Intramolecular excimer formation by phthaloyl, isophthaloyl and terephthaloyl groups in polyesters with different numbers of methylene and oxyethylene spacers

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Steady-state fluorescence spectra have been obtained for dilute solutions of 16 aromatic polyesters with the repeat unit $-A-B_m-$. The chromophore, A, is isophthaloyl or phthaloyl, and the flexible spacer, B, is methylene or oxyethylene. The number of methylene units is 2–6, and the number of oxyethylene units is 1–4. The samples are of low molecular weight. Members of the series in which A is phthalate show no detectable excimer emission. In contrast, members of the series in which A is isophthalate exhibit an excimer emission that depends on m in a manner reminiscent of that reported earlier for analogous polyesters in which A is terephthaloyl. Time-resolved emission shows that the excitation on an isolated chromophore has a lifetime of 40–50 ps. During this short time, there is little opportunity for rotational isomerism of the flexible spacer, B_m, between neighbouring chromophores. Consequently the excimer emission is dominated by segments in which $A-B_m-A$ is very near the excimer geometry at the instant of excitation. Repulsive steric interaction of the *ortho* ester groups on one chromophore with similar ester groups on another chromphore is responsible for the absence of detectable excimer emission from the series in which A is phthalate.

(Keywords: polyester; chain conformation; excimer)

INTRODUCTION

Two recent reports[1,2] describe the excimer formation in dilute solution by polymers made up of terephthaloyl groups separated by flexible spacers. The flexible spacers consist of sequences of either methylene[2] or ethylene oxide[1] units. The repeating sequences in these polymers can be written as $-A-B_m-$, where A is the terephthaloyl group, B is either CH_2 or CH_2-CH_2-O, and m is a small positive integer. The ratio of the intensities of the steady-state excimer and monomer emissions, I_D/I_M, is maximal if $m=3$ (or 2) when B is CH_2 (or CH_2-CH_2-O). This behaviour can be rationalized by an equilibrium rotational isomeric state model for the conformations accessible to the fragment $A-B_m-A$. The equilibrium model is appropriate for the analysis of the dependence of I_D/I_M on m in a given series because the dynamic contribution to the excimer population is proportional to the equilibrium excimer population at short times, as shown by application of the dynamic rotational isomeric state model to the rates of intramolecular conformational transitions in these polyesters[3]. The fluorescence lifetimes of the chromophores are indeed extremely short, as will be reported here.

The assumptions employed in the theoretical treatments of the polymers in which A is a terephthaloyl group carry with them implications for the behaviour of the related series of polymers in which A is either an isophthaloyl or phthaloyl group. Segments of the polymers in which the spacer is three methylene units are depicted in *Figure 1*. The validity of these assumptions is assessed here by the experimental characterization of the behaviour of I_D/I_M in dilute solution for four series of polymers: (1) A = isophthaloyl, $B=CH_2$, $m=2$–6; (2) A = isophthaloyl, $B=CH_2-CH_2-O$, $m=1$–4; (3) A = phthaloyl, $B=CH_2$, $m=2$–6; (4) A = phthaloyl, $B=CH_2-CH_2-O$, $m=1$–4. Excimer emission is found to be extremely weak in the two series in which A is a phthaloyl group. When A is an isophthaloyl group, excimer emission is easily observed. The dependence of I_D/I_M on m is of similar form when the chromophores are terephthaloyl or isophthaloyl groups. These experimental results closely resemble the ones expected based on the earlier analysis[1,2] of the behaviour of I_D/I_M in the polymers that contain terephthaloyl groups.

