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Inter- and Intramolecular Interactions of Polymers As Studied by Fluorescence Spectroscopy. 9. Synthesis of a Polymethacrylate Having 2-[(1-Pyrenyl)methyl]-2-[4-(dimethylamino)benzyl]ethyl Side Chains and Its Exciplex Emission Behavior

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ABSTRACT: A polymethacrylate having 2-[(1-pyrenyl)methyl]-2-[4-(dimethylamino)benzyl]ethyl side chains was prepared. An unexpected molecular weight dependence of its exciplex formation in tetrahydrofuran was studied by fluorescence spectroscopy. Concentration-dependent exciplex intensity indicated the presence of both intra- and interpolymer exciplexes. Intramolecular exciplex formation was found to be independent of DP (degree of polymerization) for the range DP = 1–2300, whereas intermolecular exciplex formation was remarkably dependent on DP. The polymers of very low DP as well as a monomer model compound (the isobutyrate instead of the polymethacrylate) and the very high DP samples exhibited almost no interpolymer exciplex emission. To understand these phenomena, ground-state association of polymer chains was considered. There was found an optimum DP to form interpolymer exciplex efficiently. The results were interpreted qualitatively as due to the combination of an increased zipping effect with increasing DP and a polymer chain entanglement and shrinking at high DP. The former will promote interpolymer association whereas the latter will hinder interpolymer association. The surface area/volume ratio of the polymer molecules is consequently a determining factor for interpolymer association.

Introduction

In a series of preceding articles,[1] we have shown that polymers bearing exciplex-forming pairs exhibit interpolymer association under extremely dilute conditions. Although such enhanced molecular association is not limited to exciplex-forming polymers,[2] valuable information is expected from the study of polymer exciplexes. Besides the concentration-dependent exciplex intensity (i.e., inter- and intrapolymer exciplex formation), the study of other controlling factors such as the degree of polymerization, solvent properties, temperature, and so forth will provide insight into "polymer effects" since an exciplex is sensitive to its environment. Nevertheless, the study of exciplex-forming polymers has been limited relative to the excimer study in polymeric systems.

This is apparently due to the preparative difficulty. Excimer-forming polymers are easy to make since the chromophores are simple aromatic hydrocarbons which are resistant to various rigorous preparative processes, including radical, anionic, or cationic polymerization. Also polycondensation processes can be easily applied. On the other hand, exciplex-forming pairs consisting of an electron donor (nucleophile) and electron acceptor (electrophile) are more difficult to build into polymers. Furthermore, equimolar amounts of donor and acceptor should be arranged along the polymer chain in an alternate fashion. To meet these requirements we have chosen polyesters starting from diols bearing D or A and diesters bearing A or D, respectively. As D/A pairs, we chose carbazole/terephthalate,[3] N,N-dimethylaniline/anthracene,[4] or N,N-dimethylaniline/pyrene.[2a,5] These samples are of well-defined structure and the results of fluorescence spectroscopy are informative. A serious drawback is the limitation of the degree of polymerization, which seems to be inevitable for polyesters bearing bulky side groups, although the situation has been improved considerably by means of the activated ester method.[6]

Avoiding the shortcoming, we present a new design of methacrylate bearing a 1-(1-pyrenyl)-3-(p-dimethylanilino)propane chromophore. This monomer sustains the good radical polymerizability of methacrylate ester, and the polymer is readily soluble in most organic solvents. Furthermore, the D–$(CH_2)_3$–A chromophore is the best studied combination,[7] and a large number of comparative results are available for the study of specific polymer effects on exciplex formation.

We have now fractionated polymer samples covering a wide range of molecular weight and are able to study interpolymer association phenomena as functions of molecular weight.

