

Identification of conformations conducive to intramolecular excimer formation in polyesters with different numbers of methylene units between aromatic rings

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Excimer formation has been studied in polyesters in which the repeating unit is represented by the formula AB_m , where A is $p\text{-OOC-C}_6\text{H}_4\text{-COO}$, B is CH_2 and $m=2, \dots, 6$. In dichloroethane, dioxane and ethyl acetate, the ratio of excimer to monomer emission, I_D/I_M , exhibits an odd-even effect, with the largest value of I_D/I_M seen in the polyester with $m=3$. The conformations conducive to excimer formation by nearest neighbour aromatic rings are identified with the aid of a rotational isomeric state analysis of $\text{C}_6\text{H}_5\text{-COO-B}_m\text{-OOC-C}_6\text{H}_5$. A single species completely dominates the excimer formation when $m=2$. As m increases more species can adopt the excimer-forming geometry. When $m=6$, no conformation accounts for more than $\sim 1/7$ of the excimers present. The equilibrium rotational isomeric state analysis can rationalize the occurrence of the largest value of I_D/I_M at $m=3$ and the existence of an odd-even effect at $m=2, \dots, 5$. However, it overestimates the importance of the excimers when $m=6$.

(Keywords: polyester; chain conformation; excimer)

INTRODUCTION

Excimer emission from polystyrene has been known about for over two decades¹. The dominant excimer is formed by phenyl groups that are part of a meso dyad in the *trans-trans* conformation^{2,3}. Excimer emission is also observed in a variety of 1,3-diarylpropanes and 2,4-diarylpentanes that contain other chromophores⁴. The photophysical behaviour of these molecules is clearly determined by the interaction of the chromophores in the local conformations accessible to the doubly labelled compounds. The overall conformation is much more important than the local conformation when the two aryl chromophores are separated by a very large number of bonds. The system that best illustrates this behaviour is provided by dilute solutions of polystyrene chains end-labelled with pyrene groups⁵. The ratio of the emission from the pyrene excimer to the pyrene monomer in the end-labelled polystyrenes decreases monotonically as the degree of polymerization increases from 60 to 2000⁵, as expected from a consideration of the macrocyclization equilibria of long chain molecules^{6,7}.

A more complicated dependence of excimer formation on degree of polymerization should be seen with smaller molecules in which there is a gradual increase in the number of rotatable bonds between the two aryl chromophores. The local conformation is of the greatest importance when the number of flexible bonds is small, and the overall conformation gradually assumes the dominant role as the number of rotatable bonds increases. The influence of the local conformations is clearly evident in the chain length dependence of excimer emission in the phenyl² and pyrene⁸ end-labelled normal

alkanes. The behaviour of the end-labelled normal alkanes implies that a series of polymers with the repeating sequence $\text{-A-B}_m\text{-}$ (where A is a chromophore that is capable of excimer formation, B is a flexible spacer, and m ranges over small integers) may exhibit a complicated dependence of excimer emission on m . A satisfactory theoretical assignment of the conformations conducive to excimer formation in these polymers should account for the observed variation of excimer emission with m . That objective has recently been achieved in a series where A is terephthalyl and B is $\text{CH}_2\text{CH}_2\text{O}$ ⁹. In this series, the excimer emission is stronger when $m=2$ than when m is either 1 or 3. Figure 1a depicts a portion of the chain that exhibits the greatest ratio of excimer to monomer emission. A theoretical identification of the

