Inter- and Intramolecular Interactions of Polymer as Studied by Fluorescence Spectroscopy XVI. Synthesis and Exciplex Emission Properties of Poly[oxy-2,2-(1-pyrenylmethyl) (4-N,N-dimethylaminobenzyl)propyleneoxycarbonyl-iminohexamethyleneiminocarbonyl]

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ABSTRACT: An exciplex forming polyurethane (**I**) ($n \leq 17$), its reference model polyurethane (**III**), and the monomer model (**II**) were prepared. The catalyst effects on the synthesis of polyurethane are discussed. From the results of absorption, emission and excitation spectra, the concentration and molecular weight effects on inter- and intramolecular interactions of **I** in 1,2-dichloroethane were compared with those of **II** and **III**. The ratio of exciplex emission intensity (F_e) to monomer emission intensity by pyrenyl groups (F_m) increased with concentration in an intermediate DP region, suggesting the interpolymer association of **I** in dilute solutions. No such tendency was observed for **II** and **III**. Clear differences in **I** and the analogous polyester **IV** were found. The maximum broadness of absorption spectra was observed in a medium DP region for **I** but not for **IV**. The maximum interpolymer association of **I** occurred in the lower DP region in contrast to **IV**. The poor solubility of the polyurethane brought about by hydrogen bonding and the resulting rigid main chain probably account for these differences. The weaker exciplex forming tendency of **I** than **IV** was attributed to the participation of DMA in the hydrogen bonding. This was supported by infrared and NMR spectroscopy.

KEY WORDS   Exciplex / Electron Donor Acceptor / Hydrogen Bonding / Polyurethane / Fluorescence / Pyrene / N,N-Dimethylaniline / Polymer Interaction / Molecular Association / Polyaddition /

In the preceding article, we have discussed the exciplex emission of 1-(1-pyrenyl)-3-(4-N,N-dimethylanilino)propane group bonded to a polyester.[1] One advantage of employing the pyrene (Py)–N,N-dimethylaniline (DMA) pair as a chromophore is the variety of choice of polymer structure. The aim of this article is to study the effect of a polymer main chain structure on intra- and interpolymer interactions. We chose polymer **I** and its monomer model compound **II** and the reference polymer **III** and compared the fluorescence and absorption characteristics with those of **IV** and **V** reported in the preceding contributions.[1,2] The polymers **I** and **IV** are isostructural except for a small difference from substituting two methylene groups in the main chain of **IV** with two imino groups in **I**. The space between the chromophore pairs is consequently nearly the same but the introduction of hydrogen bonding groups is expected to affect the features of the inter- and intrapolymer interactions.

When urethane bonds are introduced into a polymer chain, the polymer chain becomes stiff and the segment mobility of either the main or side chains is greatly reduced.[3,4] We have demonstrated the important role of hydrogen bonding urethane groups in controlling the photodimerization of anthryl groups either bonded as polymer side groups or incorporated in a polymer main chain. In comparison with the relevant polyesters, segment diffusion to a paired location suitable for photodimerization is hindered whereas the paired chro-

mophores once formed remain undisturbed in polyurethane. Although fluorescence and absorption spectroscopy of the anthryl groups provided information on the segment mobility, more detailed and intensive information can be obtained from the study on an exciplex sensitive to small changes in environments.

In the following, we are going to discuss the intra- and interpolymer interactions relevant to very weak electron donor acceptor (EDA) interaction. Since hydrogen bonding is essentially an acid-base interaction with a small contribution of a charge transfer nature,[5] hydrogen bonding and the weak EDA interaction between Py and DMA might cooperate or cancel out each other.

