Intramolecular excimer formation in polyesters from terephthalic acid and cyclohexanediols with different stereochemical compositions

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The fluorescence in dilute solution has been measured for five polyesters with terephthalate as the rigid aromatic unit and diols derived from cyclohexane as the flexible spacer. The spacers are 1,2-*cis*-cyclohexanediol, 1,2-*trans*-cyclohexanediol, a 1:2 mixture of 1,3-*cis*- and 1,3-*trans*-cyclohexanediols, a 1:2 mixture of 1,4-*cis*- and 1,4-*trans*-cyclohexanediols, and a 1:3 mixture of 1,4-*cis*- and 1,4-*trans*-cyclohexanedimethanol. The two polymers with the largest ratio of the intensities of excimer and monomer emission are those that contain either the 1:2 mixture of 1,3-*cis*- and 1,3-*trans*-cyclohexanediol or the 1:3 mixture of 1,4-*cis*- and 1,4-*trans*-cyclohexanedimethanol. A conformational analysis concludes that the spacers most conducive to excimer formation are the 1,3-*cis*-cyclohexanediol and 1,4-*cis*-cyclohexanedimethanol. This result from calculations is compatible with experimental results.

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

INTRODUCTION

Many polyesters have a repeating sequence of the form A-B_m, where A contains a rigid aromatic unit, B is a flexible spacer and m is an integer that denotes the number of repeats of the flexible spacer between successive rigid units[1–15]. The manner in which the excimer emission in dilute solution responds to changes in A, B and m depends on the fluorescence lifetime, τ, of the chromophore in A, the viscosity of the solvent, η, and the conformation and dynamics of B_m. The dynamic contribution is suppressed at small values of τ/η, which is the condition that will be of interest here. Then the fluorescence measurements for a family of polyesters with the same A, but different B and/or m, provides information on the ease with which B_m can adopt a conformation that produces a sharp bend in the chain, thereby bringing the two chromophores into the face-to-face geometry of the singlet excimer. The sharp bends, also known as hairpins[16], can play an important role in the ordering of nematic polymers[17].

The previous articles in this series[5,6,9,12–15] have investigated the fluorescence of polyesters in which B_m was a linear chain, with $B = CH_2$ or CH_2CH_2O. Here the attention is on five polyesters in which B has only limited flexibility because it contains a cyclohexane ring. Four of the spacers are 1,n-cyclohexanediols, with $n = 2$–4, and one is 1,4-cyclohexanedimethanol. Their structures are shown in *Figure 1*, and the abbreviations used are given in *Table 1*. The chromophore, A, is terephthalate. This chromophore has a very short τ value[9], thereby minimizing the impact of the dynamics of rotational isomeric state transitions on the formation of intramolecular excimers. The values of the ratio of the intensities of the emission at 390 and 324 nm obtained from the steady state fluorescence in several solvents depend strongly on the selection of the spacer. They are interpreted with the aid of a theoretical evaluation of the distribution of conformations for the fragment denoted by A-B_m-A.

METHODS

The polyesters were prepared from terephthaloyl acid chloride and five cyclohexanediols, all purchased from Aldrich. The synthesis was carried out under N_2 with stoichiometric amounts of the diacid chloride and diol in chloroform in the presence of triethylamine. Reflux was maintained for several hours. After the reaction, the solution was washed repeatedly with water and a dilute aqueous solution of sodium bicarbonate. The polymers were precipitated up to three times from the chloroform solutions with methanol (T2, CTT4, CTTT4-M) or cyclohexane (C2, CTT3). Dicyclohexyl terephthalate, synthesized in the same manner and precipitated by the addition of a small amount of methanol and then recrystallized, was used as a model compound. Samples were characterized by n.m.r. Tetrahydrofuran, 1,2-dichloroethane, p-dioxane and ethyl acetate were obtained from Aldrich (spectrophotometric or h.p.l.c. grade), and the isooctane was obtained from Fisher (spectroanalysed grade, 99%).