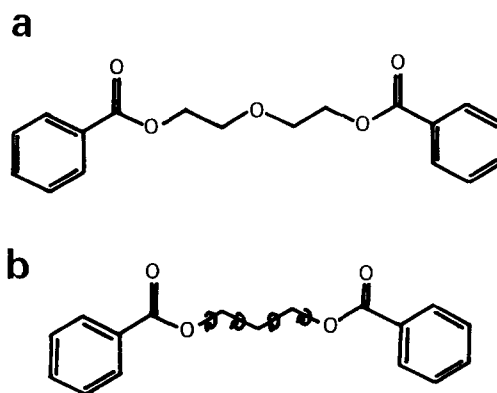


Figure 1 Fragments of the polyesters with the largest ratio of excimer to monomer emission in the series with (a) ethylene oxide and (b) methylene spacers. The bonds with the symmetric threefold rotation potentials considered in the rotational isomeric state analysis are indicated in (b)

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conformations conducive to excimer formation, achieved with rotational isomeric state theory, finds that these conformations are more easily populated when $m=2$ than when $m=1$ or 3, in agreement with the results of the fluorescence emission.

The present work shifts attention to the related series in which the flexible spacer is a polymethylene fragment, i.e. where B is CH_2 . The important experimental result is the observation of an odd-even effect in the ratio of excimer emission to monomer emission in this series of polymers when $m=2, \dots, 6$. Figure 1b depicts a portion of the polymer in which $m=3$. This chain is the member of the present series that has the largest ratio of excimer to monomer emission. A conformational analysis using rotational isomeric theory identifies the probable excimer-forming conformations. The probability for occupancy of these conformations shows an odd-even effect for $m=2, \dots, 5$. This paper first describes the experimental observations, then compares these observations with the predictions from rotational isomeric state theory, and finally describes the most important excimer-forming conformations at each m . A preliminary communication described the ratio of excimer to monomer emission and a very brief account of the rotational isomeric state analysis¹⁰.

METHODS

Fluorescence

The macromolecules studied are polyesters prepared from terephthaloyl chloride and $\text{HO}(\text{CH}_2)_m\text{OH}$, $m=2, \dots, 6$. Dimethyl terephthalate was used as a model compound. Samples of low molecular weight were prepared by a minor modification of the method described earlier for poly(terephthaloyl *trans*-2,5-dimethylpiperazine)¹¹. Based on their intrinsic viscosities in phenol:tetrachloroethane at 20°C and the tabulated viscosity-molecular weight relationships reported for poly(ethylene terephthalate) under these conditions¹², these samples have molecular weights of approximately 3000–5000. These samples were used for most of the experiments because they are more soluble than the samples of higher molecular weight. Samples of higher molecular weight were prepared by interfacial polymerization¹³. The molecular weights of these samples were not measured because of their low solubilities. Solvents of spectrophotometric grade were purchased from Aldrich and used in the fluorescence measurements without further purification.

Fluorescence measurements were performed with an SLM 8000C fluorometer equipped with a double monochromator on the excitation side. The polarizers

were set for magic angle conditions¹⁴. Slits were 8 nm for excitation and 8 nm (4 nm) for emission for dilute (concentrated) solutions. Solvent blanks were measured and subtracted from the observed spectra. Right angle and front face illumination (incident angle 60°) were used for dilute and concentrated solutions, respectively. Typical absorbances at the wavelength of excitation were 0.10–0.15 for dilute solutions, and the polymer was present at $\sim 2 \text{ g l}^{-1}$ in the concentrated solutions. All measurements were performed at 25°C.

Rotational isomeric state models

The rotational isomeric state analysis considers the fragment between two successive aromatic rings. This fragment is depicted in Figure 1b for $m=3$. The analysis also considered fragments in which $m=2, 4, 5$ or 6. The conformation partition function, Z_m , is assembled using rotational isomeric state models for polyethylene¹⁵, aromatic polyesters¹⁶ and polyoxyalkanes¹⁷. The ester group is confined to the planar *trans* conformation, and it shares this plane with the aromatic ring to which it is bonded¹⁶. The $m+1$ bonds with a symmetric threefold rotation potential are the $m-1$ $\text{CH}_2\text{-CH}_2$ bonds and the immediately adjacent O-CH_2 and $\text{CH}_2\text{-O}$ bonds. Rotation about these bonds is indicated in Figure 1b for the fragment with $m=3$. Each of the $m+1$ bonds can occupy any one of three rotational isomers, denoted by t , g^+ and g^- . The conformation partition function, Z_m , can be written as

