Dependence on spacer size of the intramolecular excimer emission from model compounds for polyesters derived from isophthalic or terephthalic acid

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Diesters with the structure C_6H_5—COO—$(CH_2)_m$—OOC—C_6H_5, $m = 2$–6, have been synthesized, and their fluorescence has been measured in dilute solution in viscous solvents. These diesters are model compounds for polyesters prepared from isophthalate or terephthalate and $HO(CH_2)_mOH$. Comparison of the fluorescence of the diesters with the fluorescence of the polyesters, reported earlier, shows that energy migration is not an important mechanism for the population of excimers in the polymers. The agreement between the experimentally determined dependence of excimer emission on m and the theoretical dependence of the population of excimer forming conformations on m is improved by consideration of interactions higher than second order, especially for the largest member of the series.

(Keywords: diesters; fluorescence; model compounds; polyesters; excimer emission)

INTRODUCTION

Polyesters prepared by the condensation of an aromatic dicarboxylic acid and $HO(CH_2)_mOH$ can be represented by the formula $[\text{-A-}(CH_2)_m]_x$, where x denotes the degree of polymerization. When the dicarboxylic acid is one of the three structural isomers of $C_6H_4(COOH)_2$, the chromophores have fluorescence lifetimes that lie in the range 20–90 ps[1]. These lifetimes are too short to permit significant rotational isomerism at the C—C and C—O bonds in the flexible spacer at ambient temperature[2]. Excimers can be formed by chromophores i and $i+1$ only if the intervening flexible spacer, at the time of excitation, is in a conformation that permits adoption of the classic sandwich geometry[3] by the aromatic units via minor adjustments in bond angles and dihedral angles within potential energy minima. In the absence of energy migration, the dependence of I_D/I_M on m becomes proportional to the relative population of such conformations for the molecules in this series. Here I_D and I_M denote the intensities of the fluorescence from the excimer and monomer, respectively. Experiments in dilute solution show that I_D/I_M exhibits an odd–even dependence on m when the chromophore is derived from terephthalate ($m = 2$–6)[1,4] or isophthalate ($m = 2$–5)[1]. None of the polymers exhibit excimer fluorescence when the chromophore is phthalate[1]. Two ester groups bonded to C_6H_4 lie in the plane of the ring when their configuration is *meta* or *para*, but they are forced out of the plane of the ring when their configuration is *ortho*[5,6]. When they are out of the plane of the ring, the esters interfere with the close approach of two C_6H_4 units that is required for the formation of a singlet excimer.

A theoretical analysis of the conformations of the flexible spacer with various values of m has provided a qualitative rationalization of the odd–even effect at $m = 2$–5 for polymers of $HO(CH_2)_mOH$ and either terephthalate or isophthalate[4]. While qualitatively successful, the analysis had two important deficiencies. Firstly, it could not account for the perpetuation of the odd–even effect to $m = 6$ in the terephthalate series. Secondly, it consistently overestimated all values of $(I_D/I_M)_{m+2}/(I_D/I_M)_m$. A possible explanation for the second deficiency might be the population of excimers in the polymers via an energy migration mechanism, the efficiency of which decreases as the size of the spacers increases. A test of that possibility calls for experiments with model compounds, C_6H_5—COO—$(CH_2)_m$—OOC—C_6H_5, for which energy migration cannot influence the excimer population. Those experiments are reported here. The results suggest that energy migration is not a significant source of excimers in the polymers. The theoretical analysis used previously is then refined, by consideration of interactions of higher than second order, so that the two deficiencies are reduced in importance.

EXPERIMENTAL

Materials

The synthesis and purification of C_6H_5—COO—$(CH_2)_m$—OOC—C_6H_5, $m = 2$–6, has been described elsewhere[7]. In brief, the diesters were prepared by stoichiometric reaction of benzoyl chloride with $HO(CH_2)_mOH$ in solution in chloroform, in the presence of triethylamine. Purification was achieved by several

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crystallizations or by column chromatography and crystallization. The purity was verified by measurement of the melting point by high performance liquid chromatography, infra-red and nuclear magnetic resonance. Ethylene glycol, glycerol and methanol of spectroscopic grade were purchased from Aldrich and used without further purification.

Absorption

Absorption spectra were measured with a Hewlett-Packard 8451A Diode Array spectrophotometer. In methanol at 25°C, the samples had an absorption maximum near 276 nm and a shoulder near 282 nm. Similar spectra were obtained in ethylene glycol and in glycerol. Optical densities for samples studied by fluorescence were about 0.15 at 276 nm, which was the wavelength of excitation.