METHODS

Preparation of the polyesters in which A is terephthaloyl has been described earlier[1,2]. All other macromolecules studied are polyesters prepared from isophthaloyl

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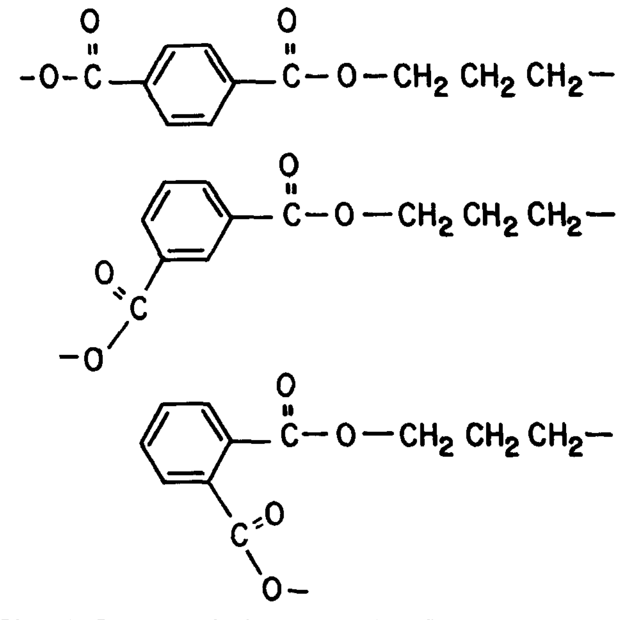

Figure 1 Fragments of polymers in which the flexible spacer is a chain of three methylene units and the chromophores (from top to bottom) are terephthaloyl, isophthaloyl or phthaloyl groups

chloride or phthaloyl chloride and $HO(CH_2)_mOH$ or $HO(CH_2CH_2O)_mH$. Dimethylisophthalate (DMI), dimethylphthalate (DMP) and dimethylterephthalate (DMT) were used as model compounds. They were purchased from Aldrich and used without further purification. The polymers were prepared by the method used for the synthesis of the polymers of terephthaloyl groups and methylene units that were of low molecular weight[2]. Dichloroethane, ethyl acetate and *p*-dioxane were of spectrophotometric grade. They were purchased from Aldrich and used in the fluorescence measurements without further purification.

An SLM 8000C fluorometer equipped with a double monochromator in the excitation path was used for the measurements of the steady-state fluorescence. Polarizers in the excitation and emission paths were set for magic angle conditions[4]. The slits were 16 nm for excitation and for emission. Solvent baselines were measured and subtracted from the fluorescence spectra obtained with the dilute polymer solutions. Excitation for each series was at the wavelength of maximal absorption for the band near 280 nm (276 nm for phthalate, 282 nm for isophthalate). Typical absorbances at the wavelength of excitation were 0.1–0.2. All measurements were performed at 25°C.

The time-correlated single-photon counting technique was used to perform the time-resolved fluorescence measurements[5]. The excitation wavelength was at 294 nm and the emission was monitored at 324 nm (monomer) and 390 nm (excimer). The specifics of the apparatus have been reported previously[6]. The instrumental response function is 60 ps full width at half maximum and 110 ps full width at one-tenth maximum. By iterative convolution of the measured decay function and an exponential decay law, fluorescence decay times as short as 10 ps can be determined with this instrument.

The rotational isomeric state analysis for the isophthaloyl series is identical with that employed earlier for the terephthaloyl series[1,2]. The analysis of the phthaloyl series differs in that the conformation at the C^{ar}–C′ bonds is changed by a rotation of 90° due to the steric interaction of the two carboxyl groups in the *ortho* position[7]. There are also changes in a few of the statistical weights. These features were incorporated in the rotational isomeric state analysis in the manner utilized by Riande for the quantitative description of the mean-square dipole moments of polyesters that contain the phthaloyl group[7].

FLUORESCENCE LIFETIMES OF TWO MODEL COMPOUNDS AND SELECTED POLYMERS

The time-resolved fluorescence from DMI and DMT in dichloroethane is summarized in *Table 1*. Upon excitation at 294 nm, the fluorescence at 324 nm can be fitted to a single exponential with a very short lifetime of 40–50 ps. The fluoroescence lifetimes (324 nm emission) for the polyesters in the terephthalate series are also very short, as shown in *Table 1*. Comparison of these times with the internal dynamics of the A–B_m–A fragment[3] shows that the polymers in which B is methylene undergo amost no conformational change during the lifetime of the excited state. There is the opportunity for a small amount of rotational isomerism during the lifetime in the more mobile chains in which B is oxyethylene.