$$Z_m = U_1 U_2 \dots U_{m+2} \quad (1)$$

After taking advantage of the condensation in matrix size permitted by the symmetry of the threefold rotation potential¹⁸, the terminal statistical weight matrices are

$$U_1 = \begin{bmatrix} 1 & 2\sigma_1 \end{bmatrix} \quad (2)$$

$$U_{m+2}^T = \begin{bmatrix} 1 & 1 \end{bmatrix} \quad (3)$$

and all remaining U_i are of the form

$$U_i = \begin{bmatrix} 1 & 2\sigma_i \\ 1 & \sigma_i(1+\omega_i) \end{bmatrix} \quad (4)$$

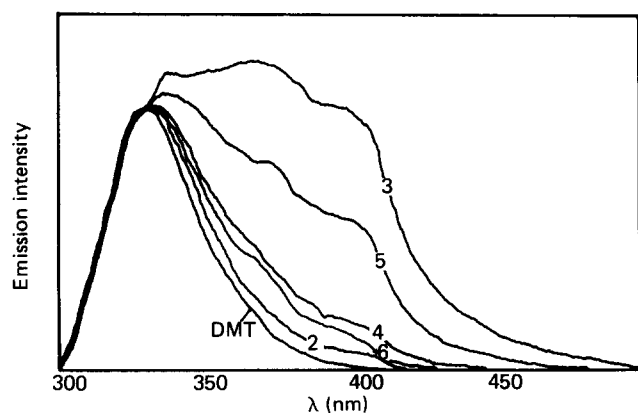
The values of the statistical weights are presented in Table 1. The first-order interaction in the $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$ fragment, and the second-order interaction in the $\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2$ fragment, are those appropriate for an unperturbed polyethylene chain at 300 K¹⁵. The statistical weights employed for the polymer with $m=2$

Table 1 Statistical weights for U_i when $m=2, \dots, 6$

	σ for					ω for				
	$m=2$	3	4	5	6	$m=2$	3	4	5	6
$i=1$	0.51	0.51	0.51	0.51	0.51					
2	3.9	2.0	1.4	1.4	1.4	0.034	0	0	0	0
3	0.51	2.0	0.43	0.43	0.43	0.034	0.51	0.39	0.39	0.39
4		0.51	1.4	0.43	0.43		0	0.39	0.034	0.034
5			0.51	1.4	0.43			0	0.39	0.034
6				0.51	1.4				0	0.39
7					0.51					0

Table 2 Bond lengths and bond angles

Bond	Length (pm)	Bond angle	Angle (deg)
C ^{ar} -C ^{ar}	140	C ^{ar} -C ^{ar} -C ^{ar}	120
C ^{ar} -C'	147	C ^{ar} -C ^{ar} -C'	120
C'-O	134	C ^{ar} -C'-O	125
O-C	144	C'-O-C	113
C-C	153	O-C-C	110
		C-C-C	112

**Figure 2** Emission spectra for dimethyl terephthalate (DMT) and the polyesters with $m=2, \dots, 6$. The solvent is dichloroethane, temperature is 25°C, excitation is at 286 nm and the emission spectra are normalized at 324 nm

are from Riande and Guzman¹⁶. All remaining statistical weights are those described for the most nearly equivalent fragment in the polyoxyalkanes studied by Abe and Mark¹⁷. Specifically, the first-order interaction for O-CH₂-CH₂-CH₂ and the second-order interactions for C-O-CH₂-CH₂-CH₂ and O-CH₂-CH₂-CH₂-CH₂ are assigned the values appropriate for poly(trimethylene oxide) and poly(tetramethylene oxide). The bond lengths and bond angles, taken from earlier work on polyethylene¹⁵ and aromatic polyesters¹⁶, are collected in Table 2. Dihedral angles for g^+ and g^- were centred 120° from the dihedral angle for t .