Fluorescence

Measurements of the fluorescence were performed with an SLM 8000C fluorometer equipped with a double monochromator in the excitation path. An enhanced sensitivity accessory (FP-018 SLM) was used because of the very low quantum yields for fluorescence by these samples. Even with this accessory, the low signal required the use of slits of 16 nm in the excitation and emission paths. Polarizers were set for magic angle conditions. Solvent blanks were measured and subtracted from the spectra of the solutions. The method used to obtain the quantum yields for fluorescence by these weak emitters has been described previously[8].

FLUORESCENCE EMISSION SPECTRA

Figure 1 depicts the fluorescence emission spectra for methyl benzoate and C_6H_5—COO—$(CH_2)_m$—COO—C_6H_5 in glycerol at 25°C. All spectra are normalized at 324 nm, which is the wavelength of maximum emission for methyl benzoate. Spectra obtained in methanol have a poorer signal-to-noise ratio, but they otherwise exhibit similar features that are blue shifted by about 3 nm. On the normalized plot, the diesters exhibit more intensity to the red of 324 nm than does methyl benzoate. This excess intensity shows an odd–even effect, with the largest values occurring when m is odd, as was also the case[4] with the polymers of terephthalate and $HO(CH_2)_mOH$.

A convenient way to summarize the spectra is as I_D/I_M *versus m*, where I_D and I_M are the intensities at 367 and 324 nm, respectively. That representation is depicted in *Figure 2*. The diester with $m = 3$ has the largest value of I_D/I_M in each solvent, and the polyester with $m = 3$ had the largest value of I_D/I_M in the solvents studied earlier[4]. Spectra for the diesters were also measured in methanol, but the results are not depicted in *Figure 2* because the uncertainties are much larger than those for spectra measured in the more viscous solvents. For the diester with $m = 3$, the values of I_D/I_M are 0.61 ± 0.04 in ethylene glycol, 0.75 ± 0.14 in 1:1 ethylene glycol: methanol, and 0.63 ± 0.26 in methanol. The uncertainty increases as the content of methanol increases, but there is no convincing evidence for any change in I_D/I_M.

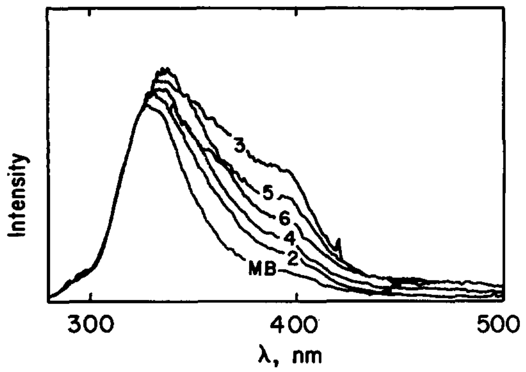

Figure 1 Fluorescence emission spectra for methyl benzoate (MB) and C_6H_5—COO—$(CH_2)_m$—OOC—C_6H_5 at 25°C in glycerol. Excitation is at 276 nm. All spectra are normalized at 324 nm

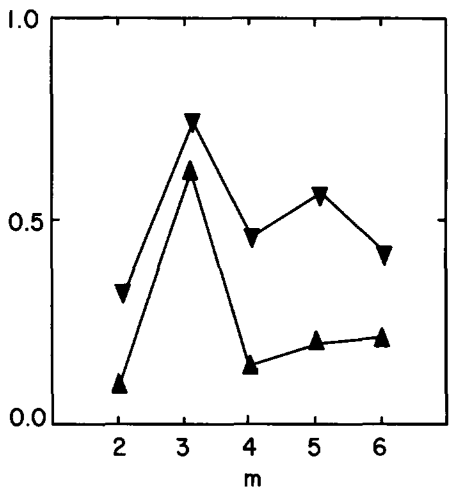

Figure 2 I_D/I_M for the diesters at 25°C in glycerol (▼) and ethylene glycol (▲)

Table 1 Comparison of $(I_D/I_M)_{m+2}/(I_D/I_M)_m$ for diesters and polymers[a]

m	Diesters	Polymers[b]
2	1.4 ± 0.1	1.6 ± 0.4
3	0.55 ± 0.25	0.55 ± 0.15
4	1.2 ± 0.3	0.65 ± 0.35

[a] Solvents: ethylene glycol and glycerol
[b] Data from reference 4. Solvents: 1,4-dioxane, ethyl acetate, and dichloroethane. I_D/I_M evaluated using 390 nm and 324 nm

If energy migration were an effective method of populating excimers in the polyesters with short flexible spacers between the aromatic rings, the values of $(I_D/I_M)_{m+2}/(I_D/I_M)_m$, at small values of m, should consistently be smaller for the polymers than for the diesters. This assertion follows from the postulates that energy migration cannot lead to an enhancement in the population of excimers in the diesters and, if present in the polymers, it must be most effective at small values of m. *Table 1* presents the ranges of the values of $(I_D/I_M)_{m+2}/(I_D/I_M)_m$ for the diesters, as calculated from the data presented in *Figure 2*. The table also contains values of $(I_D/I_M)_{m+2}/(I_D/I_M)_m$ for the polyesters. The data for the polyesters are results reported previously for measurements performed in dichloroethane, 1,4-dioxane and ethyl acetate[4]. There is no convincing indication that $(I_D/I_M)_{m+2}/(I_D/I_M)_m$ is different for the polyesters than for the diesters. Hence energy migration is not an important mechanism for population of an excimer in the polyesters.