EXPERIMENTAL

Materials

Poly[oxy-2,2-(1-pyrenylmethyl)(4-N,N-dimethyl-aminobenzyl)propyleneoxycarbonyliminohexamethyleneiminocarbonyl] (I). An anhydrous anisole solution (10 ml) containing 0.88 g (2.30 mmol) of 2-(4-N,N-dimethylaminobenzyl)-2-(1-pyrenylmethyl)propane-1,3-diol and di-n-butyltin dilaurate and triethylamine (0.1 wt% of the diol) as catalyst was stirred at 150—160°C. Anhydrous anisole solution (4 ml) containing 0.4 g (2.30 mmol) of hexamethylene diisocyanate was added in two portions, the second following 5 h after the first, by a dropping funnel. If all the isocyanate was added at once, gel formation took place. The reaction mixture was refluxed with stirring for 7 h. The polymer was precipitated in methanol. Poly[oxy-2,2-(1-pyrenylmethyl)(benzyl)propyleneoxycarbonyliminohexamethyleneiminocarbonyl] (III) was synthesized by a method similar to that described above. Analytical data for I: E.A. Calcd for $C_{37}H_{41}O_4N_3$ (repeating unit); C, 75.10%; H, 6.98%; N, 7.09%. Found: C, 76.10%; H, 7.01%; N, 6.85%. IR (KBr disk) 3420, 3330 (ν_{NH}), 1700 cm^1 ($\nu_{C=O}$). NMR (CDCl$_3$) δ 0.80—1.55 (8H, m, -(CH$_2$)$_4$), 2.91 (6H, s, -N(CH$_3$)$_2$), 3.38—3.68 (2H, m, -CH$_2$-Py), 3.81—4.26 (4H, m, -OCH$_2$-), 4.60—5.10 (2H, m, -NH-), 6.50—7.21 (4H, m, phenyl), and 7.61—8.24 (9H, m, pyrenyl).

Analytical data for III: E.A. Calcd for $C_{35}H_{36}O_4NO_2$ (repeating unit); C, 76.62%; H, 6.64%; N, 5.10%. Found: C, 76.37%; H, 6.98%; N, 5.30% IR (KBr disk) 3420, 3320 (ν_{NH}), 1720 cm^{-1}

($\nu_{C=O}$)

1,3-Bis(N-butylcarbamoyloxy)-2-(1-pyrenylmethyl)-2-(4-N,N-dimethylaminobenzyl)propane (II). To an anhydrous anisole solution (10 ml) containing 0.65 g (1.54 mmol) of 2-(4-N,N-dimethyl aminobenzyl)-2-(1-pyrenylmethyl) propane-1,3-diol was added an anhydrous anisole solution (5 ml) containing 0.7 g (3.10 mmol) of n-butyl isocyanate and a catalytic amount of di-n-butyltin dilaurate at 150—160°C under stirring. After 6 h, the solvent was removed by distillation under reduced pressure. The product was purified on a silica gel column with benzene as the eluent. Yield, 0.86 g (91.5%). mp 166—167°C. Analytical data: E.A. Calcd for $C_{39}H_{47}O_4N_3$: C, 75.33%; H, 7.60%; N, 6.75%. Found: C, 75.15%; H, 7.65%; N, 6.61%. IR (KBr disk) 3420 (shoulder), 3320 (ν_{NH}), 1720 ($\nu_{C=O}$) cm^{-1}. NMR (CDCl$_3$) δ 0.72—1.00 (6H, t, -CH$_3$), 1.00—1.55 (8H, m, -CH$_2$CH$_2$-Me), 2.81 (2H, s, -CH$_2$-DMA), 2.95 (6H, s, -N(CH$_3$)$_2$), 2.95—3.21 (4H, m, -NHCH$_2$-), 3.55 (2H, s, -CH$_2$-Py), 4.00 (4H, s, -OCH$_2$-), 4.10—4.60 (2H, m, -NH), 6.60—7.18 (4H, m, phenyl), and 7.78—8.21 (9H, m, Py).

The polyurethane sample was fractionated by gel permeation chromatography (HLC-802UR, Toyo Soda Mfg. Co. Ltd., columns for fractionation: G 2000 HG$_6$ + G 3000 HG$_6$, columns for molecular weight measurement: GMH × 2 + G 4000H + G 2500 H, eluent : chloroform, operation temperature: 35°C).

Solvent

Spectrograde 1,2-dichloroethane was further purified by distillation before use. Other solvents were purified by accepted procedures.