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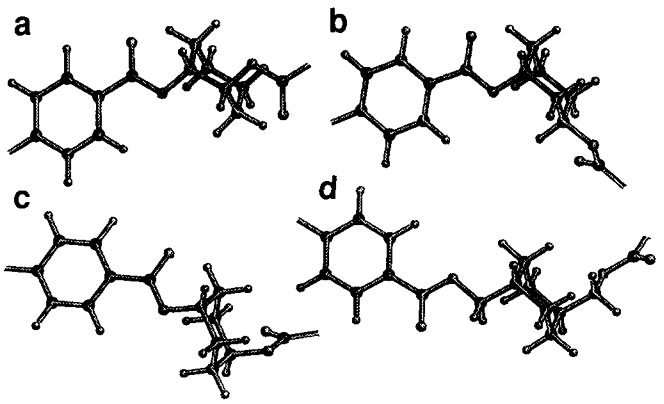

Figure 1 Covalent structures of *trans* isomers of repeat units in the polymers: (a) T2; (b) CTT3; (c) CTT4; (d) CTTT4-M

Table 1 Abbreviations for polymers with different spacers

Abbreviation	Diol used for spacer
C2	1,2-*cis*-cyclohexanediol
T2	1,2-*trans*-cyclohexanediol
CTT3	1:2 mixture of 1,3-*cis*- and 1,3-*trans*-cyclohexanediol
CTT4	1:2 mixture of 1,4-*cis*- and 1,4-*trans*-cyclohexanediol
CTTT4-M	1:3 mixture of 1,4-*cis*- and 1,4-*trans*-cyclohexanedimethanol

Fluorescence was measured using an SLM 8000C fluorometer equipped with a double monochromator in the excitation path. Polarizers were set for magic angle conditions. The low quantum yields for fluorescence required the use of slits of 16 nm for excitation and emission. Typical absorbances were in the range 0.1–0.3 at the wavelength of excitation (294 nm). Solvent signals were subtracted from the observed spectra.

FLUORESCENCE

Absorption spectra do not differ significantly from those reported previously for polyesters in which terephthalate is the chromophore[5,6]. In 1,2-dichloroethane there is a local maximum at 286 nm and a shoulder near 294 nm. Excitation spectra from the model compound and from the polymers in 1,2-dichloroethane, recorded by monitoring the emission at 324 nm, showed a single band near 294 nm. The location of the excitation band did not change upon moving the spectral region used to monitor the emission. In the case of the polymer, the wavelength for monitoring the emission could be moved to 390 nm without shifting the excitation band.

Figure 2 depicts normalized emission spectra obtained in 1,2-dichloroethane at 25°C for the five polyesters and the model compound, dicyclohexylterephthalate. Excitation is at 294 nm. No important changes in the shapes of the emission spectra are obtained upon small changes in the wavelength for excitation. The emission spectra are normalized at 324 nm, which is the location of the maximum intensity obtained in the emission from the model compound. The spectrum obtained with dicyclohexylterephthalate is similar in shape to the one reported for dimethylterephthalate[5], but the quantum yield for fluorescence is smaller for the diester with cyclohexyl groups. The polyesters exhibit more intensity near 390 nm than does the model compound, as was also the case with polyesters containing terephthalate and acyclic flexible spacers[5,6]. The broadening of the emission band in the polyesters is attributed to the intramolecular formation of an excimer, as was done previously[5,6]. In view of the very weak intensity of the emission from the model compound at 390 nm, a convenient estimate of the dependence of the excimer formation on the type of spacer is provided by the ratio of the intensities of the emission at 390 and 324 nm (denoted by I_D/I_M).

The values of I_D/I_M, averaged over several independent measurements, are summarized in *Table 2*. They vary strongly with the selection of the solvent. The smallest values are usually seen in dichloroethane, and values an order of magnitude larger are found in ethyl acetate or tetrahydrofuran. A few trends are seen among the polymers. In all five of the solvents, the largest I_D/I_M is seen with CTT3. Normalizing the values of I_D/I_M in each solvent by division by the result obtained with CTT3 yields the results presented in *Table 3*. The polymer with the mixed 1,4-cyclohexanediols as the spacer shows an atypical solvent dependence because it is the only member of the series for which the standard deviation of $(I_D/I_M)/(I_D/I_M)_{CTT3}$ is comparable with the average value. The average values of $(I_D/I_M)/(I_D/I_M)_{CTT3}$ show that the polyesters derived from the 1,2-cyclohexanediols are

