-state interactions such as

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Table I
Spectroscopic Properties of Samples

sample	no. of atoms separating pyrenyl groups	MW[a]	absorption spectra[b] ^1L_a $10^{-4}\epsilon_{max}$ at 344 nm	^1L_b ϵ_{max} at 376 nm	fluorescence spectra[c] F_d/F_m
PE(Py-2)	12	5 100	3.17	570	5.00
PE(Py-4)	14	13 000	3.11	530	4.55
PE(Py-8)	18	46 000	3.32	530	4.15
PE(Py-10)	20	11 000	3.21	530	2.51
DE(Py-2)	12	747	3.71	550	0.67
DE(Py-4)	14	775	3.70	490	1.08
DE(Py-8)	18	831	3.81	550	0.81
DE(Py-10)	20	859	3.75	570	0.97
MEPy			3.77	590	0.00

[a] From GPC.[22] [b] In THF. [c] In toluene at 20 °C; F_d at 475 nm, F_m at 376 nm, excitation at 344 nm in an Ar atmosphere atmosphere. [Py] = (1-3) × 10^{-5} M.

electron donor–acceptor (EDA),[6] hydrophobic, and Coulombic interaction.[7] Characteristics of excimer as a probe are as follows: (i) polarization or ionic effects can be neglected; (ii) thermodynamic measurements will provide information on the environment of the excimer-forming site; (iii) since a fluorescence measurement technique is used, the sensitivity is very high; (iv) excimer-forming fluorophores are, in general, stable aromatic hydrocarbons and easy to handle. Using a series of polymers of well-defined structure bearing excimer-forming fluorophores, we can expect information on the interaction between fluorophores as a function of polymer structure. Comparing with appropriate dimer or oligomer model compounds, specificity in molecular interactions in polymer will be clarified. To investigate the origin of "polymer effects" and to find out the difference between polymers and small molecules are our ultimate purpose.

Previously, we reported excimer formation by naphthyl groups attached to polyesters with designed intervals.[4a] Although the excimer formation was not particularly efficient and, therefore, the experimental results were subject to comparatively large errors, we could derive a conclusion that excimer formation by polymer-bound fluorophores was entropically favored in comparison with the dimer model compounds. For the purpose of improving the accuracy of measurements and elaborating the dimer model compounds, we chose the pyrenyl group as an excimer-forming probe in the present study. Also exact dimer models relevant to each polymer were prepared. The main advantage of using pyrenyl groups is the long singlet lifetime of the pyrenyl group and subsequent efficient excimer formation. Furthermore, the fluorescence quantum yield is higher than for the naphthyl group so emission spectroscopy can be conducted at extremely low concentrations, i.e., below 10^{-5} mol·dm^{-3}.

The conditions enabled us to study intrapolymer interactions of pendant pyrenyl groups, avoiding all complications that arise at higher concentrations.

Results and Discussion

Spectroscopic Characteristics of Samples. The structures and abbreviations of the samples are shown in Chart I and their absorption and emission characteristics are summarized in Table I. Comparison of the absorption spectra shown in Figure 1 shows that there is little difference between polymers and dimer or monomer models. While the absorption maxima corresponding to the $S_0 \rightarrow S_2$ (^1L_a) and the $S_0 \rightarrow S_1$ (^1L_b) transitions of the pyrenyl group are identical for all samples, the molar absorbance (ϵ) at 344 nm is about 20% smaller for polymers relative to dimer or monomer model compounds. A close look at the absorption spectra (Figure 1) reveals that the decrease in ϵ for polymers is probably not due to an overall decrease in oscillator strength but attributable to broadening of the spectrum. This tendency seems to be a general trend of polymer-bound chromophores as discussed for polyesters and polyurethanes bearing pendant anthryl groups.[4b] There is a significant difference between polymer and dimer whereas the spectra of dimer and monomer models are identical. Consequently, the observed spectrum broadening is not the result of neighboring group interactions but attributable to the aggregated state of the chromophores.