Spectroscopy

IR spectra were recorded on a Hitachi 260-10 type infrared spectrometer. All samples were measured in the solid state; I and III were cast on a NaCl plate from chloroform solutions while II was measured as a KBr disk. The absorption and fluorescence spectra were recorded on a Shimadzu UV-200 spectrometer and a Hitachi MPF-4 spectrofluorometer, under an argon atmosphere and no correction was made on for the fluorescence spectra. The molarity of the polymer solution was based on the "repeating unit" concentration. The NMR spectra were recorded on a 100 MHz (JEOL) JNM-PS-100 spectrometer. The exciplex emission quan-
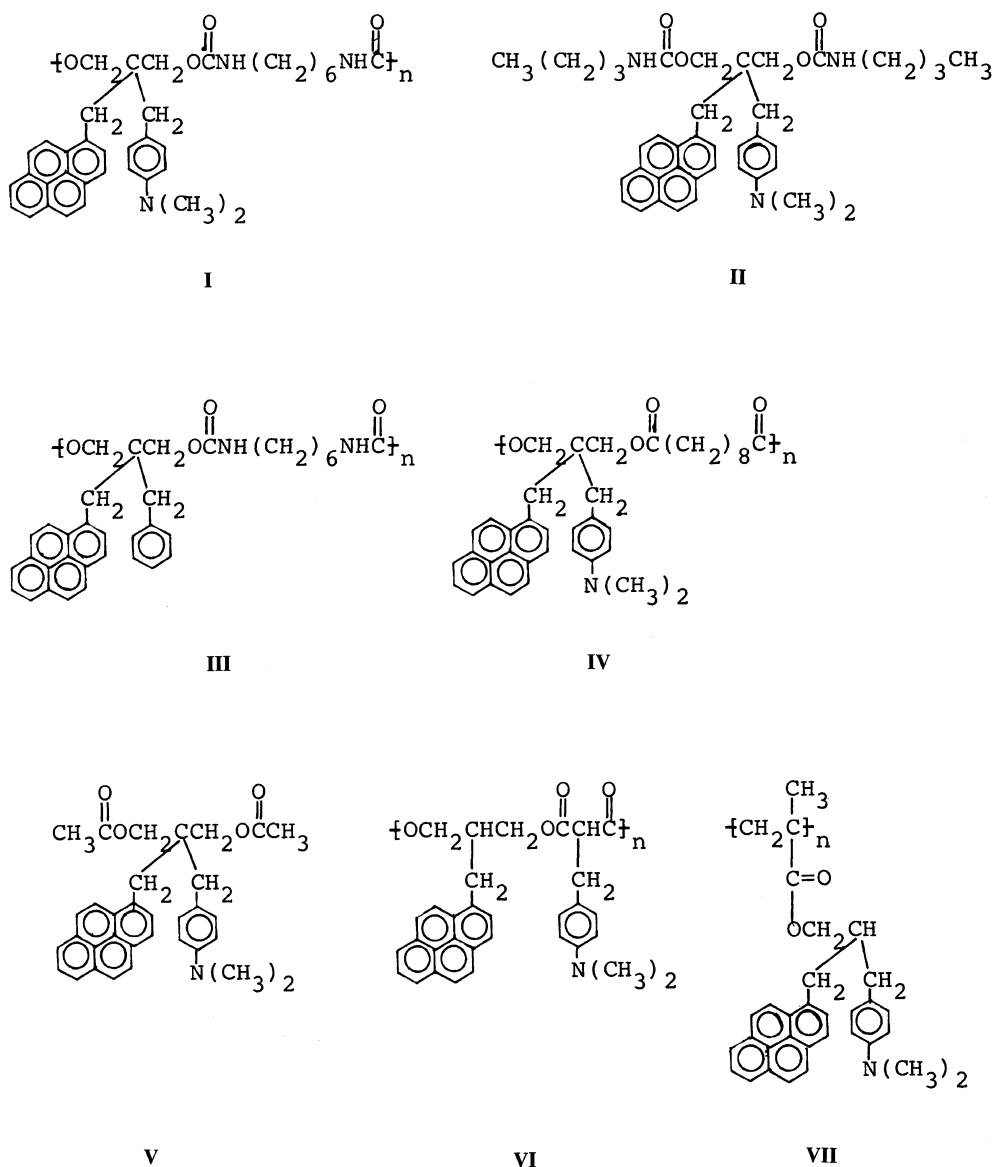
tum yield was measured as already reported.[6]

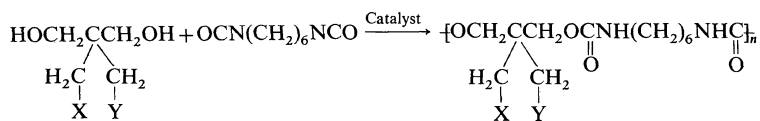## RESULTS AND DISCUSSION

Polymer Synthesis

To investigate the effects of the polymer main chain structure on inter- and intramolecular exci-

plex formation, the following polymers and the corresponding monomer model were designed. Polyurethanes **I** and **III** were prepared from the corresponding diol monomers and hexamethylene diisocyanate. For the preparation of polyurethanes, anisole or chlorobenzene commonly used as the solvent. However, the halogenated solvent was not

Scheme 1.