Experimental Section

Materials. Diethyl [[4-(Dimethylamino)benzyl](1-pyrenyl)methyl]malonate (DPM) (1). Diethyl [4-(dimethylamino)benzyl]malonate[8] (56.5 g, 0.193 mol) in 50 mL of dry benzene was added dropwise to 9.26 g of 55% sodium hydride suspended in 50 mL of dry benzene followed by dropwise addition of 1-(chloromethyl)pyrene (48.3 g, 0.193 mol) in 1800 mL of dry benzene. After the mixture was allowed to reflux for 24 h, crude 1 was separated and purified by column chromatography on silica gel: yield 50 g (51%); white-yellow plates, mp 148–150 °C; NMR ($CDCl_3$) δ 0.82–1.05 (6 H, t, CH_2CH_3), 2.93 (6 H, s, $N(CH_3)_2$), 3.42 (2 H, s, $C_6H_4CH_2$), 3.75–4.02 (6 H, m, CH_2CH_3, Py-CH_2), 6.57–7.15 (4 H, m, C_6H_4), 8.00–8.23 (9 H, m, pyrene). Anal. Calcd for $C_{33}H_{33}NO_4$: C, 78.08; H, 6.55; N, 2.76. Found: C, 77.87; H, 6.69; N, 2.90.

2-[4-(Dimethylamino)benzyl]-2-[(1-pyrenyl)methyl]ethanol (DPE) (2). A 1 M potassium hydroxide aqueous ethanol solution (130 mL; 1:1 (v/v) ethanol–water) was added to 20.82 g (0.0410 mol) of 1 dissolved in 820 mL of hot ethanol. After the mixture was allowed to reflux for 24 h, ethanol was distilled off. The last trace of ethanol was then removed by heating under reduced pressure for 1 h at 110 °C. The solid potassium salt was dissolved in 800 mL of water, and the undissolved residue was filtered off. Then, a small amount of chloroform was added to extract the unreacted ester 1. The mixture was brought to pH 4 with 1 N hydrochloric acid to precipitate the free carboxylic acid. The precipitated white powder was dissolved in 200 mL of tetrahydrofuran and reduced with an excess amount of lithium aluminum hydride by refluxing for 3 h. After the usual workup, crude 2 was separated and purified by column chromatography on silica gel: yield 8.48 g (53%); white-yellow plates, mp 26–27 °C; NMR ($CDCl_3$) δ 1.50 (1 H, br s, OH), 2.00–2.55 (1 H, m, CH),

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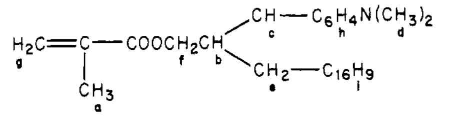
Table I
Fractionation of 4

fraction	MW × 10^{-5} [a]	$\overline{DP}$	η_{sp}/C, [b] dL/g	wt %
1	10.3	2240	0.87	33.4
2	6.06	1310	0.37	12.7
3	2.82	610	0.21	16.8
4	2.58	560	0.19	3.9
5	2.17	470	0.16	2.4
6	1.21	260	0.09	6.8
7 + 8	0.97	210	0.07	7.9
9	0.65	140	0.04	14.2

[a] Determined by light scattering measurement in chloroform. [b] 0.1 g/dL in THF at 30 °C.

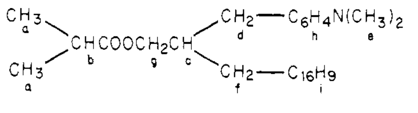
2.62–2.86 (2 H, d, $CH_2C_6H_4$), 2.92 (6 H, s, $N(CH_3)_2$), 3.20–3.47 (2 H, d, CH_2-Py), 3.47–3.80 (2 H, d, CH_2OH), 6.59–7.22 (4 H, m, C_6H_4), 7.73–8.30 (9 H, m, pyrene). Anal. Calcd for $C_{28}H_{27}NO$: C, 85.46; H, 6.92; N, 3.56. Found: C, 84.68; H, 6.93; N, 3.53.