Table 2 Conformations that contribute to $\sum p_i$

m	Conformation	p_i	Acceptable
2	$g^{+}g^{-}g^{+}$	0.0001	Yes
3	$tg^{+}g^{-}g^{-}$	0.0743	Yes
	$g^{+}g^{+}g^{-}g^{-}$	0.0189	Yes
4	$g^{+}g^{+}tg^{+}g^{+}$	0.0171	Yes
	$tg^{-}g^{-}g^{+}g^{+}$	0.0112	Yes
	$tg^{+}g^{-}g^{+}t$	0.0043	Yes
5	$tg^{+}g^{+}tg^{+}g^{+}$	0.0169	Yes
	$g^{+}g^{+}ttg^{-}g^{-}$	0.0100	Yes
	$g^{+}g^{+}tg^{+}g^{+}g^{+}$	0.0086	Yes
	$tg^{+}g^{-}ttg^{+}$	0.0047	Yes
	$tg^{-}g^{+}ttg^{+}$	0.0047	No
	$tg^{+}g^{-}g^{-}tg^{-}$	0.0020	Yes
	$tg^{+}g^{+}g^{-}g^{-}t$	0.0002	Yes
6	$tg^{+}g^{+}ttg^{-}g^{-}$	0.0100	Yes
	$tg^{+}g^{-}ttg^{+}t$	0.0076	Yes
	$g^{+}g^{+}tttg^{+}g^{+}$	0.0059	No
	$g^{+}g^{+}g^{+}ttg^{-}g^{-}$	0.0051	No
	$tg^{+}g^{+}tg^{+}g^{+}g^{+}$	0.0043	No
	$tg^{+}g^{+}g^{+}tg^{+}g^{+}$	0.0043	No
	$tg^{+}g^{+}tg^{+}g^{+}t$	0.0042	Yes
	$tg^{-}ttg^{-}g^{+}g^{+}$	0.0039	Yes
	$tg^{+}g^{-}ttg^{+}g^{+}$	0.0039	Yes
	$tg^{+}g^{-}g^{-}tg^{-}t$	0.0033	Yes
	$tg^{+}g^{-}tg^{-}g^{-}t$	0.0033	No
	$g^{+}g^{+}ttg^{+}g^{-}g^{-}$	0.0020	No
	$tg^{-}g^{+}tg^{+}g^{+}g^{+}$	0.0017	Yes
	$tg^{-}g^{+}g^{+}tg^{+}g^{+}$	0.0017	No
	$g^{+}tg^{+}g^{+}tg^{+}g^{+}$	0.0016	No
	$g^{+}ttg^{-}g^{-}tg^{-}$	0.0011	No
	$g^{+}g^{+}g^{-}tg^{+}g^{+}g^{+}$	0.0008	No
	$g^{+}g^{+}g^{-}g^{-}tg^{-}g^{-}$	0.0008	No

INCORPORATION OF HIGHER ORDER INTERACTIONS IN THE ROTATIONAL ISOMERIC STATE MODEL

The rotational isomeric state model used previously[4] was based on a discrete enumeration of all rotational isomers of A-B$_m$-A. Rotational isomers were defined as conductive to the formation of an excimer if they came sufficiently close to placing the two aromatic rings in a 'sandwich' geometry with their centres separated by about 350 pm. The geometries were classified with the aid of a Cartesian coordinate system centred on one of the rings, with its z axis normal to that ring. The criteria examine the z coordinate of the centre of the other ring, the lateral displacement, d_{xy}, defined as $r^2 - z^2$, where r is the distance between the centres of the two rings, and ψ is the angle between the z axis and the line that joins the centres of the two rings. The criteria were expressed as $335\ \text{pm} < z < 390\ \text{pm}$, $d_{xy} < 135\ \text{pm}$, and $\psi < 40°$. If rotational isomer i met this set of criteria, it was assumed to contribute to the excimer population in proportion to $p_i = w_i/Z$, where w_i is its statistical weight, as evaluated from a rotational isomeric state analysis of the flexible spacer, and Z is the conformation partition function of the spacer. All interactions of first and second order were considered in the formulation of Z, but interactions of higher order were ignored. The comparison was between the dependence on m of the measured behaviour of I_D/I_M and a quantity proportional to $\sum p_i$, where the index i runs over all rotational isomers that satisfy the criteria for z, d_{xy}, and ψ.