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Table I.

$$HOCH_2CCH_2OH + OCN(CH_2)_6NCO \xrightarrow{\text{Catalyst}} \text{+OCH}_2CCH_2OCNH(CH_2)_6NHC\text{+}_n$$

Exptl no.	X	Y	Catalyst[a]	M_w[b]	DP
1	Py	DMA	None	No polymer	
2	Py	DMA	(1)	2000	3.5
3	Py	DMA	(1)+(2)	10000	17.0
4	Py	Ph	None	No polymer	
5	Py	Ph	(1)	2000	3.5
6	Py	Ph	(1)+(2)	2000	3.5

[a] Catalyst (1) $[CH_3(CH_2)_3]_2Sn[OOC\ (CH_2)_{10}CH_3]_2$; (2) $(C_2H_5)_3N$.
[b] Estimated for unfractionated polymers by GPC; reference: standard polystyrenes.

suitable for high temperature soluion polymerization of the present diol containing amine. Addition polymerization in anisole gives an almost colorless polyurethane favorable for spectroscopic study. The molar ratio of diol/diisocyanate was strictly maintained at 1 in order to obtain a high molecular weight polymer. The results and the preparative procedure of the polyurethanes are shown in Table I. As shown in Table I (#1, #4), no polyurethanes were obtained when the catalyst was absent. The catalyst effects on the degree of polymerization (DP) of the resulting polyurethane were dependent very much on the presence of amino groups in the diol monomer. The poor reactivity of 2-(1-pyrenyl)-2-benzyl-1,3-propanediol (#5, #6) even in the presence of catalysts may be attributed to the poor solubility of **III**. When the polymer precipitates, further propagation is no longer possible. The better solubility of **I** is probably one reason for obtaining relatively high DP polymers (#3). However, this is possible only when both di-n-butyltin dilaulate and triethylamine are used (compare #2 and #3). If the tin compound is coordinated to DMA group, the catalyst may lose its activity. In this case, destruction of the coordination bond by the addition of a stronger base (triethylamine) would be required to restore the catalytic activity. The catalyst effects in the polyurethane formation are very complicated. Another explanation is that a ternary complex may be formed among the diol monomer, the tin compound and triethylamine, which might accelerate the addition polymerization.[7]

Absorption Spectroscopy

The absorption spectra of **I** and **II** are shown in Figure 1. Although the peaking wavelengths of the absorption spectrum of **I** in DCE are nearly identical with those of **II**, the broadening of the spectrum of **I** expressed by the valley/peak ratio (*i.e.*, $OD_{335}/OD_{346} = 0.39$—0.48) is more prominent than that of either **II** ($OD_{335}/OD_{346} = 0.30$) or **III** ($OD_{335}/OD_{346} = 0.32$). It seems to be a common fact that the absorption spectra of an exciplex forming polymer are broader than those of relevent low mol wt model compounds and excimer forming polymers.[8-11] Comparison of **I** with **IV** indicates that the absorption spectra of the Py–DMA pair are affected considerably by a small difference in the polymer main chain. The absorption spectra of **I** are broader than the analogous polyester **IV**. Since the separation between chromophores is identical for **I** and **IV**, the clear difference in the absorption spectra ($OD_{335}/OD_{346} = 0.39$—0.48 for **I**, and 0.33—0.36 for **IV**) results from the rigid main chain of **I**. Our previous finding that the absorption spectra of **IV** are broader in a good solvent (DCE) than in a poor solvent (mesitylene) suggests an extended polymer chain to be favorable to EDA interaction. By analogy, the broader absorption spectrum of **I** is attributable to its rigid, and therefore, extended polyurethane main chain. Since the relevent monomer models, **II** and **V**, exhibit almost identical absorption spectra, the effect of the urethane group is specific for the polymer system.

The broadness of absorption spectra of **I** is plotted against DP as shown in Figure 2. It is
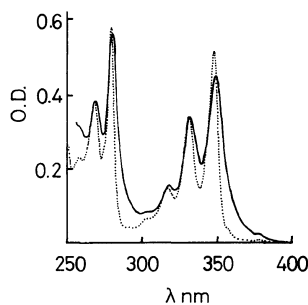
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Figure 1. Absorption spectra of **I** and **II** in DCE. [Py] = 2×10^{-5} M. **I**, (——); **II**, (------).