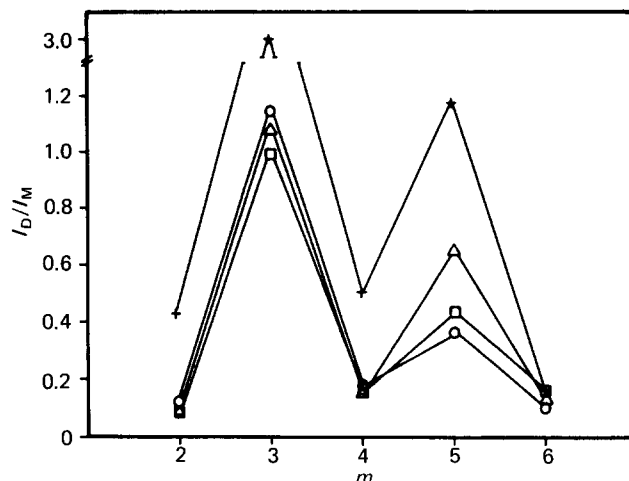
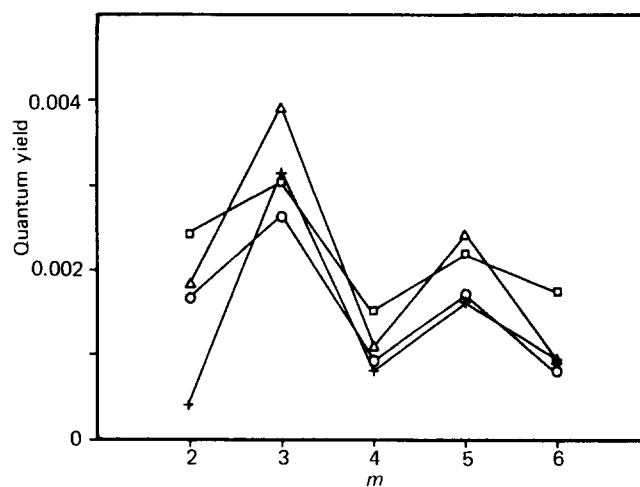
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Figure 2 depicts normalized emission spectra, observed upon excitation at 286 nm, for dimethyl terephthalate and the high molecular weight polyester series ($m=2, \dots, 6$) in dilute solution in dichloroethane. The spectra are normalized at the wavelength of the maximum emission with dimethyl terephthalate. Emission by the polymers spans a broader spectral region than that seen from the model compound, with substantial intensity far to the red of the emission from dimethyl terephthalate. The spectral range covered by the emission is similar to that seen in the series of polyesters that contain ethylene oxide spacers⁹. Dimethyl terephthalate and the polymers have similar excitation spectra (not shown). The excitation spectra for the polymers do not change when the wavelength of the emission shifts from 324 nm to 390 nm. Similar effects were observed in the polyester series in which the flexible spacer was (CH₂CH₂O)_{*m*}⁹. The broadening and red shift of the emission band in the polymers is attributed to excimer formation. Since dimethyl terephthalate shows

little emission at 390 nm, a convenient measurement of the ratio of excimer to monomer emission is provided by the ratio of the intensities at 390 and 324 nm⁶, which is denoted by I_D/I_M . Similar emission spectra are seen with the samples of low and high molecular weight.

Figure 3 depicts the behaviour of I_D/I_M as a function of the number of methylene spacer units. The spectra were obtained in dilute solution in dichloroethane, *p*-dioxane and ethyl acetate. There is an odd-even effect for I_D/I_M in each solvent. The largest value of I_D/I_M is seen for the polymer with $m=3$, and the next highest value is obtained when $m=5$. Lower values of I_D/I_M are seen for the three polymers in which m is even. The odd-even effect is also evident in the quantum yields for fluorescence in the same systems, as shown in Figure 4. The quantum yield for the polymer with $m=2$, which was synthesized as described in the 'Methods' section, is lower than that obtained with the commercial material studied earlier⁹.