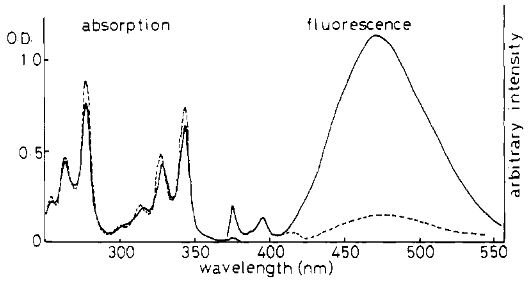
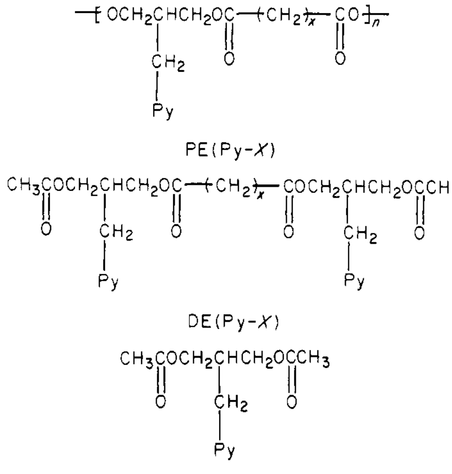


Figure 1. Absorption ([Py] = 2 × 10^{-5} M; 25 °C in THF) and emission ([Py] = 2 × 10^{-5} M; 25 °C in toluene) spectra of (—) PE(Py-2) and (---) DE(Py-2). Excitation at 344 nm.

Chart I[a]



PE(Py-X)

DE(Py-X)

MEPy

[a] Py = 1-pyrenyl.

Contrary to the absorption spectra, the emission spectra of the polymer, dimer, and monomer are prominently different. Both polymers and their dimer model compounds emit excimer fluorescence at 475 nm besides

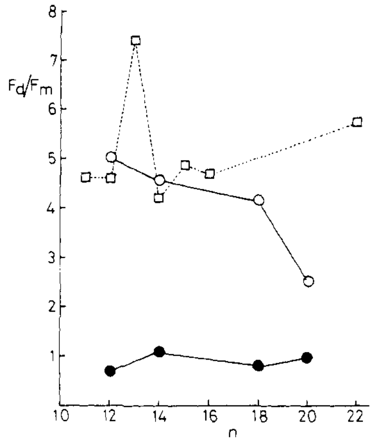


Figure 2. Excimer intensity as a function of separation between chromophores: (○) PE(Py-X), $n = X + 10$; (●) DE(Py-X), $n = X + 10$; (□) Py-$(CH_2)_n$-X.[8]

monomer fluorescence peaking at 376 nm.

An intensity difference of excimer emission by a polymer and by the relevant dimer model is a common feature for this type of polymer.[4a] In the previous article on the fluorescence study of similar polyesters with pendant naphthyl groups and their dimer model compounds, higher excimer-forming efficiency in polymeric systems was the general trend as well, and the thermodynamic parameters of excimer formation indicated that excimer formation by polymers was entropically favored over that by dimer models.[4a] However, the excimer intensity of naphthyl groups is rather weak and the measurements are accompanied by relatively large errors.

Excimer by pyrenyl groups is strong enough for precise measurements. The excimer intensity relative to the monomer intensity (F_d/F_m) decreases with increasing separation between chromophores bound to the polymer whereas the magnitude of F_d/F_m for dimer models is not simply related to the length of the spacing group as shown in Figure 2. When two pyrenyl groups are connected by a polymethylene chain, the excimer intensity also varies with the length of spacer in a complex fashion.[8] The differences between polymer and dimer is understandable if nonneighboring group participation in the polymeric system is considered. The encounter probability of chromophores in dimer is governed by the chain statistics of the spacer between the chromophores. Both experimental and theoretical studies on ring-closure reactions of X–n–Y indicate that the encounter probability of the terminally groups depends on the nature and the length of n.[9] In addition, the critical encounter distance (r_0) of X and Y below which X and Y couple to form a ring influences very much the probability as a function of n. For lactone formation, the calculated probabilities using $r_0 = 0.268$ nm agree with experiments, giving a maximum probability at $n = 19$.[10] When hydrolysis of terminal p-nitrophenyl ester by a terminal pyridyl group attached to a polysarcosine chain is compared with calculation, $r_0 = 0.4$–0.6 nm is required and the maximum probability appears at $n = 27$.[11] Excimer formation of α,ω-dipyrenylalkanes shows maximum F_d/F_m values at $n = 3$ and 13.[8] In this case, r_0 should be 0.3–0.35 nm, requiring face-to-face stacking. No comparable examples to DE(Py-X) are available.