The emission at 390 nm from four polyesters that show substantial excimer emission in the steady-state measurements reported earlier[1,2] is presented in *Table 2*. At 390 nm, each polymer exhibits a subnanosecond component reminiscent of that seen in the monomer region (*Table 1*), as well as longer components that are in the range 0.8–5.2 ns.

Detailed analysis of the time-resolved emission data is not pursued here. The crucial point is that the decay of the fluorescence from an isolated chromophore (*Table 1*) is so rapid that little internal rotational isomerism is possible during the lifetime of the electronic excited state. (The heights of the saddles between rotational isomers are larger than 2 kcal mol^{-1} (ref. 3).) Consequently

Table 1 Fluorescence lifetimes (ps) (294 nm excitation, 324 nm emission) in dichloroethane

Chromophore	Spacer	m	τ^a (%)	χ^2
Isophthalate	None[b]	0	41 (99+)	1.36
Terephthalate	None[b]	0	48 (99+)	3.06
Terephthalate	Oxyethylene	1	70 (99+)	1.38
		2	48 (98+)	2.04
		3	46 (99+)	1.58
		4	47 (99+)	1.24
Terephthalate	Methylene	2	70 (99+)	1.38
		3	40 (99+)	2.23
		4	40 (99+)	4.44
		5	31 (99+)	1.51
		6	29 (99+)	1.66

[a] Estimated error in these lifetimes is ±20 ps

[b] Denotes the model compounds, dimethylisophthalate and dimethylterephthalate

Table 2 Fluorescence lifetimes (ps) (294 nm excitation, 390 nm emission) in dichloroethane for selected polymers in which A is terephthaloyl

Space	m	τ_1 (%)	τ_2 (%)	τ_3 (%)	χ^2
Oxyethylene	2	98 (31)	1210 (25)	3530 (44)	0.98
	3	72 (60)	1050 (21)	3300 (19)	1.14
Methylene	3	91 (56)	2110 (35)	5190 (8)	1.62
	5	36 (74)	820 (14)	3450 (11)	1.35

excimer emission must arise from those pairs of chromophores that, at the instant of excitation, occupy a set of rotational isomers which can form an excimer by minor adjustments of the dihedral angles within their assigned conformational energy wells. For this reason, the extent of the excimer emission can be predicted quite well from the equilibrium rotational isomeric state model for the chain[1,2]. At early times, any dynamic contribution to the population of the excimer-forming rotational isomers will serve to maintain the relative populations deduced from the equilibrium ensemble[3].

POLYMERS THAT CONTAIN ISOPHTHALOYL GROUPS

Figures 2 and *3* depict polymer emission spectra for the series in which the chromophores are isophthaloyl groups. DMI denotes the fluorescence from the model compound, dimethylisophthalate. This emission spectrum is the one expected from the polymers if the chromophores behave independently. The flexible spacers are composed of oxyethylene and methylene groups in *Figures 2* and *3*, respectively. In each figure, the emission spectra are normalized at 310 nm. All of the polymers exhibit significant emission to the red of that seen with the model compound, as was also the case in the series in which the chromophores were terephthaloyl groups[1,2]. This red-shifted emission, with a maximum intensity near 345 nm, is attributed to the intramolecular formation of excimers. The ratio of the emission intensities at 345 and 310 nm is used as a measure of the dependence of the amount of excimer formation on m. The ratio of excimer emission to monomer emission is strongly dependent on m. It is maximal at $m=2$ in the oxyethylene series (*Figure 2*), as was also the case in the analogous series with terephthaloyl groups as chromophores[1]. The ratio I_D/I_M is maximal at $m=3$ in the methylene series (*Figure 3*). This observation was also found in the equivalent series in which terephthaloyl groups replace the isophthaloyl groups[2]. Qualitatively, the only difference in the trends seen in the terephthaloyl and isophthaloyl series with identical types of flexible spacers is in the relationship between I_D/I_M for the last three members of the methylene series, where m is 4–6. When the chromophore is the isophthaloyl group, this ratio decreases as m increases from 4 to 6, but when the chromophore is the terephthaloyl group, the polymer with $m=5$ has a larger I_D/I_M than the polymers with $m=4$ or 6 (ref. 2).