2-[4-(Dimethylamino)benzyl]-2-[(1-pyrenyl)methyl]ethyl Methacrylate (DPEMA) (3). Methacryloyl chloride (0.475 g, 4.54 mmol) in 5 mL of benzene was added to **2** (1.48 g, 3.78 mmol) and triethylamine (0.63 mL) in 15 mL of benzene under cooling. The reaction was continued at room temperature for 24 h. Crude **3** was separated and purified by column chromatography on silica gel: yield 1.16 g (67%); NMR ($CDCl_3$) δ 2.00 (3 H, s, a), 2.23–2.67 (1 H, m, b), 2.67–2.87 (2 H, d, c), 2.93 (6 H, s, d), 3.27–3.57 (2 H, d, e), 4.00–4.23 (2 H, d, f), 5.57 (1 H, m, g), 6.17 (1 H, s, g), 6.60–7.20 (4 H, dd, h), 7.72–8.28 (9 H, m, i). Anal. Calcd for $C_{32}H_{31}NO_2$: C, 83.27; H, 6.77; N, 3.03. Found: C, 83.31; H, 6.58; N, 2.87.



Poly[2-[4-(dimethylamino)benzyl]-2-[(1-pyrenyl)methyl]ethyl methacrylate] (Poly(DPEMA)) (4). Compound **3** (3.91 g) in 10 mL of DMF with 0.200 g of azobis(isobutyronitrile) was degassed by freeze–pump–thaw cycles and polymerized at 70 °C for 24 h; yield 90%. Polymer **4** was fractionated by fractional precipitation from THF solution, with methanol as a precipitant. The NMR spectrum was broad and not analyzable. Anal. Calcd for $C_{32}H_{31}NO_2$: C, 83.27, H, 6.77; N, 3.03. Found: C, 82.17, H, 6.69; N, 2.91.

2-[4-(Dimethylamino)benzyl]-2-[(1-pyrenyl)methyl]ethyl Isobutyrate (Monomer Model Compound, DPEIB) (5). This was prepared by reaction of **2** with isobutyryl chloride in benzene containing an equimolar amount of triethylamine and purified by column chromatography on silica gel (10:1 benzene–acetone): yield 59%; viscous oil; NMR ($CDCl_3$) δ 1.19–1.31 (6 H, dd, a), 2.06 (1 H, s, b), 2.23–2.60 (1 H, m, c), 2.60–2.87 (2 H, d, d), 2.96 (6 H, s, e), 3.32–3.50 (2 H, d, f), 3.97–4.13 (2 H, d, g), 6.70–7.27 (4 H, m, h), 7.80–8.30 (9 H, m, i). Anal. Calcd for $C_{32}H_{33}NO_2$: C, 82.90; H, 7.17; N, 3.02. Found: C, 81.71; H, 7.21; N, 3.09.



Solvents. All solvents were purified by conventional procedures.

Determination of the Molecular Weight of the Polymer. The weight-average molecular weight was determined in chloroform with a low-angle light scattering photometer (Chromatix KMX-6).

Fluorescence Spectroscopy. The fluorescence spectra were measured with a Hitachi MPF-4 fluorescence spectrometer. Fluorescence spectroscopy was conducted at 30 °C under an argon atmosphere. The fluorescence spectra were not corrected for the wavelength-dependent sensitivity of the spectrometer.