The polymers can be examined in more concentrated solutions in trifluoroacetic acid because they have greater solubility in this medium. The behaviour of I_D/I_M is depicted in Figure 5. The odd-even effect is not as dramatic in this solvent system as in the less strongly

**Figure 3** I_D/I_M for the polyesters of low (□) and high (△) molecular weight in dichloroethane, and for the polyesters of low molecular weight in *p*-dioxane (○) and ethyl acetate (+)**Figure 4** Quantum yields for fluorescence for the polyesters considered in Figure 3, using the same symbols

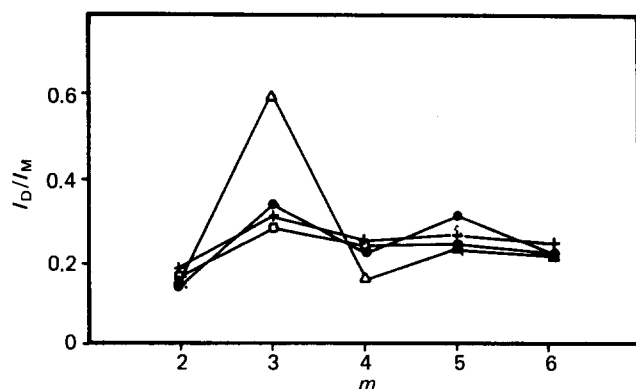


Figure 5 I_D/I_M in trifluoroacetic acid for the polyesters of low molecular weight in dilute (\square) and concentrated (+) solutions, and the series of high molecular weight in dilute (\circ) and concentrated (\triangle) solutions. Solvents are 99% and 60% trifluoroacetic acid for the dilute and concentrated solutions, respectively

interacting media, but it is still evident, particularly at $m=3$.

ROTATIONAL ISOMERIC STATE ANALYSIS

Conformations conducive to excimer formation by nearest neighbour aromatic rings were identified in the manner initially described in the investigation of the polyester series with ethylene oxide spacers⁹. The ideal target is a conformation that 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 of the rings are separated by 350 pm. Some tolerance must be used for these criteria because the rotational isomeric state analysis does not continuously sample conformational space. The tolerances are most easily described in terms of a Cartesian coordinate system with its origin at the centre of mass of one of the rings. Its z -axis is perpendicular to the plane of this ring. A conformation is accepted if the centre of mass of the other ring has an absolute value of the z -coordinate, denoted by $|z|$, in the range $z_{\min} < |z| < z_{\max}$ and a radial distance in the x - y plane in the range $0 < (x^2 + y^2)^{1/2} < xy_{\max}$, and the angle between the normals to the rings, ψ , is in the range $0 < \psi < \psi_{\max}$.

The usual rotational analysis for the aromatic polyesters assigns three rotational isomers to each of $m+1$ bonds, giving 3^{m+1} conformations for the fragment. In the present application, this set is enlarged to 9^{m+1} conformations by assignment of three dihedral angles, instead of a single dihedral angle, to each rotational isomer. One dihedral angle is 180° , 60° or -60° , depending upon whether the rotational isomer is a *trans* or *gauche* state. The other two dihedral angles are symmetrically displaced by 20° about the usual value. The purpose of the three dihedral angles for each rotational isomer is to sample more closely the conformational space that becomes accessible as a result of thermally induced oscillations of a dihedral angle near the minimum in the conformational energy well. It is assumed that the fragment represented by a particular string of $m+1$ letters selected from t , g^+ and g^- will form an excimer if any one of its 3^{m+1} conformations satisfies the tolerances described in the preceding paragraph. Therefore it is assumed that the excimer is a trap and that oscillations

within a conformational energy well are much more rapid than the decay of the excited state.

