

Intramolecular excimer formation in model compounds for polyesters prepared from 2,6-naphthalene dicarboxylic acid and eight different glycols

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Fluorescence has been measured in dilute solutions of model compounds for polymers of 2,6-naphthalene dicarboxylic acid and eight different glycols. The glycols are HO-(CH₂)_i-OH, *i* = 2–6, and H-(OCH₂CH₂)_j-OH, *j* = 1–4. The ratio of excimer to monomer emission depends on the glycol used. Studies as functions of temperature and solvent show that, in contrast with the analogous polyesters in which the naphthalene moiety is replaced with a benzene ring, there can be a substantial dynamic component to the excimer emission. Extrapolation to media of infinite viscosity shows that in the absence of rotational isomerism during the lifetime of the singlet excited state, there is an odd–even effect in the series in which the flexible spacers differ in the number of methylene units, but not in the series in which the flexible spacers differ in the number of oxyethylene units.

(Keywords: conformation; dynamics; excimer; fluorescence; polyester)

INTRODUCTION

Intramolecular excimer emission can be observed in dilute solutions of many polymers that have a repeating sequence denoted by -A-B_m-, where A is a chromophore that is capable of the formation of an excimer, and B is a flexible spacer. The number of flexible spacers will be denoted by *m* for the general case. When the discussion is specialized to methylene or oxyethylene spacer, *m* will be replaced by *i* or *j*, respectively. In the absence of energy migration, the dominant process for the production of an intramolecular excimer depends on the relationship between the fluorescence lifetime of the chromophore and the time required for conversion of B_m from one rotational isomer to another. When A is terephthalate or isophthalate, the fluorescence lifetime in dichloroethane at ambient temperature is less than 0.1 ns¹. This lifetime is much shorter than the time required for first passage of B_m from a set of rotational isomers that does not support the formation of an excimer to another set conducive to the formation of an excimer². Under these circumstances, excimer formation is achieved by minor adjustments, achieved without crossing energy barriers between stable rotational isomers, of the conformations of molecules that were close to the geometry required for an excimer at the moment of excitation. For this reason, the dependence upon *m* of the ratio of the intensities of emission from excimer and monomer, *I_D/I_M*, in these polymers is susceptible to rationalization by rotational isomeric state theory³. This theory is used for evaluation of the population of -A-B_m-A- that occupy a set

of rotational isomers from which an excimer can be formed without crossing an energy barrier larger than ~1 kcal mol⁻¹ (refs 1, 4 and 5).

Substitution for terephthalate by a chromophore with a sufficiently longer fluorescence lifetime will permit the opportunity for the formation of an excimer as a consequence of rotational isomerization in B_m. The theoretical evaluation of this addition mechanism for the formation of an excimer requires knowledge of the rate of first passage of -B_m- from the set of rotational isomers that cannot form an excimer to a set that can². An attractive set of polymers for this purpose is provided by the family of polyesters in which A is derived from 2,6-naphthalene dicarboxylic acid. The substitution of this chromophore for terephthalate should permit an important lengthening of the fluorescence lifetime without major alteration in the short range interactions that influence the conformation of B_m. The basis for the similarity of the short range interactions that affect the conformation of B_m is apparent by comparison of the two structures in *Figure 1*.

A potential complicating factor is presented by the increase in the Förster radius⁶ that accompanies replacement of the terephthalate by the substituted naphthalene. The increase in the Förster radius opens up the possibility of another dynamic contribution to the formation of an excimer, as a consequence of intramolecular migration of the electronic excitation^{7–10}. This potential complication is avoided if every molecule contains two chromophores.

Here we describe the synthesis and steady state fluorescence of the model compounds of the form A-B_m-A, where A is a naphthalene that is substituted in

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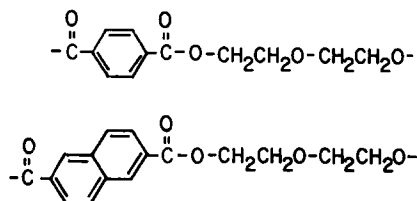


Figure 1 Two segments of $-A-B_2-$ in which A is derived from either terephthalic acid or 2,6-naphthalene dicarboxylic acid and B is oxyethylene

position 2. The flexible spacers used are methylene, for which i is 2–6, and oxyethylene, for which j is 1–4. The influence of the viscosity of the solvent on the intensity of the excimer emission in these compounds demonstrates the presence of a greater dynamic contribution to the population of excimers than was the case in the polymers in which A is terephthalate.