Unlike DE(Py-X), a chromopohore in a polymer chain has a chance to meet a number of partners and consequently the concept of local chromophore concentration should be introduced. With increasing length of spacing group, the local chromophore concentration certainly decreases and the value of F_d/F_m decreases.

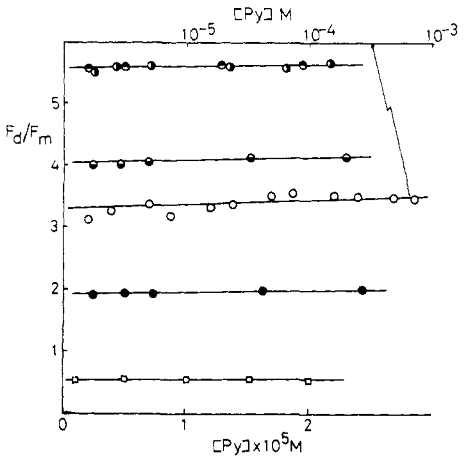


Figure 3. Concentration dependence of excimer intensity in THF. Low-concentration region: (◑) PE(Py-2); (◓) PE(Py-4); (⊖) PE(Py-8); (●) PE(Py-10); (□) DE(Py-2). F_d at 475 nm, F_m at 376 nm. High-concentration region: (○) PE(Py-10). F_d at 475 nm, F_m at 397 nm.

At this stage of the discussion we cannot attribute all of the differences between polymer and dimer to a concentration effect. Determination of thermodynamic parameters for excimer formation will provide the key information as discussed in the following sections.

Concentration Dependence of F_d/F_m. Although a study of the properties of dilute polymer solutions is generally based on the assumption that every polymer molecule exists independently from each other, we have many pieces of spectroscopic evidence supporting interpolymer association in extremely dilute solutions, even when the chromophore concentration is less than 10^{-1} mol·dm^{-3}. The condition for interpolymer association is to have weak ground-state interactions such as electron donor–acceptor (EDA)[3a,b,d,e] and hydrophobic interactions.[12] Even if these interactions are not detectable between isolated chromophores, interactions between polymer-bound chromophores are enhanced owing to a cooperative or zipping effect.[3e]

In comparison with exciplex-forming or micelle-forming polymers, interpolymer interactions of excimer-forming polymers in organic media are very weak.[4] For example, polyesters bearing pendant (1-naphthyl)methyl groups were shown to self-associate only at concentrations well above 10^{-3} mol·dm^{-1}.[4a] The same is true for polyesters bearing pendant (9-anthryl)mentyl groups.[4b,13] On the contrary, when the same (9-anthryl)methyl pendant groups were attached to polyionene as hydrophobic chromophores, interpolymer association in aqueous solution was suggested by the concentration-dependent excimer emission.[12] The present excimer-forming polyesters do not show any tendency for interpolymer excimer formation in the concentration region of 10^{-5} M as shown in Figure 3. As a matter of course, DE(Py-X) exhibit intramolecular excimer formation alone. An example is shown in Figure 3. Because of the small Stokes shift of the pyrenyl group, the emission spectra at high concentration are complicted. Since the monomer emission at 376 nm is subject to a reabsorption effect by the ^1L_b band of pyrene, we took the weaker monomer emission at 397 nm as a standard, and the concentration dependence of F_d/F_m was studied up to 10^{-3} mol·dm^{-3} as shown in Figure 3. The slope is only slightly positive. Above 10^{-3} mol·dm^{-3}, where previous polyesters bearing naphthyl or anthryl groups exhibited interpolymer excimer formation, we could not obtain reliable F_d/F_m values because of the reabsorption problem. The interpolymer association of anthracene polymers

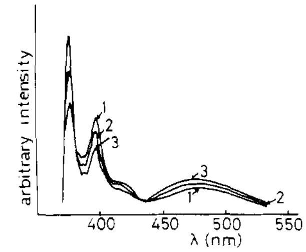


Figure 4. Fluorescence spectra of DE(Py-4) at various temperatures: (1) −39 °C; (2) −29 °C; (3) −19 °C. [Py] = 2×10^{-5} mol·dm^{-3} in toluene.

might be attributed to the tendency of ground-state dimer formation by anthracene. Consequently, we are dealing with intrapolymer excimer alone in our standard conditions of fluorescence measurements at the chromophore concentration of 2×10^5 mol·dm^3. The monomer model MEPy does not show excimer emission in the concentration region studied.