The theoretical rationalization for the dependence of I_D/I_M on the number of oxyethylene[1] or methylene[2] spacers between terephthaloyl groups was based on a rotational isomeric state analysis of the fragment A–B$_m$–A. The only concession to chain dynamics in this analysis was the incorporation of nine, rather than three, rotational isomers for each bond about which rotation can occur. The motivation for this assignment was to allow for the independent oscillations of each rotatable bond within the conformational energy well for a rotational isomer. Each of the conformations of A–B$_m$–A was examined to see whether it would bring the pendant aromatic rings into the sandwich geometry[8] of an excimer. The sums of the probabilities of the excimer-forming conformations were evaluated as a function of m in each series. The sum was maximal at $m=2$ in the oxyethylene series and at $m=3$ in the methylene series.

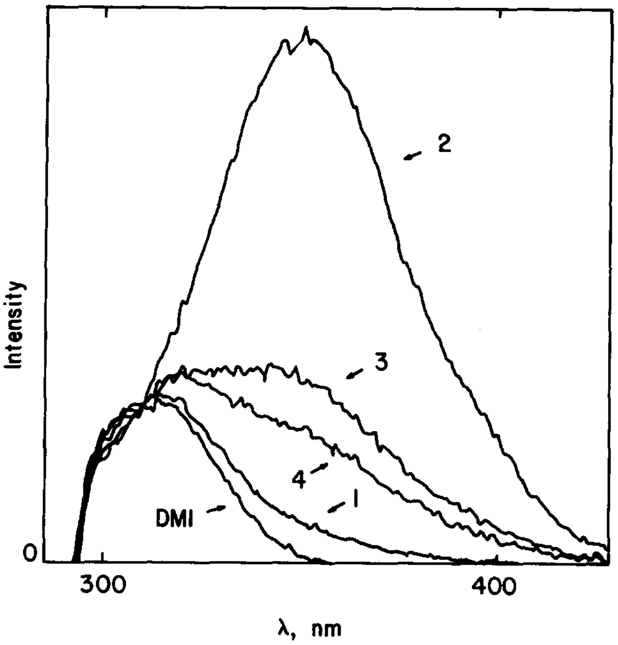

Figure 2 Fluorescence emission (normalized at 310 nm) for dimethylisophthalate (DMI) and polyesters in which isophthaloyl units are separated by m oxyethylene units. The values of m, ranging from 1 to 4, are noted for each curve

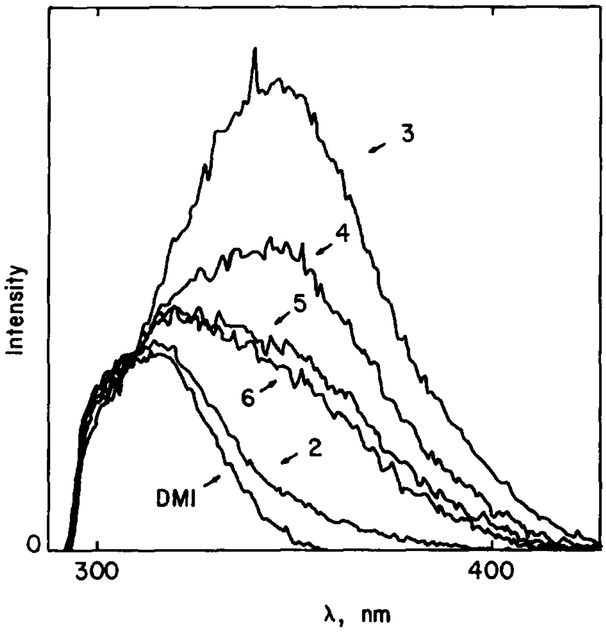

Figure 3 Fluorescence emission (normalized at 310 nm) for dimethylisophthalate (DMI) and polyesters in which isophthaloyl units are separated by m methylene units. The values of m, ranging from 2 to 6, are noted for each curve