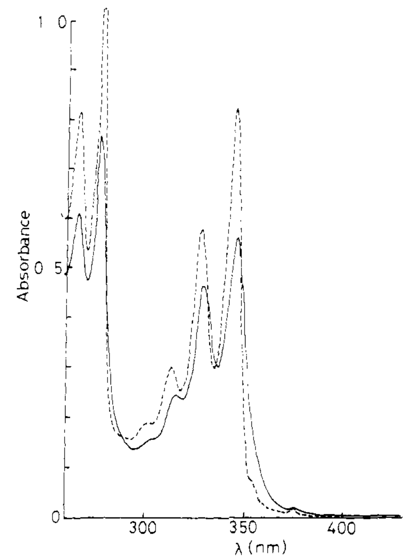
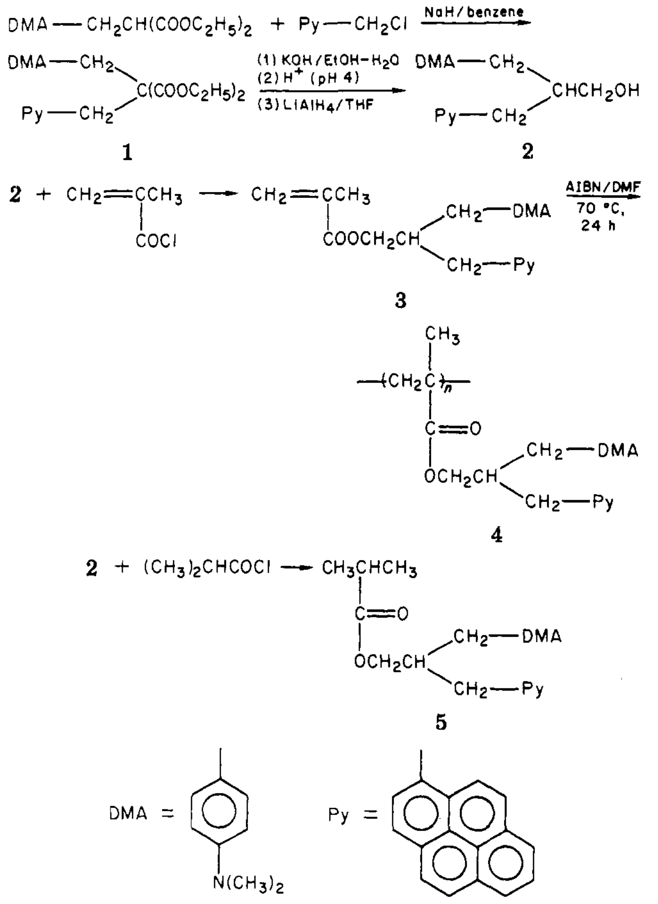


Figure 1. Absorption spectra of poly(DPEMA) and DPEIB: (—) unfractionated poly(DPEMA); (---) DPEIB. [Py] = 2 × 10^{-5} M in THF.

Scheme I



Results and Discussion

Poly[2-[4-(dimethylamino)benzyl]-2-[(1-pyrenyl)methyl]ethyl methacrylate] (4). The outline of the polymer sample preparation is shown in Scheme I. The monomer is readily converted to polymer by conventional radical polymerization. As shown in the reaction scheme, the monomer model compound (DPEIB) was similarly prepared. Molecular weight data of the fractionated

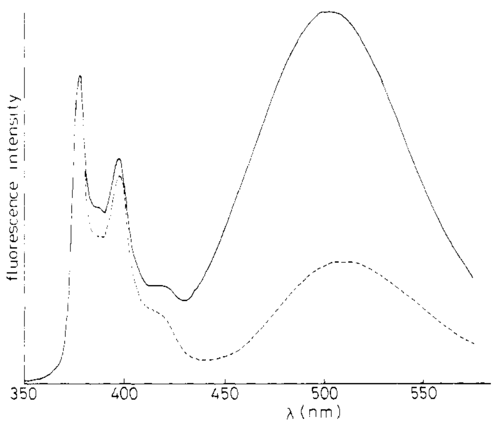


Figure 2. Fluorescence spectra of poly(DPEMA) and DPEIB: (—) unfractionated poly(DPEMA); (---) DPEIB. [Py] = 1 × 10^{-5} M in THF.