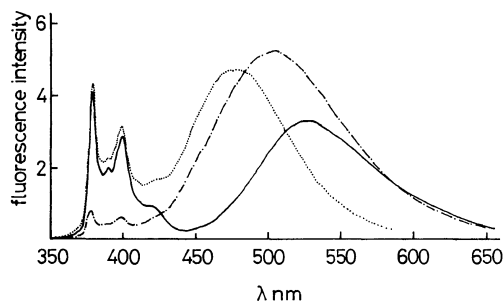**Figure 3.** Fluorescence spectra of **I** (Fraction 5), **II**, and **III** in DCE. Excitation at 346 nm, [Py] = 5×10^{-5} M. **I**, (– – – –); **II**, (——); **III**, (------).

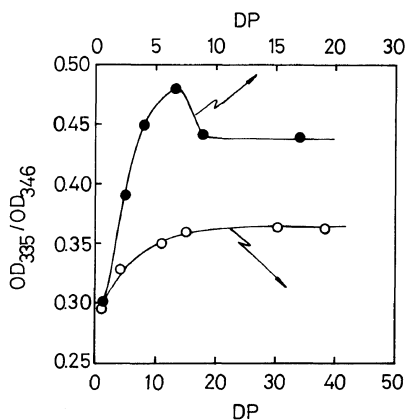**Figure 2.** Comparison of **I** with **IV** in DP dependent broadening of the absorption spectra in DCE. [Py] = 2×10^{-5} M. **I**, (●); **IV**, (○).
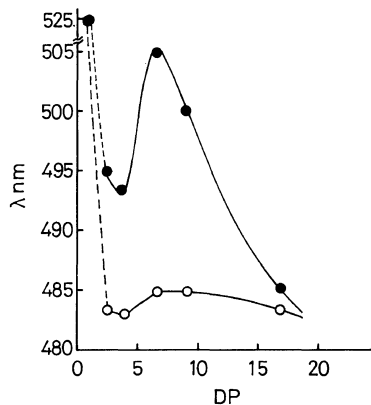

Figure 4. DP dependence of the maximum exciplex emission wavelength of **I** in DCE. Excitation at 346 nm. [Py] = 5×10^{-5} M (●) and $< 1 \times 10^{-6}$ M (○).

interesting to note that the maximum broadness of absorption spectra of **I** was found for a medium sized polyurethane. For **IV**, the absorption spectra become broader with increasing DP whereas the origin of the broadening is the intrapolymer interaction as indicated by obedience to the Beer's law. The fraction 5 of **I** is very specific, as will be discussed in the following section, and many physical values show the maximum value in this DP region.

Fluorescence Spectroscopy

The fluorescence spectra of **I**, **II**, and **III** are shown in Figure 3 and the emission characteristics are shown in Table II along with the reported results on **IV**.[1,2] The maximum wavelength of the exciplex emission by **I** depends on DP as plotted in Figure 4. The complexed shape of the plots at $c =$

5×10^{-5} M seems to be a reflection of mixed inter- and intrapolymer exciplexes as well as excited EDA complexes. The contribution of each component depends on DP and the concentration of **I**. Comparing Figure 4 with Figure 7 and Table II, it can be seen that the open circles in Figure 4 represent the intrapolymer exciplex and possibly the EDA complex almost exclusively whereas the black circles include both the inter- and intrapolymer exciplexes. In particular, the fractions 3 and 5 are prone to the interpolymer exciplex formation so that the wavelengths of peaking emission are practically of the interpolymer exciplex. The results in Figure 4 are contrasting to those in Figure 10 in the previous report.[1] For **IV**, the inter- and intrapolymer exciplexes appeared at the same wavelength whereas the interpolymer exciplex by **I** emits in a longer wavelength region than the intrapolymer

Table II.

Sample	No.	$M_w{}^a$	DP	Broadness[b] of absorption spectra	Fluorescence spectra			
					λ_m^{max} [c]	λ_e^{max} [c]	$\lambda_e^{max}{}_{c \to 0}$ [d]	$(F_e/F_m)_{c \to 0}$
					nm	nm	nm	
	1	10500	17.0	0.44	377, 398	485	483	0.5
	3	5500	9.0	0.44	377, 398	500	485	0.6 ± 0.3
I	5	3900	6.5	0.48	377, 398	505	485	0.5 ± 0.3
	7	2000	3.5	0.45	377, 398	493	482	0.5
	9	1600	2.5	0.39	377, 398	495	483	0.5
II	Monomer model	621.8	1	0.30	377, 398	525	525	0.5
III	Reference polymer	2000[e]	3.5	0.32	377, 398	476	478	1.1 (excimer)
IV	Polyester	17800	30.0	0.36	377, 398	515	482	4.0
V	Monomer model of IV	507.4	1	0.28	377, 398	525	525	2.2

[a] Determined by GPC (reference: polystyrene).
[b] OD_{335}/OD_{346} (valley/peak ratio).
[c] Pyrene monomer and exciplex emission maximum wavelength at $[Py] = 5 \times 10^{-5}$ M.
[d] Maximum wavelength of exciplex (excimer) emission at the high dilution limit.
[e] Unfractionated sample. The F_e/F_m value is independent of concentration.

exciplex. The contribution of EDA emission seems rather small judging from the weak EDA emission even in a frozen matrix (Figure 5). The lower energy emission by **II** in comparison with **I** is comparable to the same relation between **IV** and **V**. Reduced solvation and steric hindrance in polymers accounts for this.