Since there is negligible short-range steric interaction between the two ester groups bonded to a given terephthaloyl or isophthaloyl unit, a rotational isomeric state analysis for A–B$_m$–A, at the level of approximation used previously[1,2], will be unaffected by the substitution of terephthaloyl for isophthaloyl units. Therefore it is expected that the qualitative trends observed in *Figures 2* and *3* should be similar to those reported earlier[1,2] for the polymers that contain terephthaloyl groups. A more subtle rotational isomeric state analysis will be necessary to explain the differences between the terephthaloyl and isophthaloyl series with oxyethylene spacers and $m=5$ and 6.

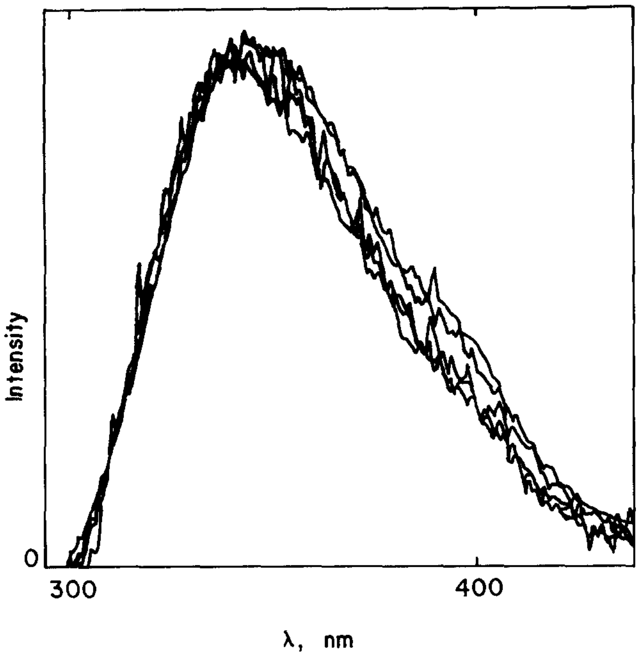

Figure 4 Fluorescence emission (normalized at 345 nm) for dimethylphthalate (DMP) and polyesters in which phthalate units are separated by 1, 2, 3 or 4 oxyethylene units. The five curves plotted are not readily distinguishable because the differences between them barely exceed the noise in the individual spectra. The curve for DMP tends to be the one with the lowest intensity in the spectral region to the red of the maximum

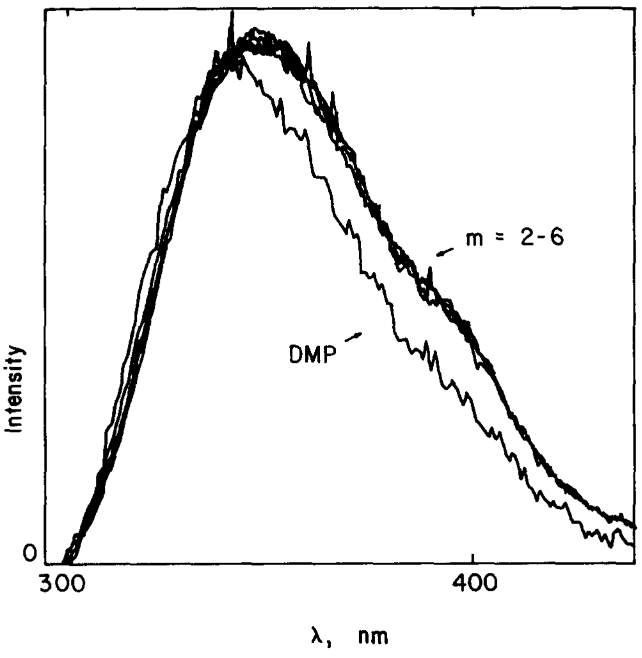

Figure 5 Fluorescence emission (normalized at 345 nm) for dimethylphthalate (DMP) and polyesters in which phthalate units are separated by *m* methylene units. The values of *m* range from 2 to 6, inclusive. The spectra for the five polymers are not experimentally distinguishable