Thermodynamic Parameters of Intramolecular Excimer Formation. The kinetics of excimer formation is well established.[14] Assuming the elementary processes shown in eq 1[15] and steady-state concentrations for the excited state of the pyrenyl group ([M*]) and the excimer ([D*]), kinetic expression 2 is derived, where M denotes the ground state of the pyrenyl group.

$$\begin{tikzcd}
M \arrow[r, "h\nu"] & M^* \arrow[rr, shift left, "k_{Da}[M]"] \arrow[dl, "k_{Mf}"'] \arrow[d, "k_{IC}"] & & D^* \arrow[ll, shift left, "k_{Dd}"] \arrow[d, "k_{DIC}"'] \arrow[dr, "k_{Df}"] & \\
M + h\nu_f & M & & 2M & 2M + h\nu'_f
\end{tikzcd} \qquad (1)$$

$$F_d/F_m = k_{Df}k_{Da}[M]/k_{Mf}(k_{Df} + k_{Dd} + k_{DIC}) \qquad (2)$$

To derive the thermodynamic parameters, the following conditions were assumed: (i) $k_{Dd} \gg k_{Df} + k_{DIC}$ in the high-temperature region; (ii) $k_{Dd} \ll k_{Df} + k_{DIC}$ in the low-temperature region; (iii) $k_{Df} + k_{DIC}$ is independent of temperature. These assumptions are the same as those used in the previous study.[4a] The validity of assumption iii is shown by the clear isoemissive point at 428 nm at low temperature as shown in Figure 4. Following the same context discussed previously, we obtained two kinetic expressions applicable to the low- and high-temperature regions.

(i) Low-Temperature Region (Nonequilibrium System) ($k_{Dd} \ll k_{Df} + k_{DIC}$):

$$F_d/F_m = k_{Da}[M]/k_{Mf}$$

$$k_{Da} = Ke^{-\Delta G_{Da}^{\ddagger}/RT} \qquad (3)$$

where K is defined by $\kappa k_B T/h$ (κ = transmission coefficient and k_B = Boltzmann constant). Then

$$\log (F_d/F_m) = -\frac{\Delta H_{Da}^{\ddagger}}{2.303R}\frac{1}{T} + \frac{\Delta S_{Da}^{\ddagger}}{2.303R} + \log \frac{K[M]}{k_{Mf}} \qquad (4)$$

(ii) High-Temperature Region (Equilibrium System) ($k_{Dd} \gg k_{Df} + k_{DIC}$):

$$F_d/F_m = k_{Df}k_{Da}[M]/k_{Mf}k_{Dd} \qquad (5)$$

$$\log (F_d/F_m) = -\frac{\Delta H}{2.303R}\frac{1}{T} + \frac{\Delta S}{2.303R} + \log \frac{k_{Df}[M]}{k_{Mf}} \qquad (6)$$

Plots of log (F_d/F_m) vs. T^{-1} show a positive slope at high temperature, corresponding to the enthalpy of excimer formation, and a negative slope at low temperature, corresponding to the activation enthalpy of excimer formation as shown in Figure 5.

Table II
Thermodynamic Parameters of Excimer Formation

sample	$\Delta H_{Da}^{\ddagger}$, kcal/mol	$\Delta H_{Dd}^{\ddagger}$, kcal/mol	$-\Delta H$, kcal/mol	$\frac{\Delta S_{Da}^{\ddagger}}{2.303R} + \log \frac{K[M]}{k_{Mf}}$	$\frac{(\Delta S_{Da}^{\ddagger})_{PE} - (\Delta S_{Da}^{\ddagger})_{DE}}{2.303R} + (\log [M]_{PE} - \log [M]_{DE})^a$
PE(Py-2)	3.4 ± 0.05	15.9 ± 0.35	12.5 ± 0.8	3.23	1.99
PE(Py-4)	3.3 ± 0.04	13.9 ± 0.64	10.6 ± 0.6	3.11	1.59
PE(Py-8)	3.5 ± 0.05	15.0 ± 0.85	11.5 ± 0.8	3.22	1.30
PE(Py-10)	3.6 ± 0.08	15.8 ± 0.28	12.2 ± 0.2	3.11	0.96
DE(Py-2)	1.9 ± 0.04	10.6 ± 1.04	8.7 ± 1.0	1.24	
DE(Py-4)	2.0 ± 0.03	10.8 ± 0.43	8.8 ± 1.0	1.52	
DE(Py-8)	2.7 ± 0.02	13.1 ± 0.52	10.4 ± 0.5	1.92	
DE(Py-10)	2.9 ± 0.04	13.2 ± 0.34	10.3 ± 0.3	2.15	
MEPy[b]	3.1 ± 0.08	15.4 ± 1.28	12.3 ± 1.2		

