

**Inter- and Intramolecular Interactions of Polymers
as Studied by Fluorescence Spectroscopy XIV.
Emission by Pyrene-*N,N*-Dimethylaniline
Pair in Glassy 2-Methyltetra-
hydrofuran Matrix**

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ABSTRACT: Emission and absorption spectra of a polyester having pyrene and *N,N*-dimethylaniline groups (**I**) were studied in 2-methyltetrahydrofuran (MTHF) between room temperature (r.t.) and 77 K and the results were compared with a series of model compounds (**II**, **III**, and **IV**). The following important results were obtained: i) **I** emits fluorescence from excited EDA (electron donor acceptor) complex ($\lambda_{\max} \approx 440$ nm) in a glassy matrix below ~ 90 K while **II** hardly does so. ii) Exciplex emission by **I** at r.t. decreases with lowering temperature and the locally excited state of pyrene alone is observed at an intermediate temperature region. iii) EDA emission relative to pyrene emission is intensified by increasing the degree of polymerization (DP) of **I** whereas the concentration effect is not observed indicating that intrapolymer EDA complexes are formed with possible non-neighboring group participation. iv) The absorption spectrum of **I** at 77 K is much broader than that of **II** in support of EDA complex formation by **I**. v) In accordance with the results of absorption spectroscopy, the excitation spectrum monitored at 440 nm at 77 K is broader than that monitored pyrene emission. This is a good indication that the origin of absorption spectrum broadening is relevant to the EDA emission. Since these findings are very different from emission characteristics of a polymer bound exciplex at r.t., comparative study on EDA and exciplex emission was conducted and the possible factors controlling these emissions are discussed.

KEY WORDS Polyester / EDA Complex / Exciplex / Glassy Matrix / Charge Transfer / 2-Methyltetrahydrofuran / Pyrene / *N,N*-Dimethylaniline / Fluorescence /

Interpolymer association is a general characteristic of exciplex forming polymers consisting of regular repeating units.¹⁻⁷ From a comparison between exciplex- and excimer forming polymers with identical backbone structures, we were able to confirm that the driving force is a weak electron donor acceptor (EDA) interaction between pyrenyl (Py) and *N,N*-dimethylanilino (DMA) groups.⁸ If this is actually the case, the ground state interaction should reflect the absorption and excitation spectra. Besides the emission spectra, there are many small but clear difference between the excimer- and the

exciplex-forming polymers such as the line broadening of absorption spectra^{6,8} and the dependence of excitation spectra on the monitoring emission wavelength in the latter.^{3,6} Although these results support the ground state interactions in the exciplex forming polymers, the contribution is minor and the major part of the long wavelength structureless emission is attributed to a *true* exciplex (*i.e.*, the excited complex state is formed *via* a locally excited state of one of the components). Preliminary measurements on the rise and decay of a exciplex emission⁹ showed that the exciplex rise is mea-

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surably slow for interpolymer exciplex systems. That is, chromophore mobility is a necessary condition for exciplex formation even if the polymers are in an associated state. Consequently, separate measurements on excited EDA complex are not possible in liquid media.

Under such circumstances, a possible approach for distinguishing the ground state complex formation from excited state interactions is to freeze molecular motions so that the excitation of ground state EDA complexes alone can be achieved. In this article, we chose a polyester bearing Py and DMA in an alternate fashion which had been subjected to a detailed study in regard to exciplex behavior,⁶ and the spectroscopic properties in a 2-methyltetrahydrofuran (MTHF) glassy matrix were studied.

EXPERIMENTAL

Materials

Preparation of samples **I**,⁶ **II**,⁶ **III**,¹⁰ and **IV**⁸ and fractionation of **I** and **IV** have already been reported. 2-Methyltetrahydrofuran (Spectrograde) was dried over sodium metal and distilled before use.