METHODS

Naphthyl groups were attached to the ends of the glycol by the reaction of a slight excess of 2-naphthoyl chloride (2.5 mol) with the glycol (1 mol) in the presence of triethyl amine in chloroform at room temperature. The glycols used were $HO(CH_2)_iOH$, $i=2-6$, and $H(OCH_2CH_2)_jOH$, $j=1-4$. (The member of the former series with $i=2$ is identical with the member of the latter series with $j=1$. No other molecule is common to both series.) After washing the solution sequentially with water, aqueous sodium bicarbonate, and excess water, the crude product contains the disubstituted glycol as well as the acid and a small fraction of the monosubstituted glycol. Separation of the components was achieved by column chromatography on silica gel. Elution was achieved with a mixture of chloroform and ethyl acetate. The ratio of the volumes of chloroform and ethyl acetate was in the range 5–15, depending on the glycol used. It was chosen so that the R_f values for the three components differed by more than 0.3. After removal of the solvent from the fraction that contained the disubstituted glycol, the product was dissolved in chloroform and reprecipitated by the addition of methanol.

Steady state measurements of the fluorescence were performed with an SLM 8000C fluorometer equipped with a double monochromator in the excitation path. Slits were 4 nm for excitation and 2 nm for emission. Magic-angle conditions were employed¹¹. Solvents of spectrophotometric grade were purchased from Aldrich Chemical Co. and used without further purification. Solvent blanks were measured and subtracted from the observed spectra. Typical absorbances at the wavelength of excitation, 292 nm, were about 0.1.

RESULTS AND DISCUSSION

Excimer emission

All samples had similar excitation spectra. *Figure 2* depicts the excitation spectra for 2-methyl naphthoate and for the diethylene glycol labelled with naphthalene at each end. The peaks in the excitation spectra are found near 295, 320, and 338 nm.

Figures 3 and 4 depict emission spectra for methyl 2-naphthoate and the four end-labelled samples with oxyethylene spacers. Spectra presented in *Figure 3* were

obtained in methanol, which has a viscosity of 0.547 cp at 25°C. Ethylene glycol, for which the viscosity is 16.32 cp at 25°C, was used as the solvent in *Figure 4*. Spectra in each figure are normalized at the maximum emission of methyl 2-naphthoate. This maximum occurs at 363 nm in methanol and at 366 nm in ethylene glycol. To the red of the wavelength used for normalization of the spectra, the end-labelled samples with oxyethylene spacers exhibit greater emission than methyl 2-naphthoate. This enhancement in the emission is attributed to intramolecular formation of excimers by the naphthalene groups at the chain ends. Inspection of the figures shows that the excimer emission for a particular sample is always higher in the less viscous solvent, and, in a particular solvent, it is greatest when the number of oxyethylene spacers is two. A simple means for comparing the ratio of excimer to monomer emission, denoted by I_D/I_M , in several spectra is

$$I_D/I_M = [I(m, 400) - I(0, 400)]/I(\text{norm}) \quad (1)$$

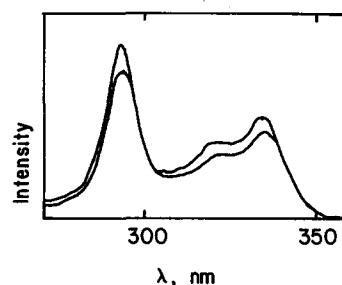


Figure 2 Excitation spectra for 2-methyl naphthoate (upper line) and diethylene glycol (lower line) esterified at both ends with 2-naphthoate. Emission is monitored at 400 nm

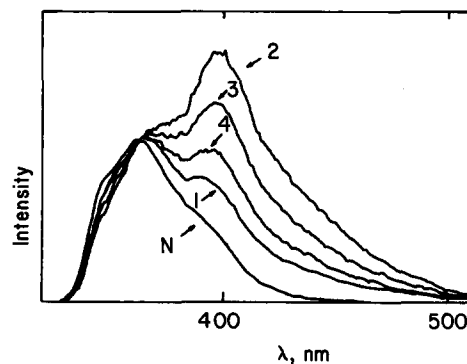


Figure 3 Emission spectra, normalized at 363 nm, for methyl 2-naphthoate (denoted by N) and oligomers of ethylene glycol esterified at both ends with 2-naphthoate. Integers denote the number of oxyethylene units in the flexible spacer. The solvent is methanol