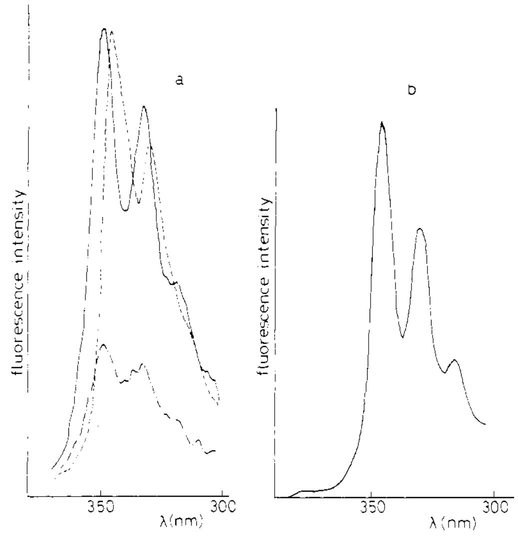


Figure 3. Excitation spectra of poly(DPEMA) and DPEIB. (a) Poly(DPEMA) fraction 3: emission monitored at 470 and 500 (—), 440 (-·-), and 376 nm (---). (b) DPEIB. The excitation profile is not affected by the wavelength of monitoring emission. Solvent THF; maximum absorbance 0.05.

polymers are given in Table I.

Absorption Spectra of 4 and 5. The absorption spectra for 4 and 5, shown in Figure 1, are nearly identical. As generally observed in polymer solutions, the absorption spectrum of 4 is broader than that of monomer model compound 5. The S_0–S_2 absorption peaks at 346 nm (ϵ = 2.66 × 10^4) and 344 nm (ϵ = 4.15 × 10^4) for 4 and 5, respectively. Broadening is the result of interchromophore interaction between pyrenyl and *N*,*N*-dimethylanilino groups.[7] Apparent hypochromicity due to line broadening is much smaller for polymers bearing pyrenyl groups alone.[6a] In this case, reduction in ϵ in polymer systems is about 10% in comparison with the relevant monomer model compound.

Fluorescence Spectra of 4 and 5. Fluorescence emission and excitation spectra for 4 and 5 are shown in Figures 2 and 3, respectively. When the ^1L_a band of the pyrenyl groups is excited in THF, 4 emits an intense exciplex emission peaking at ~500 nm. Compound 5 similarly forms an exciplex but with considerably lesser efficiency. The peak wavelength of the exciplex of 5 is red shifted by ~10 nm in comparison to that of 4. This is supposedly due to protection of the exciplex from solvation in moderately polar THF by the nonpolar polymer chain. As already reported for a polyester bearing 9-anthryl and *N*,*N*-dimethylanilino groups,[4] the apparent dipole moment of a polymer-bound exciplex is smaller than that of model compounds owing to hindered solvation. This polymer effect is particularly prominent in poor solvents in which the polymer chain is contracted.

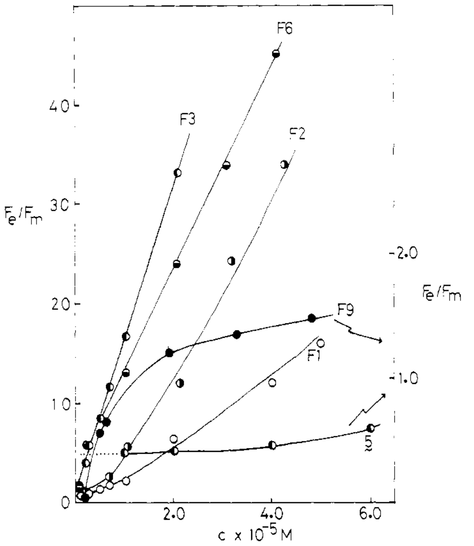


Figure 4. Concentration-dependent exciplex intensity (F_e) relative to monomer emission (F_m). Solvent THF. The unit of F_e/F_m is on the left scale unless otherwise specified.