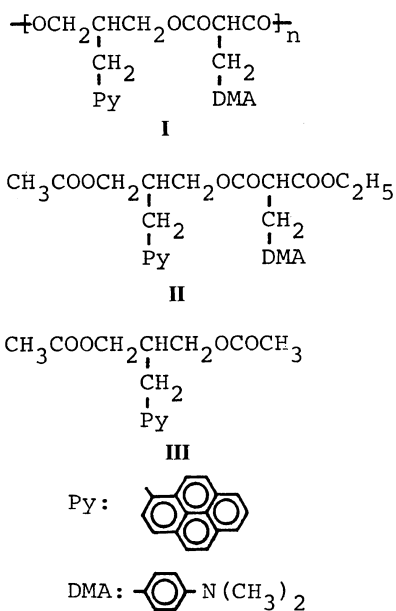
Spectroscopy

Absorption and emission spectra were measured by a Shimadzu UV-200 spectrometer and a Hitachi MPF-4 spectrofluorometer, respectively. Fluorescence spectroscopy was conducted under an argon atmosphere with emission and excitation slit widths of 3 nm. The excitation wavelength was 346 nm except for the measurement of the excitation spectra. Temperature controlled spectroscopy was conducted in a thermostatted Dewar bottle (Oxford type). Constant temperature was maintained by means of a cold flowing nitrogen stream and intermittent heating controlled by a thermocouple attached to the sample cell.

RESULTS AND DISCUSSION

Comparison of Electronic Spectra at 77 K and Room Temperature

Absorption spectra of the polymer (**I**), the dimer model (**II**), and the monomeric pyrene (**III**) are shown in Figure 1. All spectra at 77 K are sharper than those at room temperature (r.t.) while **I** gives a broader absorption than **II** or **III** even at 77 K. The



Scheme 1.

single peak around 345 nm at r.t. tends to split into two at 77 K. This tendency is more pronounced for **II** than for **I**. In addition, a new absorption band develops in the long wavelength region at 77 K. After the peak intensity at 345 nm was normalized for all **I**, **II**, and **III**, the spectrum of **III** was subtracted from those of **I** and **II** to give the difference spectra depicted in Figure 2. When the ground state interactions between Py and DMA influence the absorption spectra, the contribution of EDA complexes should be more at 77 K since the EDA complex formation accompanies a negative enthalpy change. As a general trend of temperature effect on the shape of spectra, all the samples exhibit sharper spectra at 77 K. Nevertheless, the differences in relative broadness between **I** and **II** and between **II** and **III** shown in Table I increase from 0.14 to 1.55 and 0.04 to 1.69, respectively, when the temperature is lowered from 303 K to 77 K. This is a good indication that the tendency of EDA interaction is enhanced more for **I** than for **II** at 77 K. The prominent line broadening of **I** on a relative scale is attributed to the reduced solubility of **I** at low temperatures. The shrunken polymer chain is probably favorable for intrapolymer EDA interaction. The higher intensity of the difference spectrum of **I**—**III** than that of **II**—**III** supports this con-

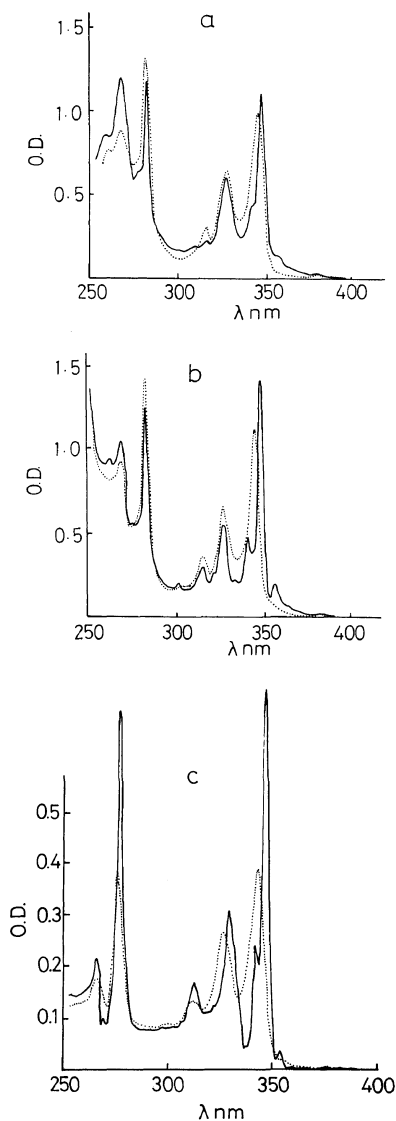


Figure 1. Absorption spectra of I(a), II(b), and III(c) in MTHF at 77 K (glassy matrix, —) and at room temperature (-----). $[\text{Py}] = 5 \times 10^{-5} \text{ M}$ for I and II, $1.5 \times 10^{-5} \text{ M}$ for III. Sensitivity of spectrometer was doubled for the measurements of I and II at r.t.