It is of interest to recognize the difference in λ_e^{max} (Table II) between **I** and **IV**. Since the monomer models **II** and **V** emit an identical exciplex emission, the higher exciplex energy of **I** than **IV** may be attributed to hydrogen bonding which reduces the electron donor properties of DMA. Hydrogen bonding also brings about a rigid main chain so that the relaxation of the exciplex is retarded, giving rise to a blue shifted exciplex emission.

The ground state interaction is shown in Figures 5 and 6. In a glass matrix at 77K (Figure 5), the formation of a "true" exciplex is prohibited and the remaining broad emission extending over 500 nm is considered as due to an excited EDA complex. The EDA emission was observed more or less for all polymers containing Py and DMA groups. Particularly, **VI** and **VII** in Scheme 1 exhibited strong emission peaking around 440 nm.[9] **II** or **III** hardly exhibited the EDA emission. The excitation
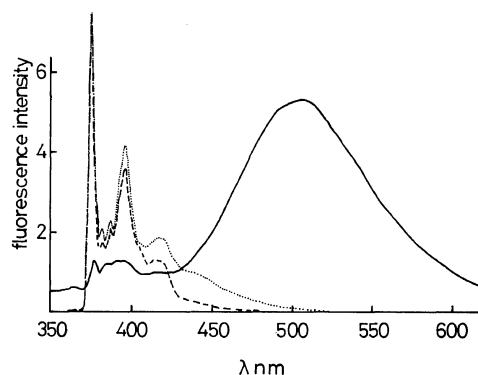

Figure 5. Fluorescence spectra in a glassy MTHF matrix. $[Py] = 5 \times 10^{-5}$ M, excitation at 346 nm. **I** (Fraction 5) at 77 K (------) and at room temp (——— fluid solution). **III** at 77 K (----).

profiles in Figure 6 and the deduced results in Table III unequivocally confirm the participation of a ground state complex. The excitation spectrum of **I** depends considerably on the monitored wavelength whereas that of **II** is scarcely so as shown in Table III. Furthermore, the excitation spectrum of **III**, independent of the monitored wavelength, indicates that the excimer system consists of a single absorb-

ing species. Similar results were obtained for other polymers in solution. The excitation spectrum for the exciplex emission is broader than that for the monomer emission as expressed by the valley/peak ratio of the excitation spectrum manifesting that there is a broad and weak absorption band overlapping the $S_2 - S_0$ band of Py responsible for a part of emission in the exciplex region.
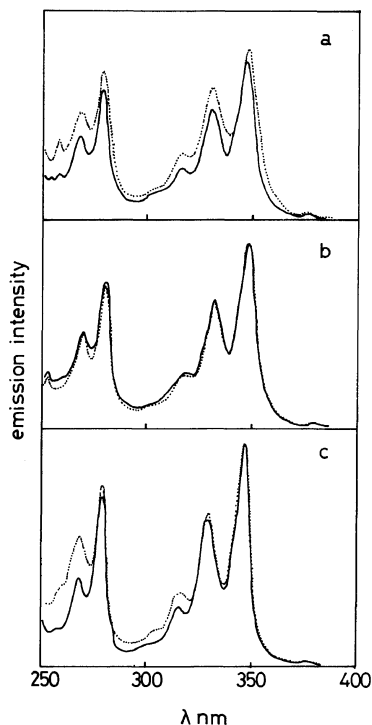

Figure 6. Excitation spectra of **I** (a), **III** (b), and **II** (c) in DCE. Monitored wavelength, 377 nm (——) and 500 nm (------). Absorbance ≤0.05.