[a] Difference of the temperature-independent term between polymer (PE) and relevant dimer model (DE). K and k_{Mf} are same for PE and DE from their definition.
[b] [MEPy] = 1.0×10^{-2} M.

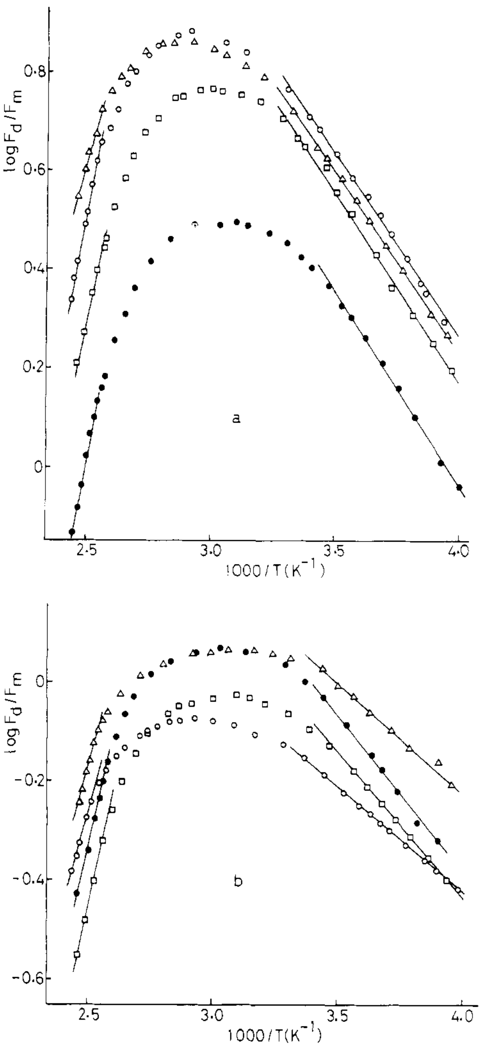


Figure 5. Temperature dependence of F_d/F_m in toluene. (a) PE(Py-X): (○) $X = 2$; (△) $X = 4$; (□) $X = 8$; (●) $X = 10$. (b) DE(Py-X): (○) $X = 2$; (△) $X = 4$; (□) $X = 8$; (●) $X = 10$.

The thermodynamic parameters calculated from the data in Figure 5 are tabulated in Table II.

Comparison of Excimer Formation by Polymer and Dimer. Origin of Polymer Effects. If the stronger excimer emission in polymers is attributable only to the higher chromophore concentration, the enthalpy terms should not be so different for polymer and dimer as shown in Table II. However, the enthalpy terms seem to reflect the chain strain. In dimer models both $\Delta H_{\mathrm{Da}}^{\ddagger}$ and $\Delta H_{\mathrm{Dd}}^{\ddagger}$ increase with spacing between pyrenyl groups. Excimer formation is a diffusion-controlled process and the energy barrier for the process is small. In particular, the dimer models with short spacing groups (DE(Py-2) and DE(Py-4)) are not likely to form a head-to-tail excimer as judged by a molecular model study, and translational diffusion of pyrenyl groups to find a partner for excimer formation will not be much required. This would be a reason for the small $\Delta H_{\mathrm{Da}}^{\ddagger}$ value. With increasing spacing, the thermodynamic parameters for dimers approach those for the monomer model (MEPy). The sequence of $\Delta H_{\mathrm{Dd}}^{\ddagger}$ for dimers would indicate the sequence of chain strain. The looped structure of DE(Py-2) would be more highly strained than that of DE(Py-10). Consequently, the excimer by the former is less stable than that by the latter.