clusion. In order to confirm the role of the EDA pair in I, we attempted to carry out an absorption measurement of IV which has an identical structure with I, but bears no EDA pair. However, the solubility of IV in MTHF at low temperature was very poor and a clear glassy state could not be obtained.

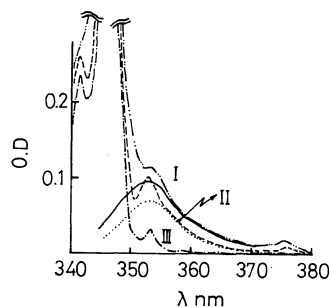


Figure 2. Difference spectra of I—III (—) and II—III (-----) in glassy matrix at 77 K. All spectra of I (-----), II (-----), and III (-----) are normalized for the peak at 346 nm.

Fluorescence emission spectra are shown in Figure 3. The shape of fluorescence by I at 77 K is very different from that at r.t. (Figure 3a). The fluorescence at 77 K consists of emission from the locally excited state of Py and that from some kind of excited complex peaking at $\sim 440 \text{ nm}$. It was difficult to elucidate the change of fluorescence at 77 K as a result of the wavelength shift of exciplex emission. The loss of segment mobility at 77 K prevents the formation of the most stable Py-DMA arrangement and also the rearrangement of solvent molecules to stabilize the excited EDA pair is prohibited so that the exciplex emission if any should shift towards the shorter wavelength region. The magnitude of the shift is however far too big to be attributed to solvent effects. Furthermore, the segment mobility is a necessary condition for the exciplex formation by I at r.t. as judged by the exciplex rise and decay profiles.⁹ Consequently, the emission peaking around 440 nm apparently does not originate from the exciplex. This conclusion is supported by the temperature dependence of fluorescence spectra. In an intermediate temperature region, both the EDA and the exciplex emission disappear indicating that their origins are different. The details for this will be discussed later.

In comparison with I, II emits a very weak emission from the excited EDA complex at 77 K as a small shoulder while exciplex emission is clearly observed at r.t. as shown in Figure 3b. The spectrum of II at 77 K (Figure 3b) is, however, much broader than those of III or polyesters prepared from 2[(1-pyrenyl)methyl]-1,3-propanediol and dibasic acids²⁴ which exhibit emission from the locally excited state of Py alone in the MTHF matrix at

Table I. Broadening of absorption spectra due to EDA interaction

	303 K		77 K	
	OD ₃₃₅ /OD ₃₄₆ ^b	Relative broadness ^c	OD ₃₃₅ /OD ₃₄₈ ^b	Relative broadness ^c
I ^d	0.429	1.18	0.250	4.24
II	0.378	1.04	0.159	2.69
III	0.365	1.00	0.059	1.00
Difference (I—II)	0.051	0.14	0.091	1.55
IV	0.372	1.02	Not determined	

^a Solvent, 2-methyltetrahydrofuran.

^b The valley/peak ratio of the pyrene S₀–S₂ absorption as a measure of broadness.

^c Broadness relative to the monomer model I.

^d MW = 6200 determined by GPC (reference, PS).

77 K. The difference between **I** and **II** in fluorescence behavior is in good agreement with the absorption characteristics of these compounds in Table I. As a matter of course, the isolated Py group in **III** shows fluorescence from the locally excited state alone either in a liquid solution or in a glassy matrix (Figure 3c). Chain entanglement of **I** would promote the ground state pair formation. The excitation spectra as a function of the monitoring wavelength are very informative for distinguishing ground state complexes and exciplexes. The results in Figure 4 explicitly indicate that F_m and F_{440} originate from different species. In the S₀–S₂ transition, the excitation profiles for F_m and F_{440} are nearly identical regardless of the monitoring wavelength. When F_{440} is monitored, the excitation profile is somewhat broader, reflecting the contribution of the possible EDA absorption band depicted in Figure 2 as the difference spectra. The discrepancy of the excitation profiles is enhanced in the short wavelength region where the absorption band of DMA overlaps indicating that the excitation of DMA brings about the monomer emission by an energy transfer to Py whereas the excited DMA cannot be converted to the species fluorescing at 440 nm.