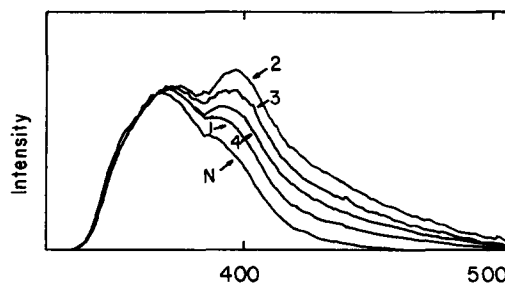


Figure 4 Emission spectra, normalized at 363 nm, for methyl 2-naphthoate (denoted by N) and oligomers of ethylene glycol esterified at both ends with 2-naphthoate. Integers denote the number of oxyethylene units in the flexible spacer. The solvent is methanol

where $I(m, 400)$ denotes the normalized intensity at 400 nm for the end-labelled species with m spacers, $I(0, 400)$ is the normalized intensity obtained with methyl 2-naphthoate at 400 nm, and $I(\text{norm})$ is the intensity at the wavelength used for normalization of the spectra. This procedure contains a correction for the emission by the monomer at 400 nm, but it does not attempt to introduce a correction for any emission by the excimer at the wavelength used for normalization.

Figures 5 and 6 depict the normalized emission spectra for the methyl 2-naphthoate and $\text{HO}(\text{CH}_2)_i\text{OH}$ that has been esterified at both ends with 2-naphthoate. At each value of i , the value of I_D/I_M is larger in the less viscous solvent, as was also the case in the samples with oxyethylene spacers. The samples with $j=2$ in Figures 3 and 4, and with $i=5$ in Figures 5 and 6, have 10 bonds between the naphthalene rings. The only difference in these two compounds is the substitution of an oxygen atom for a methylene group at the junction of the fifth and sixth bonds between the two aromatic rings. Although the aromatic rings are separated by the same number of bonds, the values of I_D/I_M are different. Excimer emission is stronger when the spacer is derived from diethylene glycol, rather than pentamethylene glycol. This observation undoubtedly has its origin in the greater flexibility of polyoxyethylene than polymethylene.

Influence of viscosity and temperature

Similar measurements were performed in mixed solvents prepared from methanol and ethylene glycol. The results

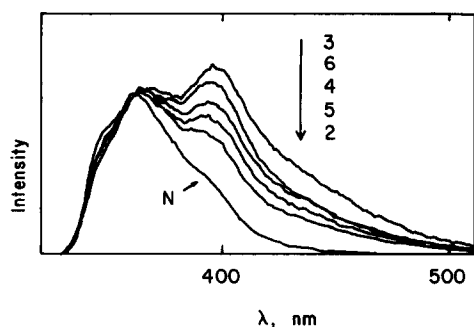


Figure 5 Emission spectra, normalized at 363 nm, for methyl 2-naphthoate (denoted by N) and $\text{HO}(\text{CH}_2)_i\text{OH}$ esterified at both ends with 2-naphthoate. The values of i are shown for each spectrum. The solvent is methanol

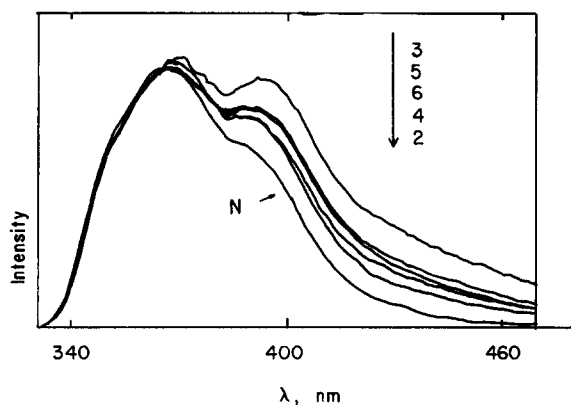


Figure 6 Emission spectra, normalized at 366 nm, for methyl 2-naphthoate (denoted by N) and $\text{HO}(\text{CH}_2)_i\text{OH}$ esterified at both ends with 2-naphthoate. The values of i are shown for each spectrum. The solvent is ethylene glycol