The excitation spectra monitored at 376 nm (emission from the local excited state of pyrene, F_m) and at ~500 nm (exciplex emission, F_e) (Figure 2) are slightly different. Although the shapes of the spectra are qualitatively the same, the excitation spectra for the exciplex emission are broader than those for the monomer emission. The difference in the excitation spectra for the monomer and the exciplex emission is particularly prominent for the polymer. Not much attention has been paid to the ground-state interactions of exciplex-forming pairs.[9] Being an electron donor–acceptor pair, however, it would not be surprising if very weak ground-state interactions were reflected in the excitation spectra. We now have accumulated evidence that very weak EDA pairs bound to polymer exhibit ground-state association[1] which is not detected unless the chromophores are bonded to polymer. A detailed discussion in relation to the broadening of the absorption spectra will be a subject of future publications.

Molecular Weight and Concentration Dependence of Exciplex Emission. Exciplex-forming polymers are particularly prone to interpolymer association. Emission from all of the exciplex-forming polymers which we have so far studied is strongly concentration dependent.[3-5] The present polymer is no exception. Plots of F_e/F_m vs. polymer concentration (Figure 4) indicate interpolymer association in the concentration region below 10^{-5} M whereas the monomer model compound 5 shows no tendency of intermolecular exciplex formation in this concentration region. A change in polymer chain conformation with concentration is inconceivable in the present concentration region ([Py] < 10^{-4}; i.e., [4] ≪ 10^{-6} M). In addition, excimer emission by polymers such as 6, 8, and those reported previously[10,11] is sensitive to the nature of the solvent affecting the polymer chain conformation whereas the excimer intensity ratio F_d/F_m is independent of concentration, at least below 10^{-3} M.

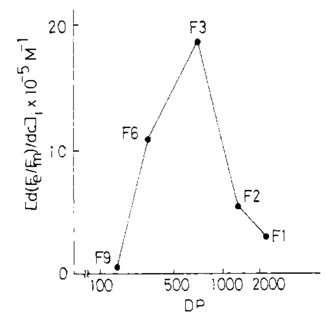
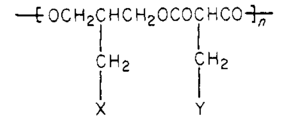


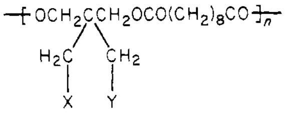
Figure 5. Dependence of the initial slopes of plots in Figure 4 on the degree of polymerization (DP).

Peculiar features of exciplex emission as functions of polymer concentration and DP are as follows. First, although the extent of concentration dependence of exciplex intensity varies depending upon DP of the polymers, the F_e/F_m value at infinite dilution is the same for all samples, indicating identical intramolecular exciplex formation. This is a different conclusion from that readied for the exciplex formation between side-group carbazole and main-chain terephthalate.[3c] Second, the ease of interpolymer exciplex formation as judged by the initial slope of Figure 4 depends on DP in an unusual manner. It is striking to observe that exciplexes of both the lowest DP sample (fraction 9) and the highest DP sample (fraction 1) are nearly concentration independent while a strongly concentration-dependent exciplex is demonstrated by samples of moderate DP. The plots of the initial slopes in Figure 4 vs. DP are given in Figure 5.

The DP-dependent F_e/F_m vs. C plots might look curious from the viewpoint of a conventional solution property study. However, we have accumulated pieces of evidence in agreement with the present observations. We have just accomplished photophysical measurements with the following newly designed samples in dilute solution:[12,13]


$-\!\!\left[\text{OCH}_2\text{CH(CH}_2\text{X)CH}_2\text{OCOCH(CH}_2\text{Y)CO}\right]_n\!\!-$

5, X = Py; Y = DMA
6, X = Py; Y = phenyl


$-\!\!\left[\text{OCH}_2\text{C(CH}_2\text{X)(CH}_2\text{Y)CH}_2\text{OCO(CH}_2)_8\text{CO}\right]_n\!\!-$

7, X = Py; Y = DMA
8, X = Py; Y = phenyl

Although the polymer structures are very different from 4 and these polycondensation polymers are of low molecular weight relative to 4 (MW < 10^5), the exciplex-forming behavior as a function of DP and concentration are remarkably similar to those of 4.