The excitation profiles of EDA emission are also quite different from those of exciplex emission since the excitation of a DMA group paired with Py or anthracene³ induces an exciplex formation efficiently at r.t.

Dependence of F_{440} on the Degree of Polymerization (DP) and Concentration

The intensity ratio, F_{440}/F_m of **I** increases with DP as shown in Figure 5. This trend is different from what was observed for **I** in liquid solutions. The DP dependent exciplex formation at r.t. was interpreted as due to a zipping type interpolymer association which is most efficient at an appropriate DP region,⁴ depending on the solvent. In high DP regions, the polymer chain seems to shrink, resulting in a decrease in the surface area/volume ratio of a polymer molecule to reduce the tendency of interpolymer exciplex formation. In the present concentration region, the F_c/F_m at r.t. is attributed mostly to an interpolymer exciplex whereas the F_{440}/F_m in the glassy matrix is of intrapolymer origin. As depicted in Figure 6, F_{440}/F_m is nearly independent of concentration whereas F_c/F_m is not. The results in Figures 5 and 6 are consistent with the reported results of the absorption spectroscopy of **I** at r.t.⁶ The spectral broadening of **I** in a solvent at r.t. increases with DP whereas the absorbance obeys the Lambert–Beer's law indicating that line broadening is unaffected by concentration. All the information supports that the origins of EDA emission and broadening of absorption spectra are closely related.

Temperature Dependence of Excited EDA Complex Emission and Exciplex Emission

The shape of spectra in Figure 3a and the plots of relative emission intensity vs. temperature in Figure 7 indicate that the conversion of the exciplex

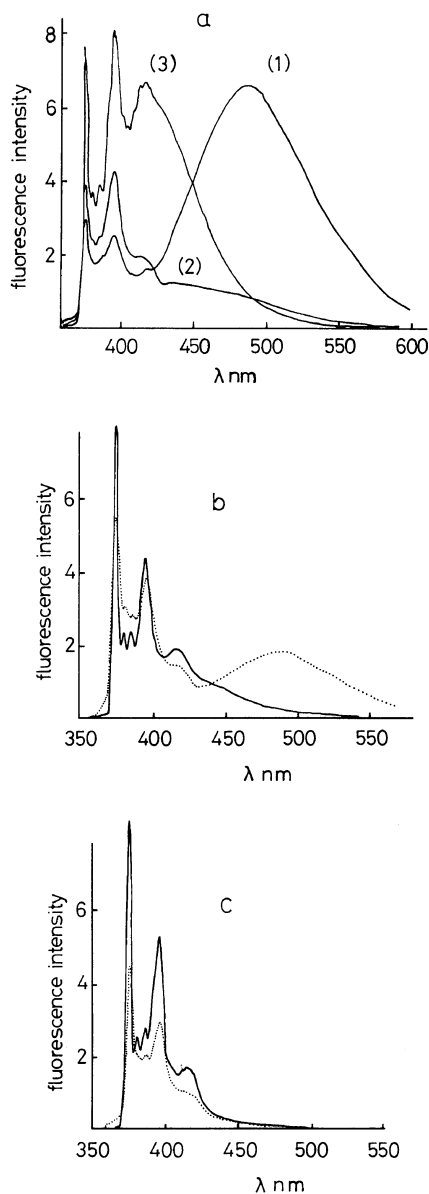


Figure 3. Fluorescence spectra of I, II, and III in MTHF. a: I, $[Py] = 6 \times 10^{-5}$ M; (1), 303 K; (2), 89 K; (3), 77 K. b: II, $[Py] = 6 \times 10^{-5}$ M; -----, 303 K; —, 77 K. c: III, $[Py] = 5 \times 10^{-5}$ M; -----, 303 K; —, 77 K.