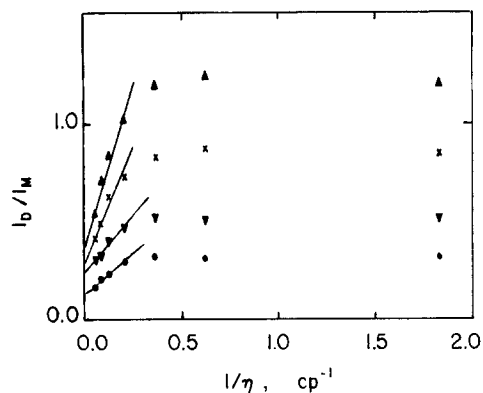


Figure 7 Dependence of I_D/I_M on the reciprocal of the viscosity of the solvent for oligomers of ethylene glycol esterified at both ends with 2-naphthoate. The change in viscosity is produced by changing the ratio of methanol to ethylene glycol in the solvent. $j=1, 2, 3, 4$ for ●, ▲, ×, ▼ respectively

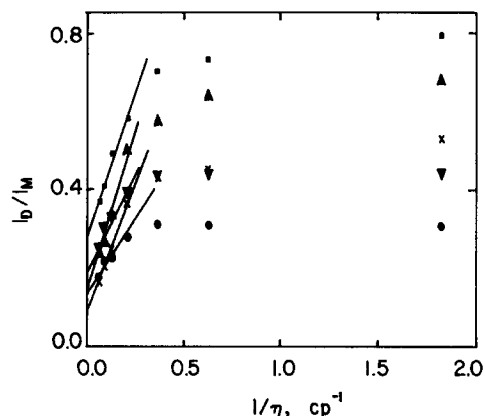


Figure 8 Dependence of I_D/I_M on the reciprocal of the viscosity of the solvent for $\text{HO}(\text{CH}_2)_i\text{OH}$ esterified at both ends with 2-naphthoate. The change in viscosity is produced by alteration in the ratio of methanol to ethylene glycol in the solvent. $i=2, 3, 4, 5, 6$ for ●, ■, ×, ▼, ▲ respectively

are presented in Figures 7 and 8 as I_D/I_M vs. the reciprocal of the viscosity of the mixed solvent. The four samples with oxyethylene spacers (Figure 7) experience a monotonic decrease in I_D/I_M with increasing solvent viscosity as η rises above ~ 3 cp. The values of I_D/I_M become nearly independent of η at lower solvent viscosities. At any η , the values of I_D/I_M change with j as $1 < 4 < 3 < 2$.

The series of five samples with methylene spacers behave somewhat differently, as is shown in Figure 8. In the most viscous medium, I_D/I_M exhibits an odd-even effect, with the larger values being obtained when i is odd. The values of i , in the order of increasing I_D/I_M , are $4 < 2 < 6 < 5 < 3$. The odd-even effect is absent in the least viscous medium, where the order is $2 < 5 < 4 < 6 < 3$.

Spectra were also measured as a function of temperature in ethylene glycol. The results are depicted in Figures 9 and 10, using the same format as that employed in Figures 7 and 8. In Figures 7 and 8, the variation in viscosity is obtained by the isothermal change in solvent composition, and in Figures 9 and 10 it is obtained by changing the temperature of a solvent that contains a single component. The values of I_D/I_M for the lower viscosities in Figure 10 are smaller than the values of I_D/I_M at the same viscosities in Figure 8. As the temperature rises above $\sim 30^\circ\text{C}$, it has an effect on I_D/I_M that cannot be accounted for simply by the thermally induced change in the viscosity of the solvent. The