We have noticed that improvement in the agreement between experiment and theory can be obtained by examination of all conformations that satisfy the criteria for z, d_{xy} and ψ for the possible occurrence of prohibitive interactions of third or higher order, and rejection of such conformations from those counted in $\sum p_i$. The basis for this statement is presented in *Table 2*. This table summarizes the rotational isomers that made the most important contributions to $\sum p_i$ when first and second order interactions only are considered. The p_i listed for each rotational isomer in the third column includes the contribution for the mirror image and for reversal of the sequences. For each m, the rotational isomers are listed in the order specified by the values of their p_i. The final column presents the new information in the form of an assessment of the influence of interactions higher than second order. This column contains a 'Yes' if the rotational isomer retains an acceptable conformation after consideration of these higher order interactions, and a 'No' otherwise.

All the rotational isomers that contribute to $\sum p_i$ are acceptable when $m = 2$–4. Only one of the rotational isomers merits a 'No' when m is 5. Exclusion of this structure from $\sum p_i$ reduces the value of the sum by only 10% because other rotational isomers contribute most of the population that can form an excimer. In contrast, when m is 6, many of the rotational isomers counted previously in $\sum p_i$, based on first and second order interactions, are found to have untenable interactions of higher order. Elimination of these rotational isomers from $\sum p_i$ reduces the value of the sum by almost one-half, as shown in *Table 3*.

The qualitative nature of the improvement obtained by inclusion of the influence of interactions of higher order can be seen by comparison with the behaviour of the measured values of I_D/I_M for $m = 4$–6 in *Figure 2*. This figure shows that I_D/I_M has nearly identical values for $m = 4$ and 6 in the most viscous solvent, and a value about 20% larger at $m = 5$. In contrast, $\sum p_i$ increases continuously as m rises from 4 to 6 if only first and second order interactions are evaluated (second column of *Table 3*). The desired dependence of $\sum p_i$ on m in this range is obtained upon inclusion of the interactions of higher order (third column of *Table 3*), primarily as a consequence in the reduction of $\sum p_i$ at $m = 6$.

The computational method employed here does not attempt to account for the population of excimers as a consequence of rotational isomerism by the flexible spacer during the lifetime of the singlet excited state. The justification for this approach is provided in the present case by the very short fluorescence lifetime[1] and the high viscosity of the solvents. In other systems that might permit extensive rotational isomerism of the flexible spacer during the fluorescence lifetime, a simulation of the molecular dynamics of A-B$_m$-A provides an attractive approach to the rationalization of the dependence of I_D/I_M on m. The molecular dynamics simulation will naturally take into account the influence of the third and higher order interactions that appear to play the

Table 3 $\sum p_i$ including different interactions

m	First and second order interactions	All interactions
2	0.0001	0.0001
3	0.0932	0.0932
4	0.0326	0.0326
5	0.0473	0.0427
6	0.0655	0.0352

important role in reducing I_D/I_M for C_6H_5—COO—$(CH_2)_6$—OOC—C_6H_5 below the value expected on the basis of first and second order interactions alone. Since the method described in the present work requires much less computational power than does the computation of a molecular dynamics trajectory, it offers practical advantages for systems with very short fluorescence lifetimes, observed in media of high viscosity.

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REFERENCES

1 Mendicuti, F., Patel, B., Waldeck, D. H. and Mattice, W. L. *Polymer* 1989, **30**, 1680
2 Bahar, I. and Mattice, W. L. *J. Chem. Phys.* 1989, **90**, 6783
3 Braun, H. and Förster, Th. *Ber. Bunsenges. Phys. Chem.* 1966, **70**, 1091
4 Mendicuti, F., Patel, B., Viswanadhan, V. N. and Mattice, W. L. *Polymer* 1988, **29**, 1669
5 Riande, E., de la Campa, J., Schlereth, D. D., de Abajo, J. and Guzman, J. *Macromolecules* 1987, **20**, 1641
6 Mendicuti, F., Saiz, E., Patel, B., Dodge, R. and Mattice, W. L. *J. Phys. Chem.* 1990, **94**, 8374
7 Mendicuti, F., Rodrigo, M. M., Tarazona, M. P. and Saiz, E. *Macromolecules* 1990, **23**, 1139
8 Mendicuti, F. and Mattice, W. L. *Polym. Bull.* 1989, **22**, 557