emission to the EDA emission with lowering temperature is not continuous. Since the exciplex formation is a diffusion controlled process even if interpolymer association provides favorable exciplex forming sites, the low temperature, and hence high viscosity is an unfavorable condition for the proc-

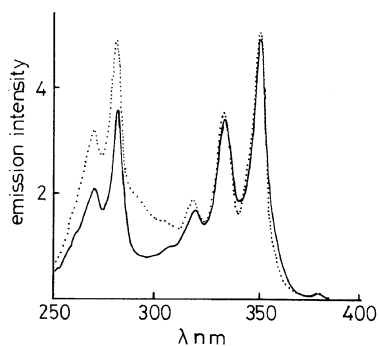


Figure 4. Excitation spectra of I in MTHF at 77 K. $[Py] = 6 \times 10^{-5}$ M. Monitoring wavelength at 377 nm (-----) and 440 nm (—).

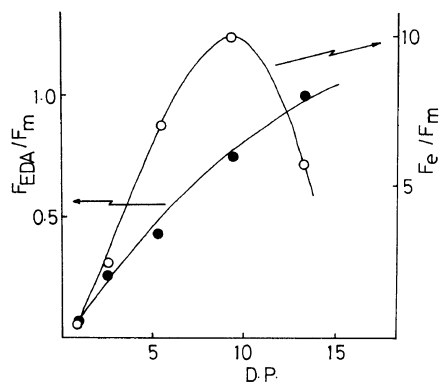


Figure 5. Intensity of EDA complex (F_{EDA}) and exciplex (F_e) emission relative to emission from the locally excited state of Py (F_m) as a function of the degree of polymerization (DP). $[Py] = 6 \times 10^{-5}$ M in MTHF; ●, F_{EDA}/F_m at 77 K; ○, F_e/F_m at 303 K. Since F_{EDA} and F_m were superimposed at 440 nm, the overall F_{440} was corrected to give F_{EDA} by means of subtracting F_m at 440 nm estimated from the value of F_{440}/F_{376} for III and the peak intensity at 376 nm in the spectrum concerned.

ess. The EDA complex emission starts to appear below ~ 90 K, which nearly agrees with the T_g (glass transition temperature) of MTHF. Obviously, the exciplex and the excited EDA complex are not interconvertible. Enhancement of emission intensity at low temperature is a general tendency and the absolute value of F_{440} at 77 K is comparable to or more than that of F_e at r.t. It is therefore unlikely that F_{440} overlapping with the strong exciplex emission at r.t. gradually becomes noticeable as the exciplex emission discipates with lowering temperature. This does not necessarily mean that the EDA emission does not at all mix with the

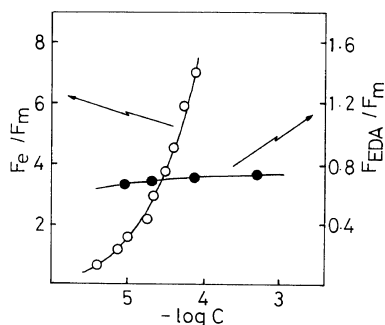


Figure 6. Concentration dependence of EDA complex emission and exciplex emission by I in MTHF. Molecular weight of I = 6,400; ●, EDA complex emission at 77 K; ○, exciplex emission at 303 K.

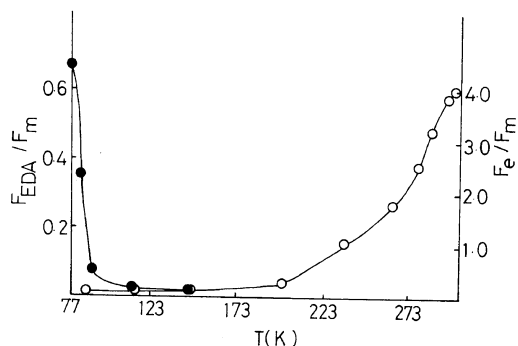


Figure 7. Temperature dependence of EDA complex emission and exciplex emission by I in MTHF. [Py] = 6×10^{-5} M; MW = 4600; ●, F_{EDA}/F_m ; ○, F_e/F_m .