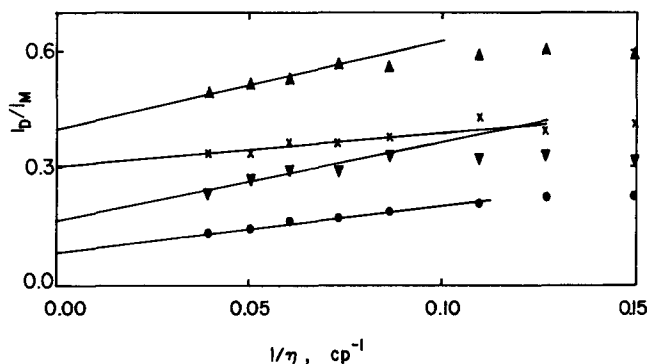


Figure 9 Dependence of I_D/I_M on the reciprocal of the viscosity of the solvent for oligomers of ethylene glycol esterified at both ends with 2-naphthoate. The change in viscosity is produced by alteration in the temperature. Symbols as in Figure 7

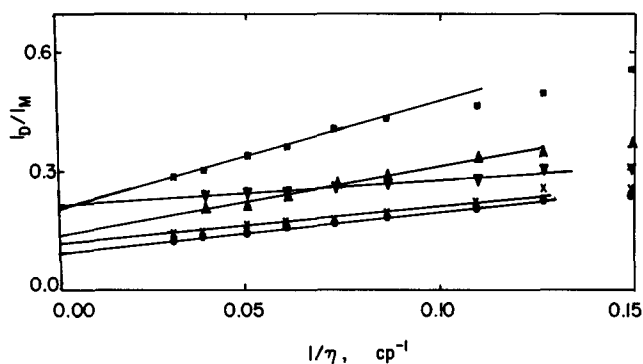


Figure 10 Dependence of I_D/I_M on the reciprocal of the viscosity of the solvent for $\text{HO}(\text{CH}_2)_4\text{OH}$ esterified at both ends with 2-naphthoate. The change in viscosity is produced by alteration in the temperature. Symbols as in Figure 8

decrease in I_D/I_M at the higher temperatures is consistent with the activation of an additional mechanism for the non-radiative dissociation of the excimer as the temperature rises above $\sim 30^\circ\text{C}$. This effect is also apparent in the series with methylene spacers, as can be seen by a detailed comparison at viscosities near 6 cp of the I_D/I_M in Figures 8 and 10. However, the influence of the thermally activated process is clearly smaller in the series with methylene spacers than in the series with oxyethylene spacers. Since polyoxyethylene is a more flexible chain than polymethylene, the results suggest that the thermally activated process may be dissociation of the excimer to an excited monomer and a ground-state monomer, as a consequence of a change in conformation of the flexible spacer.

Limiting results at high viscosities

Estimation of the dependence of I_D/I_M on m , in the limit of very high viscosity, can be obtained either from the isothermal data with mixed solvents prepared from methanol and ethylene glycol, or from the data obtained as a function of temperature in ethylene glycol. None of the plots of I_D/I_M vs. $1/\eta$ are linear over the entire range of η covered in the experiments. Deviations from linearity are most noticeable in the data obtained with the mixed solvents, which extend to lower viscosities. The straight lines in Figures 7–10 are drawn through the four points with the highest viscosities. Linear extrapolation to $1/\eta=0$ provides estimates for I_D/I_M in media so viscous that rotational isomerism cannot occur during the lifetime of the electronic excited state.

The limiting values of I_D/I_M obtained from these linear extrapolations are given in Table 1. The differences in the limiting values obtained by the two methods range from 0.02 to 0.08. Both approaches find the same order for I_D/I_M in the oxyethylene series, and they both predict an odd–even effect in the methylene series. These estimates show how the probability for formation of an intramolecular excimer depends on the number of bonds in the flexible spacer when the excimer must be populated without allowing rotational isomerism between *trans* and *gauche* states in the spacer. The results are therefore susceptible to analysis by a rotational isomeric state treatment that identifies all combinations of rotational isomers that can form an intramolecular excimer, and assigns probabilities to these conformations.

The odd–even effect in the methylene series is lost at sufficiently low viscosity, as shown by the emission spectra depicted in Figure 5 and by the behaviour of I_D/I_M depicted in Figures 8 and 10. When the rate of rotational isomerism becomes sufficiently high so that interchange of *trans* and *gauche* states can occur during the lifetime of the electronic excited state, there is a new dynamic contribution to the population of excimers. A challenge to a dynamic rotational isomeric state treatment of these fragments is to explain why the activation of this route to the population of an excimer results in the loss of the odd–even effect.