In polymer systems high values of $\Delta H_{\mathrm{Da}}^{\ddagger}$ are explainable as a result of high viscosity in the polymer matrix. Unlike ethylenic polymers, no preformed excimer site was detected for the polyester. These polymers as well as the dimer models do not emit excimer fluorescence in a frozen 2-methyltetrahydrofuran matrix at 77 K. Segment mobility is therefore absolutely necessary for the present systems. Coiling or entanglement of polymer molecules will hinder the segment motion so that $\Delta H_{\mathrm{Da}}^{\ddagger}$ is higher for a polymer than that for the relevant dimer model. Although the overall difference between polymer and dimer is understandable, our recent measurements have revealed that the excimer formation process in the present polymers is not a single-step process.[16] The results of picosecond laser photolysis indicate the presence of a small fraction of a very fast excimer formation process followed by a normal slow process occurring over a few nanoseconds for PE(Py-2). The fast buildup of excimer decreases with increasing space between pyrenyl groups and eventually almost disappears for PE(Py-10). It is not observed for the dimer models. The fast excimer formation will be a low activation energy process whereas the overall $\Delta H_{\mathrm{Da}}^{\ddagger}$ is unfavorable for polymer. When k_{DM} consists of two rate constants, strict interpretation within the framework of Birks kinetics is not possible.

When excimer is anchored by a polymer, the dissociation process is energetically very unfavorable in comparison with the dimer model. Excimer formation and dissociation in polymer are both energetically more unfavorable than those in dimer models while the dissociation process is more disfavored in polymer, resulting in a higher $-\Delta H$ value. Now, a question arises as to why the chain strain does not reduce the value of $\Delta H_{\mathrm{Dd}}^{\ddagger}$ in polymeric systems. There is strong evidence for nonneighboring group participation in the present polymer so that the strain due to looping of the polymer chain by excimer formation is not so important as for dimer models.[17] Consequently, the reduced segment mobility brings about a positive effect on $\Delta H_{\mathrm{Dd}}^{\ddagger}$, and the excimers by polymers, as enthalpically more or equally stable in comparison with that by MEPy.

The entropy term of excimer formation ($\Delta S_{\mathrm{Dd}}^{\ddagger}$) is obtained from measurements in the low-temperature region. Although the concentration term and the entropy term are inseparable, the differences between polymer and the relevant dimer model shown in Table II are not attributable to a concentration effect. Supposing a polymer molecule to be linear, the chromophore concentration in the polymer will be doubled in comparison with the dimer model compound. Since a polymer molecule in solution is by no means linear, the chromophore concentration enhancement would be larger than a factor of 2, depending upon the coordination number and the degree of nonneighboring group participation. If the difference in the temperature-independent term is to be explainable as the concentration increase in M, the chromophore concentration in PE(Py-2) should be nearly 10^2 times higher than that in DE(Py-2). This is totally impossible from the viewpoint of the limited coordination number of the pendant pyrenyl groups. The difference in the temperature-independent term between polymer and dimer decreases with increasing separation between pyrenyl groups. This trend suggests that the main reason for the polymer–dimer difference is not a concentration difference. The temperature-independent term of the dimer model increases with increasing size of spacer whereas that of the polymer is almost constant and independent of the polymer structure. If the differences are to be attributed to the local concentration increment in polymeric systems brought about by nonneighboring group participation, the values would be higher for the PE(Py-10)–DE(Py-10) pair than for the PE(Py-2)–DE(Py-2) pair. The chain flexibility is expected to increase in the order PE(Py-2) < PE(Py-4)

$<$ PE(Py-8) $<$ PE(Py-10) and the importance of nonneighboring group participation will follow the same order. The experimental results do not agree with the guess. Namely, the difference in the temperature-independent term between polymer and dimer increases with decreasing spacing between chromophores. This finding supports strongly that the temperature-independent term is determined mostly by the entropy term. The loss of entropy by loop formation will be more for a small loop. Excimer formation by DE(Py-2) is therefore entropically less favorable than that by DE(Py-10). However, excimer by polymer is not limited to neighboring chromophore interaction and the size of loop is not fixed. This discussion leads to the expectation that $\Delta S_{\mathrm{Da}}{}^{\ddagger}$ in the polymer would be controlled not so much by the structure of the repeating unit as by the total length of the polymer, namely, the unit length of the repeating unit multiplied by the degree of polymerization. Phenomenologically, this is a reflection of nonneighboring group participation. It should be remembered that the discussions are relativisic in the sense of comparing polymers with their dimer models.