POLYMERS THAT CONTAIN PHTHALOYL GROUPS

Figures 4 and *5* depict the emission spectra, normalized at 342 nm, for dimethylphthalate (DMP) and polyesters of phthalate with different numbers of oxyethylene or methylene groups in the flexible spacers. There are two important qualitative differences between the results reported in these two figures and the results obtained with polyesters in which the chromophores are terephthaloyl[1,2] or isophthaloyl groups (*Figures 2* and *3*). First, in neither *Figure 4* nor *Figure 5* do the normalized emission spectra depend on *m* in a manner that convincingly exceeds the noise in the individual spectra. Secondly, the normalized spectra for the polymers in these two figures differ very little from that of the model compound, dimethylphthalate. The population of excimers in the two phthalate series of polymers is so small that it eludes detection.

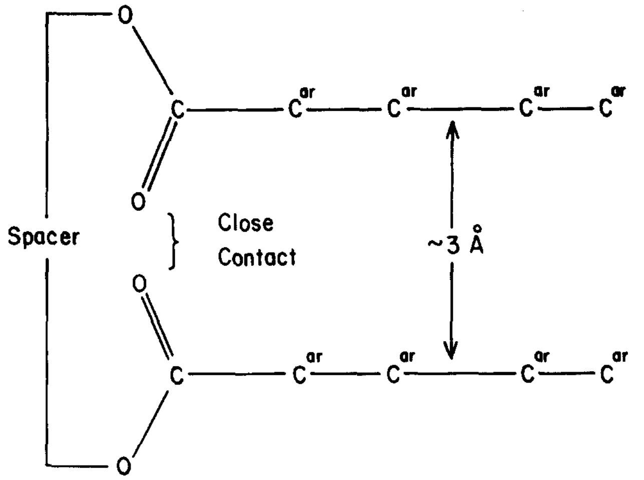

Figure 6 Schematic representation of A–B_m–A when B_m brings the two chromophores close to the sandwich geometry of an excimer. The aromatic rings are coplanar in the conformation depicted, and the view is from the mean plane of these rings. Ester groups are oriented perpendicular to the plane of the aromatic ring to which they are bonded, as expected in phthalate. The ester groups would be in the plane of the aromatic rings in isophthalate and terephthalate, thereby alleviating the 'close contact' in the figure

The initial step in the development of an explanation for the molecular origin of the different behaviour of the phthalate series begins with the realization that there is interaction between the two ester groups bonded to a single phthalate group. The preferred conformation of the ester groups in terephthalate and isophthalate is one that is coplanar with the aromatic ring[1,2,9]. However, adoption of this conformation by the two ester groups in phthalate generates unacceptable repulsive steric interactions, as is suggested in *Figure 1*. For this reason, the plane of each ester group in phthalate is perpendicular to the plane of the aromatic ring. The rotational isomeric state analysis of A–B_m–A is therefore different when A is phthalate than when A is either terephthalate or isophthalate. If only the customary short-range interactions, i.e. those of first and second order, are included in the rotational isomeric state analysis, one still finds that there are accessible conformations of –B_m– that bring the pendant aromatic rings into the close face-to-face interaction that characterizes an excimer. The dearth of excimers in the phthalate series arises not from the short-range restraints on –B_m–, but instead from unfavourable steric interaction of the oxygen atoms in the ester groups on one phthalate unit with the oxygen atoms on the ester groups on the other phthalate unit as they approach the face-to-face sandwich. The origin of this repulsion is suggested in *Figure 6*. Repulsive interaction of these oxygen atoms is alleviated if the ester groups are coplanar with the aromatic ring to which they are bonded, as they are in isophthalate and terephthalate.

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