Concentration Dependence of Exciplex Emission

As a measure of intra- and intermolecular interactions, the intensity ratio of the exciplex emission (F_e) to that from the locally excited state of Py (F_m) was taken, and the results obtained in DCE are plotted in Figure 7. The other solvents used previously (mesitylene, o-xylene, dioxane, and others) are not usable because of the poor solubility of the present polymer. In the medium DP region, (Fr-5, MW = 3900, DP = 6.5), a strong concentration dependence of the exciplex formation was found and an optimum DP for the interpolymer exciplex formation was obtained. The presence of an optimum DP for the interpolymer exciplex formation was common to all exciplex forming polymers investigated. In contrast to **IV**, the peak in Figure 8 appears in a lower DP region and furthermore, the sharp profile of the plots indicates specific interpolymer association in a limited DP region. The difference between **I** and **IV** or **VI** is in part attribut-
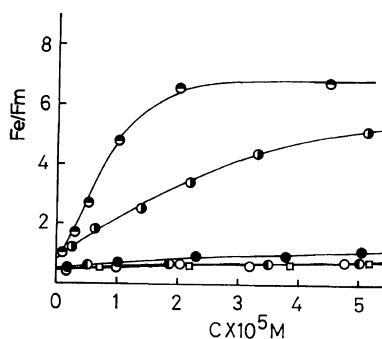

Figure 7. Concentration dependence of exciplex emission in DCE. Excitation at 346 nm. **I**, fraction 9 (○), 7 (◐), 5 (◓), 3 (◑), and 1 (●); **II**, □.

Table III. The valley/peak ratio of excitation spectra of **I**, **II**, and **III** at different monitored wavelength[a]

Monitored wavelength	F_{337}/F_{346}[b]			F_{322}/F_{346}[b]		
nm	I	II	III	I	II	III
377	0.402	0.331	0.402	0.298	0.233	0.281
515	0.502	0.361	0.403	0.370	0.278	0.278
Difference %	+24.8	+9.1	±0	+24.2	+19.3	±0

[a] Conditions: The maximum OD of sample solution was maintained below 0.05 ([Py] < 10^{-6} M). Solvent, 1,2-dichloroethane. **I** (Fr-5, M_w = 3900), **II** (urethane monomer model), and **III** (reference polyurethane, unfractionated M_w = 2000).

[b] Suffixes indicate excitation wavelength in nm.

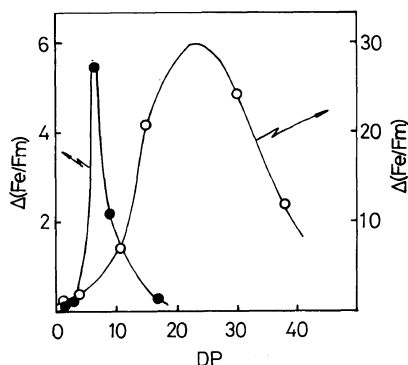**Figure 8.** DP dependence of interpolymer interaction in DCE. $\Delta(F_e/F_m) = (F_e/F_m)_{2 \times 10^{-5}M} - (F_e/F_m)_{c \to 0}$. **I**, (●); **IV**, (○).
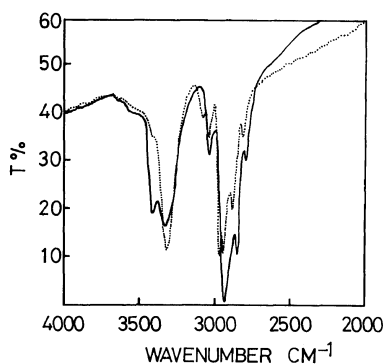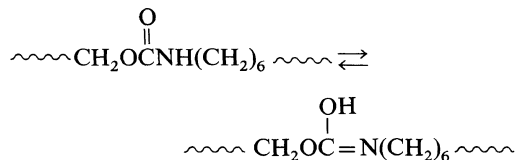

Figure 9. Infrared absorption spectra of **I** and **II**. **I**, (——); **II**, (------).

able to the poorer solubility of **I** than **IV** and **VI**. When the same plots as in Figure 8 were depicted for **IV** and **VI** (ref 1, Figure 8 and ref 7, Figure 12) in poor solvents, the optimum DP value decreased and the plots became sharper but not as much as those for **I** in Figure 8. The hydrogen bonding tendency of the polyurethane is relevant to the difference between **I** and **IV**. The infrared absorption spectrum of **I** (Figure 9) provides explicit evidence for hydrogen bonding which results not only in polymer interactions but also brings about a stiff main chain. The amount of hydrogen bonding in **I** and **III** is considerably larger than that in **II**. The intensity ratios of the IR absorption at 3420 cm^{-1} (hydrogen bonded NH groups) to that at 3320 cm^{-1} (free NH groups) are 0.87 and 0.78 for **I** and **III**, respectively, whereas the value is 0.3 for **II** for which the absorption at 3420 cm^{-1} is observed only as a