Another factor to be considered is the entropy difference in the initial state. This problem has already been discussed for polyesters with pendant naphthyl groups. Since the mobility of polymer side groups is limited, a polymer molecule is essentially in a low entropy state, which reduces the entropy loss accompanied by the face-to-face packing of chromophores in excimer formation. All these results indicate entropically favored excimer formation in polymeric systems.

In the preceding discussions the role of energy migration has been neglected. When energy migration along the polymer chain is efficient, the excitation energy will be transferred to excimer-forming sites and the excimer intensity of the polymer tends to be higher than that of the relevant dimer model. This is a different interpretation. For ethylenic polymers, excimer formation assisted by energy migration seems to take place.[18] For example,[18c] fluorescence spectroscopy of poly(vinylnaphthalene-*co*-methyl acrylate) indicated that the excimer intensity is proportional to the product of the mole fraction of the aromatic pair sequence and the mean sequence length of the aromatic monomer while the fluorescence depolarization in a frozen matrix as an index of energy migration is proportional to the mean sequence length of the aromatic monomer. Even in ethylenic polymers, in which chromophores are congested, excessive emphasis on energy migration was recently questioned.[19] We have determined the fluorescence depolarization of the present polyesters in 2-methyltetrahydrofuran at 77 K.[20] The degree of fluorescence polarization is 0.097 for MEPy whereas the values for PE(Py-X) (X = 2, 4, 8, and 10) range between 0.037 and 0.091. In comparison with similar polymers bearing anthryl groups, these figures suggest relatively inefficient energy migration in the pyrenyl polymers. Assuming the Förster mechanism[21] to be applicable, the inefficient energy migration among pyrenyl groups is anticipated from the long singlet lifetime, on the order of 10^2 ns. Furthermore, the separation between chromophores is much larger than in ethylenic polymers, which reduces the energy migration efficiency.

Conclusion

Elucidation of polymer effects either on reactions or on molecular interaction must be based on comparison of polymers with their well-defined dimer models. Neighboring group effects was not confined to polymer systems and are better not to be included. Strictly speaking, polymer effects should be limited to those phenomena inherent to cooperation of multiple chromophores and to the fact that chromophores are bonded to a polymer chain. Simple local concentration effects could be realized by methods other than binding chromophores on polymers. Although the enhancement of local chromophores concentration in polymers is certainly responsible for part of the difference in $F_{\mathrm{d}}/F_{\mathrm{m}}$ between PE and DE, the concentration effect alone could not explain the thermodynamic parameters for excimer formation. Both the entropy and enthalpy of excimer formation are apparently functions of polymer chain structure. Comparison between PE and DE reveals that polymer effects are more pronounced when the chromophore population along the polymer chain is high. Clear differences between PE and DE would indicate nonneighboring group participation as functions of molecular weight and polymer chain conformation. In the present study, we focused the discussions on the primary structure of polymers. However, in the context of the present discussions, the size and conformation of the polymer chain seem to equally important parameters for intrapolymer excimer formation by the present series of polyesters. Studies with fractionated samples in different solvents are now under way.

Experimental Section

Materials. Sample Preparation. The polymer samples an the monomer model used in this work were those already reported.[22] The dimer models were prepared as follows.

1-[2-(Acetoxymethyl)-2-(hydroxymethyl)ethyl]pyrene (I). 2-[(1-Pyrenyl)methyl]propane-1,3-diol was half-esterified by acetyl chloride. The crude product was chromatographed on alumina (developer, 1:1 chloroform/ether).

Acetoxy-2-[(1-pyrenyl)methyl]trimethyleneoxysuccinyloxy-2-[(1-pyrenyl)methyl]trimethyleneoxyacetoxy (DE(Py-2)) (II). A 486-mg sample of I and 114 mg of succinyl chloride were reacted in the presence of pyridine (0.12 mL) at room temperature. The reaction product was chromatographed on alumina (developer, 1:1 chloroform/ether): yield 356 mg (65.3%); viscous oil; NMR ($CDCl_3$) δ 2.01 (6 H, s, CH_3), 2.40–2.55 (2 H, m, methine), 2.61 (4 H, s, $C(=O)CH_2$), 3.30 (4 H, d, CH_2-Py), 4.00–4.38 (8 H, m, OCH_2), 7.55–8.34 (18 H, m, aromatic H). Anal. Calcd: C, 77.19; H, 5.68. Found: C, 76.05; H, 6.00.