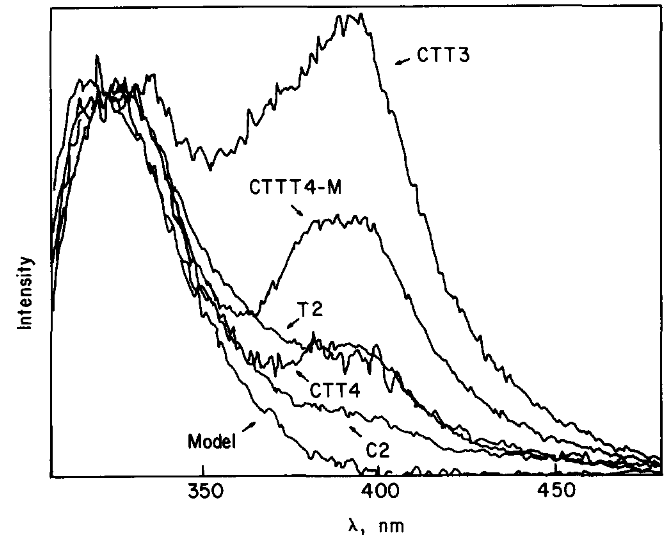

Figure 2 Emission spectra, normalized at 324 nm, for the model compound and the five polymers in 1,2-dichloroethane at 25°, using excitation at 294 nm. *Table 1* contains the abbreviations for the polymers

Table 2 Values of I_D/I_M at 25°C

Sample	Solvents[a] DCE	*p*-Dioxane	Iso:DCE	EA	THF
C2	0.09	0.22	0.41	0.52	0.19
T2	0.30	0.46	0.75	1.60	1.20
CTT4	0.16	0.78	0.37	5.30	0.00
CTTT4-M	0.63	2.50	0.76	7.20	4.50
CTT3	2.40	2.60	4.80	11.00	14.00

[a] DCE, dichloroethane; Iso:DCE, 1:1 mixture of isooctane and DCE; EA, ethyl acetate; THF, tetrahydrofuran. *Table 1* gives the abbreviations for the polymers

Table 3 Normalized values of I_D/I_M

	$(I_D/I_M)/(I_D/I_M)_{CTT3}$	
Sample	Average	Standard deviation
C2	0.05	0.04
T2	0.14	0.03
CTT4	0.19	0.18
CTTT4-M	0.48	0.29
CTT3	1.00	0.00

not conducive to excimer formation, the values being 0.05 ± 0.04 and 0.14 ± 0.03 for C2 and T2, respectively. The mixed 1,4-cyclohexanediols are somewhat more effective, with CTT4 having a value of 0.19 ± 0.18. The mixed 1,4-cyclohexanedimethanol polymers merit a still larger value of 0.48 ± 0.29. In order to understand the behaviour of the average values of $(I_D/I_M)/(I_D/I_M)_{CTT3}$ for these polymers, the family of conformations accessible to the fragment that contains two chromophores and a single spacer is now considered.

CONFORMATIONAL ANALYSIS

Eight bichromophoric diesters were used in the modelling. They were the *cis* and *trans* isomers of the diesters with a spacer consisting of 1,2-, 1,3- and 1,4-cyclohexanediol, and also 1,4-cyclohexanedimethanol. Each of these eight covalent structures was studied starting from chair and boat conformations of the cyclohexane ring. After minimization of the conformational energy, the boat conformations sometimes became twist-boat conformations. Conformations distinguishable by virtue of whether the substituents were in axial or equatorial positions were also studied. *Figure 3*, for example, shows two different starting conformations (one diequatorial, the other diaxial) for the chair conformation of the 1,2-*trans*-cyclohexanediol derivative.

A search was performed using the three local minima (*trans*, *gauche*$^+$, *gauche*$^-$) obtained by rotating about the O—C^{cyc} bonds (for C2, T2, CTT3, CTT4) and both the O—CH_2 and CH_2—C^{cyc} bonds (for CTTT4-M), where C^{cyc} denotes a carbon atom in the cyclohexane ring. The conformation at each local minimum was optimized using the force field supplied with Sybyl 5.41 (Tripos Associates, Inc., St Louis, MO, USA) by allowing variation of bond lengths, bond angles and dihedral angles. Then a conformational partition function, Z, was assigned to each unit as

$$Z = 3^N \sum_i \exp\left(-\frac{E_i}{RT}\right) \tag{1}$$

where N denotes the number (four for CTTT4-M, two for the other spacers) of rotatable O—C^{cyc} and O—CH_2 bonds, and the summation extends over all of the rotational isomers. The factor 3^N is included in the evaluation of Z because the assessment of the population of conformations conducive to an excimer evaluates

$$p_i = Z^{-1} s_i \exp\left(-\frac{E_i}{RT}\right) \tag{2}$$

$$p = \sum_i p_i \tag{3}$$

Each rotational isomer is examined in 3^N minor variants, which arise from independently changing each variable dihedral angle by −20°, 0° and +20°. This fluctuation provides an approximation to the conformational space that might be swept out by rapid torsional oscillations of the dihedral angles about their preferred values. The value of s_i is the number of these variants of rotational isomer i that satisfy the tolerances on the geometric criteria. The geometric properties examined[5] are the distance, d, between the centres of the two aromatic rings, the angle, ψ, between the normals to the mean planes of these two rings, and their lateral offset, d_{xy}. The results presented here use the tolerances $3.35\,\text{Å} < d < 3.9\,\text{Å}$, $0 < d_{xy} < 1.35\,\text{Å}$ and $0 < \psi < 40°$.