shoulder. If a rod-like polymer chain begins to bend above a critical DP region, polymer association may be difficult above the threshold value whereas the cooperative effect in interpolymer association[12]

$$\sim\!\!\sim\!\!\sim CH_2O\overset{\overset{\displaystyle O}{\|}}{C}NH(CH_2)_6 \sim\!\!\sim\!\!\sim \rightleftharpoons$$

$$\sim\!\!\sim\!\!\sim CH_2O\overset{\overset{\displaystyle OH}{|}}{C}=N(CH_2)_6 \sim\!\!\sim\!\!\sim$$

is lacking in very low DP polymers. Hydrogen bonding is however not direclty responsible for the interpolymer association. Had this been the case, **III** should have exhibited the interpolymer excimer formation. No such tendency was observed.[2]

The role of hydrogen bonding is therefore to impart rigidity to the main chain. This does not necessarily require interpolymer hydrogen bonding. Intrapolymer interaction involving the tautomeric structure shown above is possible.

The rigid and extended polymer chain of **I** seems relevant to the nearly DP independent intrapolymer exciplex intensity (($F_e/F_m)_{c \to 0}$ in Figure 7 and Table II). Non-neighboring group participation is not permitted for **I** at least in the present DP region. In contrast, **IV** showed strongly DP dependent intrapolymer exciplex in poor solvents but not in a good solvent (DCE)[1] in which the polymer chain is extended. This is a reasonable consequence supported by the previous results on the DP independent intrapolymer exciplex by poly[oxy-2-(1-pyrenylmethyl)propyleneoxy-(4-N,N-dimethyl-aminobenzyl)malonyl] (**VI**) having bulky congested side groups.[8]

The maximum F_e/F_m value in Figure 7 is about 6.5, which is much smaller than the corresponding value for **IV** exceeding 25.[1] The energy level of the interpolymer exciplex in **I** is higher than that in **IV** by at least 400 cm^{-1}. Such differences can be explained by hydrogen bonding effects on exciplex as discussed in the following section.

A red shift of up to 20 nm in the exciplex peaking wavelength is observed for **I** by increasing concentration (Figure 4 and Table II) as a reflection of the wavelength difference between the intra- and interpolymer exciplex emissions. A similar trend was reported for **IV** in DCE,[1] but not in poor solvents.
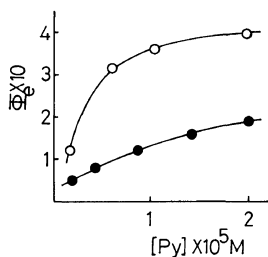
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Figure 10. Quantum efficiency of exciplex emission as a function of concentration in DCE. Excitation at 346 nm. (●), **I**; (○), **IV**.

Hydrogen Bonding Effects on Exciplex Emission

We have shown that hydrogen bonding influenced the exciplex characteristics of **I** indirectly *via* affecting the polymer chain rigidity. Another possibility is the effect on exciplex energy levels. In the preceding section, we considered the hydrogen bonding between carbonyl and imino groups. The DMA group is equally a hydrogen acceptor. Its basicity is higher than the carbamoyl group. The hydrogen bonding to DMA reduces the donor property and the resultant decrement in exciplex forming capability is observed. This is actually the case in Figure 8. Furthermore, the blue shifted exciplex emission by **I** (*i.e.*, unstable exciplex) is consistent with this interpretation. The quantum efficiency of exciplex emission (ϕ_e) is very much increased with increasing concentration. This provides direct support for the interpolymer association which promotes the exciplex formation.[6] ϕ_e of **I** is considerably smaller than that of **IV** in all concentration regions as shown in Figure 10. This is also reminescent of the reduced donor property of DMA in **I**.

NMR spectroscopy of the methyl group in DMA provides good support for the participation of hydrogen bonding. The singlet NMR signal for the methyl groups in DMA appears at 2.91 for **I**, 2.81 for **IV**, and 2.95 for **II** (δ, ppm). The small but considerable down field shift of **I** and **II** indicates reduced electron density owing to hydrogen bonding.

CONCLUSION

A small difference in polymer main chain architecture alters the overall picture of inter- and intrapolymer exciplex formation and the emission properties. The major effect of introducing urethane linkages to the main chain on exciplex emission is explainable by the change in main chain rigidity. However, the direct effect of hydrogen bonding on the donor-acceptor properties of DMA should also be taken into account.

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