Other dimer models were similarly prepared by the reaction of I with adipyl chloride (DE(Py-4)), sebacyl chloride (DE(Py-8)), or decanoyl chloride (DE(Py-10)). All dimer models were obtained as pale yellow oils. Elemental analysis and NMR agreed.

Solvents. Toluene and THF (both guaranteed grade) were further fractionally distilled after drying over $LiAlH_4$ (for THF) or sodium hydride (for toluene).

Electronic Spectroscopy. A Shimadzu UV-200 spectrofluorometer was used for absorption spectroscopy. A Hitachi MPF-4 spectrofluorometer equipped with a quartz Dewar bottle with transparent windows was used for fluorescence spectroscopy. For variable-temperature measurements, the Dewar bottle with a sample cell was once cooled or warmed to limiting temperatures and then allowed to warm up or cool down spontaneously. F_{d} and F_{m} were determined with appropriate intervals while the temperature change was continuously monitored by a thermocouple attached on the sample cell. All fluorescence measurements were conducted under an argon atmosphere. Since relative values of $F_{\mathrm{d}}/F_{\mathrm{m}}$ were required, fluorescence spectra were not corrected for the wavelength dependence of the spectrometer sensitivity.

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Fluorescence of the Diastereoisomers of 2,4-Di(*N*-carbazolyl)pentane and the Two Excimers Observed in Poly(*N*-vinylcarbazole)

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ABSTRACT: The two diastereoisomers of 2,4-di(*N*-carbazolyl)pentane were synthesized and characterized by NMR. Their respective emission in the excimer region, at 420 nm for the meso isomer and 370 nm for the racemic isomer, can be related to the two excimers observed in poly(vinylcarbazole).

A recent publication[1] proposing an interpretation of the excimer kinetics of poly(*N*-vinylcarbazole) in solution prompts us to report preliminary results on the emission properties of 2,4-di(*N*-carbazolyl)pentanes. We have already shown[2] that the classical kinetic scheme for intermolecular complex formation could not be extended to systems where substantial barriers prevent fast conformational equilibrium. The role of conformational equilibrium upon intramolecular excimer formation was also suggested by Morawetz.[3] As was pointed out by Bovey,[4] one should, in the case of polymers such as polystyrene, consider configurational aspects. Monnerie[5] has shown that the excited-state properties of 2,4-diphenylpentane are substantially different for the meso and the racemic diastereoisomers, especially their capacity to form the excimer.[5b] The nonvalidity of the classical kinetic scheme of intermolecular excimer formation in poly(2-vinylnaphthalene)[6] could also be related to differences in excited-state properties of meso and racemic model systems.[6b]

Table I
^{1}H NMR Data of Diastereoisomers of 2,4-Di(*N*-carbazolyl)pentane in CD_2Cl_2 at 313 K

δ	multiplicity	group of protons	*J*, Hz
		Sample B (meso)	
1.58	d	CH_3	
2.76 (A), 2.90 (B)	ABX_2	H_ACH_B	$^2J_{AB} = -14.2$
4.53	ABX_2, q	CH	$^3J_{AX} = 7.8$, $^3J_{BX} = 7.6$
6.9–7.4	m		
7.98–8.05	m	carbazolyl	
		Sample A (*dd*,*ll*)	
1.39	d	CH_3	
3.02	$AA'XX'$	$CH_{2AA'}$	$^2J = -14.85$
4.40	$AA'XX'$, q	$CH_{XX'}$	$^3J_{AX} = 4.45$, $^3J_{AX'} = 10.80$
6.2–7.6	hump		$J_{XX'} = 0$
7.9–8.05	m	carbazolyl	

Poly(vinylcarbazole) has, however, in the realm of the polyvinyl aromatic systems a particular aspect: dual excimer emission is observed, one excimer emitting at 380 nm (high-energy excimer, trap II) and the other (low-energy excimer) at 420 nm.[7] Attempts to interpret the fluorescence properties of poly(vinylcarbazole) were made on the basis of a scheme in which an equilibrium between the two excimers is included.[1,8] It had, however, been noted[9] that "the intensity of the high-energy excimer in-

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