Findings pertinent to the interpretation of the present results are as follows. First, the relation between interpolymer exciplex formation and DP is expressed by plots comparable to those of Figure 4 for exciplex-forming polymers 5 and 7. There was observed an optimum DP to facilitate interpolymer association, which shifts toward the low molecular weight region in poor solvents. Second, relevant excimer-forming polymers 6 and 8 do not show any tendency of interpolymer association, and the intrapolymer excimer intensity increases with increasing DP.

Together with the finding of a zipping-type association of 5,[2a] all results strongly support that polymer association is a function of molecular size and conformation. With increasing molecular weight to a certain limit, the interpolymer association is promoted by a zipping-type interaction. On the other hand, solubility of polymer decreases with increasing DP, and the polymer chain of high DP is thought to be more contracted, provided that the interpolymer association is due to contact of a polymer particle but not due to penetration into a coiled polymer chain by another extended polymer chain; i.e., relatively low DP polymers will be in a better position for the interpolymer association. When a polymer chain is coiled, the surface area/volume ratio decreases and the effective contact area is reduced. Furthermore, an increase in DP will bring about a decrease in chain mobility, which is again a negative factor for interpolymer association. In support of the importance of segment mobility, exciplex at ~500 nm disappears at 77 K in a 2-methyltetrahydrofuran matrix.[10]

Before concluding our discussion, we should carefully examine other possible interpretations. An alternative explanation for the DP effect is to take into account the possible branching of high molecular weight samples. Since polymerization was conducted up to a high conversion (~90%) and the polymer contains benzylic hydrogens on the side chain, there is a good possibility of branched polymer formation. The branching might be more prominent in high molecular weight fractions.[15] The fact that the viscosity number of 4 is relatively low while the molecular weight determined by light scattering is high would be an indication of branched polymer formation and subsequent contracted-chain conformation. If the degree of branching could increase with DP, the DP effect might in part be attributed to the change in polymer primary structure. Intramolecular entanglement of branched polymer chain might hinder interpolymer association for high DP fractions. This is essentially the same argument as that developed in the foregoing section, emphasizing the importance of surface area/volume ratio in interpolymer association. Although at the moment we cannot conclude what the role of branching is in the observed DP-dependent fluorescence phenomena, polymers 5 and 7 which are undoubtedly of linear structure, exhibit behavior identical with that shown in Figure 5. The optimum DP for maximum interpolymer association is, however, smaller for these condensation polymers than for 4.

The major difficulty in studying mutually interacting polymers is the ambiguity in molecular weight determination. In the concentration region of light scattering measurements, 4 is supposedly in an aggregate state. The concentration for viscosity measurement is even higher than that for light scattering measurement so the degree of polymer association and hence the polymer chain contraction is greater in the former measurement. Consequently, the viscosity number tends to be smaller than that expected from light scattering experiments. In any case, the molecular weight listed in Table I should be considered "apparent".

The discussions above suggest the importance of polymer conformation in interpolymer exciplex formation as functions not only of DP but also solvent, temperature, tacticity, branching, and so forth. Research is being undertaken along these lines and detailed results will be published elsewhere in near future.

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(2) Our present understanding is that any weak interchromophoric interactions in the ground state such as electron donor-electron acceptor and hydrophobic interactions promote interpolymer association. (a) Tazuke, S.; Yuan, H. L.; Iwaya, Y.; Sato, K. *Macromolecules* **1981**, *14*, 267. (b) Suzuki, Y.; Tazuke, S. *Polym. Prepr., Jpn.* **1979**, *28*, 1342. (c) Tazuke, S.; Yuan, H. L. *J. Phys. Chem.*, in press.

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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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