Rotational isomeric state analysis

The rotational isomeric state model used is identical with that described in the previous work, in which the phenyl groups are replaced by 2-naphthyl groups¹. Two additional bonds are added, each connecting the centres of the two aromatic rings forming an individual naphthalene moiety. The assumed target conformation has the two rings oriented so that the normals to their planes are parallel, the line joining the centres is parallel to the normals, and the centres are separated by 350 pm. Some tolerance must be used for these criteria because the rotational isomeric state analysis does not sample conformational space continuously. The statistical weights used and the restraints (tolerances) applied are exactly identical to those described in a previous paper¹. Because of the larger structure of the naphthalene as compared with benzene, there will be more conformations conducive to excimer formation. Each naphthalene unit has two aromatic rings, and two different types of excimers were distinguished in the calculations. Both aromatic rings of each naphthalene unit overlap in one type, and only one

Table 1 Estimates of I_D/I_M in media of infinite viscosity^a

Spacer	m	I_D/I_M (solvent)	I_D/I_M (T)	Range
Oxyethylene	1	0.14	0.09	0.12 ± 0.03
Oxyethylene	2	0.40	0.43	0.42 ± 0.02
Oxyethylene	3	0.30	0.30	0.30 ± 0.00
Oxyethylene	4	0.24	0.17	0.20 ± 0.04
Methylene	2	0.14	0.09	0.12 ± 0.03
Methylene	3	0.29	0.20	0.24 ± 0.05
Methylene	4	0.08	0.12	0.10 ± 0.02
Methylene	5	0.21	0.20	0.20 ± 0.01
Methylene	6	0.11	0.13	0.12 ± 0.01

^a I_D/I_M (solvent) is estimated from the data in mixed solvents, and I_D/I_M (T) is estimated from the data at various temperatures in ethylene glycol. The last column presents the range covered by these two estimates of I_D/I_M

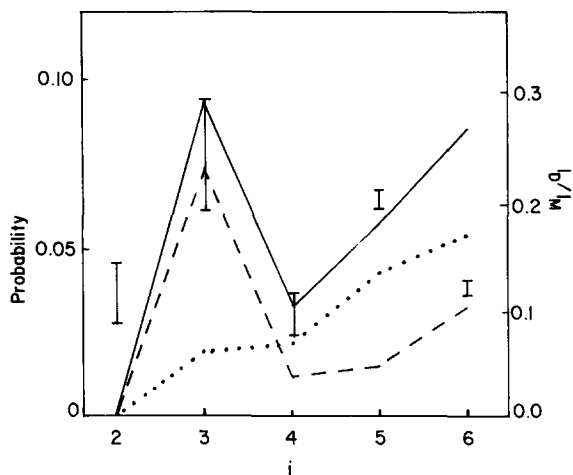


Figure 11 Dependence of the probability of excimer formation on the number of methylene spacers separating the two 2-naphthoate units, when both rings (---) or only one ring (.....) in each unit experiences overlap. The solid line denotes the sum. The calculation does not permit crossing of rotational energy barriers during the lifetime of the excited state. Experimentally determined values of I_D/I_M , extrapolated to infinite viscosity (Table 1), are plotted as the vertical bars

of the aromatic rings of each naphthalene unit participates in overlap in the other type.

Figure 11 depicts the change in the probability of excimer formation as a function of i , the number of methylene spacers separating the naphthalene units. The analysis does not permit the crossing over from one rotational isomer to another during the fluorescence lifetime. Only oscillations about the dihedral angles are permitted. The estimates of excimer formation should hence correspond to the I_D/I_M extrapolated to a media of infinite viscosity (which suppressed the crossing of

energy barriers between rotational isomers during the lifetime of the excited state), obtained from steady-state fluorescence experiments. For the case where both of the naphthalene rings overlap, the probability increases with the number of spacer units. The contribution of conformations which lead to the overlap of at least one of the rings must be included if the maximum value calculated for I_D/I_M is to occur at $i=3$. An odd-even effect is observed for i between 2 and 5. The rotational isomeric state analysis overestimates the probability of excimer emission when i is 6, perhaps due to the neglect of higher order interactions that become of greater importance as i increases.

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