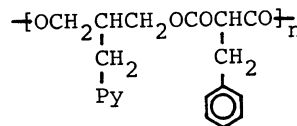
Table II. Comparison of EDA and exciplex emissions by I

	EDA (77 K)	Exciplex (r.t.)
Emission wavelength	~440 nm	~490 nm
Effect of DP on the intensity	Increase with DP	Optimum DP value
Effect of concentration on the intensity	None	Increase with concentration
Effect of temperature on the intensity	Increase at low temperature	Decrease at low temperature
Interaction modes	Intrapolymer phenomena	Intra- and interpolymer phenomena

exciplex emission at r.t. As already reported,⁶ the exciplex emission shifts towards blue when the long wavelength limit of absorption at 365 nm is excited, indicating the participation of at least two emitting species having different excitation profiles.

Environmental Effects on EDA Complex and Exciplex Emissions

The results shown in Figures 1–6 lead to the conclusion that there are differences in the emission behavior of I at r.t. and 77 K. As summarized in Table II. The emission at 77 K apparently arises from the preformed complex whereas that at r.t. requires segment mobility. All circumstantial evidence suggest the emission at 440 nm to be that of an EDA complex. The aggregated Py groups do not exhibit the fluorescence characteristics shown in Figure 3. The polymer containing Py alone as chromophore (IV) is capable of excimer formation in a liquid solution while in a glassy matrix, the emission from only the locally excited state of Py can be observed as shown in Figure 8.



IV
Scheme 2.

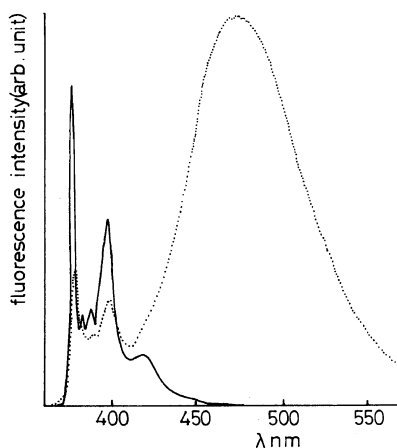
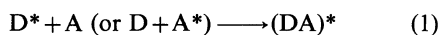


Figure 8. Fluorescence spectra of excimer forming polymer (IV) in MTHF. [Py] = 5×10^{-5} M; MW = 5600; —, 77 K; ·····, 303 K.

Ground state pairing of an exciplex forming donor and acceptor is a point of active investigation.¹¹⁻¹⁸ In principle, (DA)* formed either *via* a locally excited state of D or A(1), or *via* a direct excitation of paired DA(2) should emit fluorescence from an identical energy level. For intermolecular complexes (*i.e.*, D and A are not chemically linked), the generally accepted view is that both reactions (1) and (2) yield the same fluorescent state.¹¹⁻¹⁷ There is, however, a discrete view that both the exciplex and excited EDA complex are simultaneously observed at



77 K for organic cations such as acridinium, acridizinium, and 1-azophenanthrene cations quenched by aromatic donors.¹⁸ In such systems, the apparent exciplex emission and the excitation profiles depend on the wavelength of excitation and the monitoring wavelength, respectively. Furthermore, the fluorescence decay of the pairs is non-exponential, indicating the presence of more than two complexes. Ground state pairing and subsequent emission from an energy level different from that of an exciplex is suspected for more common exciplex forming pairs such as aromatic hydrocarbon-amine combinations in glassy matrix.^{19,20} The reason for the existence of two fluorescent states is considered to be the retarded relaxation due to the steric effects and/or high viscosity in the matrix.¹⁸ However, there seems to be strict steric requirements for an EDA complex to fluorescence differently from an exciplex.²¹ Direct excitation of a complex formed at a low temperature does not necessarily lead to an EDA complex emission. Thus, even in pure DMA as solvent, no anthracene-DMA exciplex is observed at 77 K,²² whereas for Py-DMA or *N,N*-diethylaniline pairs, an EDA complex emission can be observed to some extent.²³