The sums of the probabilities of the conformations conducive to the formation of an excimer are vanishingly small ($< 10^{-4}$) for all of the compounds with *trans* stereochemistry at the cyclohexane unit, and for *cis* units from 1,2- or 1,4-cyclohexanediols. Significantly larger values (0.22 and 0.05) are obtained with 1,3-*cis*-cyclohexanediol and 1,4-*cis*-cyclohexanedimethanol units, respectively. The identification from the calculation of these two species as the most likely excimer formers is compatible with the experimental results summarized in *Table 3*. It also places the emphasis on the components of the mixtures that have the *cis* configuration for the attachment of the esters to the cyclohexane ring.

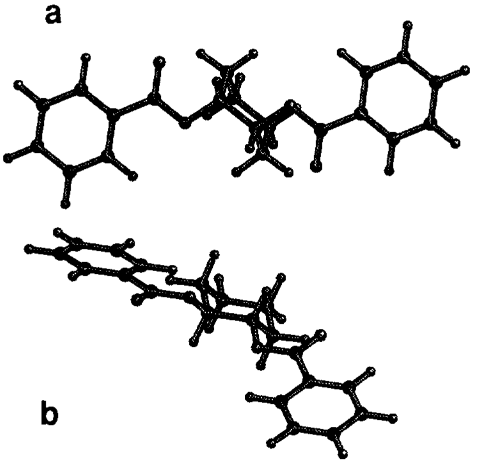

Figure 3 Bichromophoric unit from 1,2-*trans*-cyclohexanediol with diaxial (a) and diequatorial (b) conformations

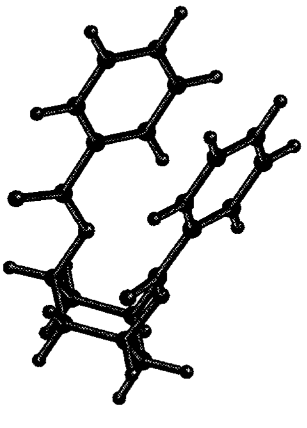

Figure 4 Conformation of the 1,3-*cis*-cyclohexanediol unit that places the two aromatic rings in a conformation conducive to excimer formation. The cyclohexane ring is in a chair. The values of d, d_{xy} and ψ are 3.46 Å, 0.86 Å and 19.4°, respectively

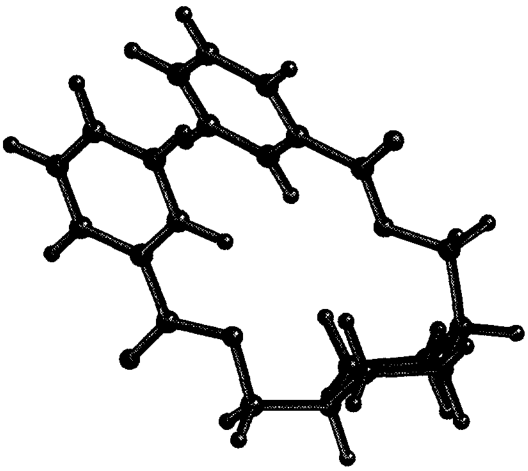

Figure 5 Conformation of the 1,4-*cis*-cyclohexanedimethanol unit that places the two aromatic rings in a conformation conducive to excimer formation. The cyclohexane ring is in a chair. The values of d, d_{xy} and ψ are 3.73 Å, 0.60 Å and 17.7°, respectively

Two conformations that contribute strongly to the larger probabilities for these two fragments are depicted in *Figures 4* and *5*. They both have chair conformations for the cyclohexane rings. For the other units, which have lower computed probabilities for excimer formation, the most likely excimer-forming candidates have the less stable boat conformation for the cyclohexane rings.

The results indicate that a method for introducing a few tight bends, the hairpins described by de Gennes[16], into a copolyester would be to incorporate a few spacer units consisting of 1,3-*cis*-cyclohexanediol or 1,4-*cis*-cyclohexanedimethanol, with the former compound likely to be the more effective of the two.

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