The confusion in the definition of an excited EDA complex and exciplex would further complicate an understanding of the literature data. If one is going to define an exciplex by process (1), one immediately encounters the difficulty of classifying the case when D and A form a pair but are not complexed so that the exciplex state can be formed without diffusion even in a glassy matrix. An ambiguous situation occurs as well for process (2), such

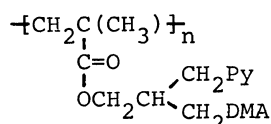
as the participation of a contact charge transfer complex whose concentration is not measurable. We consider that the simplest way to distinguish an exciplex from an excited EDA complex would be to examine the complete agreement between the excitation spectra with monitoring emissions from a locally excited state and an apparent excited complex state. Consequently, regardless of the pairing of D with A, if the photoabsorbing species are spectroscopically identical with the isolated D or A, we call the new broad emission an exciplex emission. There are, however, few examples of quantitative investigation in which excitation spectra as a function of the monitoring wavelength are compared.

As we learned from the study of polymer-bound exciplexes and excimers, the effects of a polymer consist not only of an increase in local chromophore concentration but also protection of the exciplex from solvation.^{1,3,5-7} Segment mobility in a polymer environment is subjected to a higher energy barrier in comparison with the relevant small molecular models.²⁴ Polymer environments may consequently provide more favorable conditions for excited EDA complexes than for genuine exciplexes requiring segment mobility in general. The difference between **I** and **II** in fluorescence behavior (Figures 3a and b) cannot be interpreted by the difference in chromophore concentration. For an ideally stretched polymer, the local chromophore concentration should differ from that of the dimer model only by a factor of 2. Although the polymer chain entanglement would multiply the factor to some extent as a result of the non-neighboring group participation, the difference between **I** and **II** is far too great to be explainable by the concentration term alone. **II** emits fluorescence mainly from the locally excited state at 77 K, suggesting that the EDA complex formation between neighboring groups is sterically disadvantageous. This argument is consistent with the DP effect on the EDA emission by **I** (Figure 5) since the non-neighboring group participation should increase with DP.

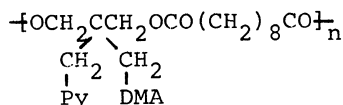
The DP effect is also consistent with the intrapolymer phenomena of the excited EDA complex formation. A very different concentration and DP dependence of the exciplex and the EDA complex emission are understandable on the condition that the former is a mostly interpolymer diffusion-

controlled dynamic event driven by a zipping effect while the latter is an intrapolymer static phenomenon. A difficult question to be answered is the reason why the interpolymer association favorable for the exciplex formation does not bring the EDA complex formation. Although we have no ready answer for this, the shrinking of a polymer chain at low temperature might reduce the tendency of interpolymer association. More fundamentally, as demonstrated for various small molecular systems, the strict conformational requirements for EDA complex emission but not for exciplex formation would be responsible for this. This problem is still in a rudimentary stage of exploration.

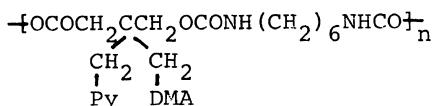
The problem of dual complex formation is remarkably dependent on polymer structure, even if equimolar Py and DMA are incorporated into polymers. For example, V emits extremely strong fluorescence from the EDA complex at 77 K in MTHF while the extent of this is much less for VI and VII. On the other hand, all polymers exhibit



V



VI



VII

Scheme 3.

inter- and intrapolymer exciplex formation. In reference to the discussions mentioned above, the controlling factors will be congestion of chromophores in polymers, solubility, molecular weight, rigidity of polymer chain and interpolymer interactions. These factors are expected to affect the balance between intra- and interpolymer interactions. Detailed studies on the exciplex and EDA complex formation by V, VI, and VII with emphasis

on their structural differences will be dealt with in forthcoming publications.

CONCLUSION

The emission of an EDA complex is a general phenomenon for polymers containing Py and DMA in a glassy matrix. The intensity of the emission depends very much on the polymer structure and DP. Since weak but definite interchromophore attraction in the ground state is an essential requirement, the excimer forming polymers do not exhibit such a trend of ground state interaction at all.

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