Computational labour is reduced by examination of only a single member of each pair of mirror images and by invoking the assumption that an excimer-forming conformation must have at least one *gauche* placement. The number of conformations to be examined is thereby reduced from 9^{m+1} to $(9^{m+1} - 3^{m+1})/2$. For $m=2, \dots, 6$, the numbers of conformations examined are 351, 3240, 29403, 265356 and 2390391, respectively.

Equally weighted conformations

When all σ_i and ω_i are assigned a value of 1, Z_m is the number of combinations of conformational energy wells accessible to the fragment, i.e. $Z_m = 3^{m+1}$. The probability for observation of a specific combination of conformational energy wells is simply $1/Z_m$. The dashed lines in Figure 6 depict the sums of the probabilities of those combinations of conformational energy wells that satisfy either of two sets of criteria for excimer formation. Set A has $z_{\min} = 325$ pm, $z_{\max} = 400$ pm, $xy_{\max} = 140$ pm and $\psi_{\max} = 40^\circ$. Set B employs the more selective criteria $z_{\min} = 335$ pm, $z_{\max} = 390$ pm, $xy_{\max} = 135$ pm and $\psi_{\max} = 40^\circ$. Both sets yield the same results for $m=2$. The more selective criteria yield smaller probabilities for $m=3, \dots, 6$. Both sets yield an odd-even effect for $m=2, \dots, 5$. This feature is in qualitative agreement with the behaviour of I_D/I_M depicted in Figure 3. The most important discrepancy between these probabilities and the I_D/I_M in Figure 3 is seen at $m=6$. This polymer has an I_D/I_M that propagates the odd-even effect seen at smaller

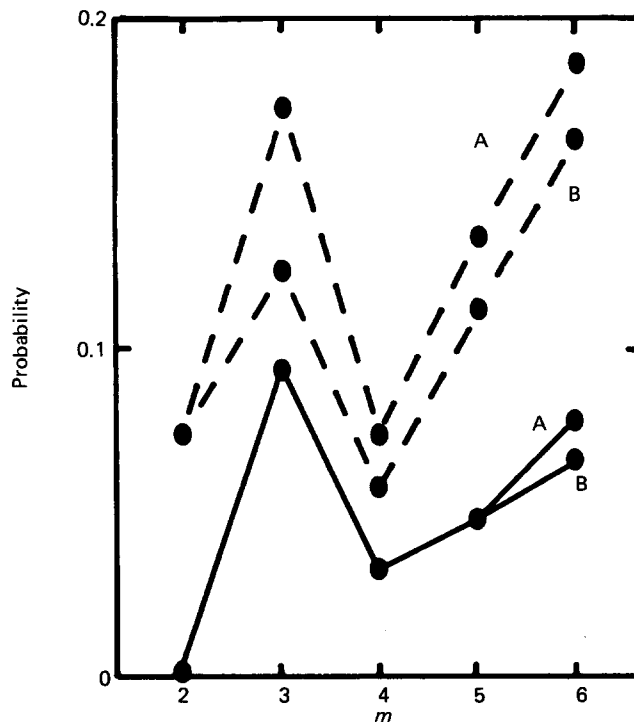


Figure 6 Probabilities, calculated from equilibrium rotational isomeric state theory, for the occupancy of conformations conducive to excimer formation by nearest neighbour aromatic rings. The dashed line depicts the results when all conformations are weighted equally, and the solid line is calculated utilizing a realistic set of statistical weights (Table I). Set A employs $z_{\min} = 325$ pm, $z_{\max} = 400$ pm, $xy_{\max} = 140$ pm and $\psi_{\max} = 40^\circ$, and set B employs $z_{\min} = 335$ pm, $z_{\max} = 390$ pm, $xy_{\max} = 135$ pm and $\psi_{\max} = 40^\circ$

Table 3 Dominant excimer-forming conformations

<i>m</i>	Conformation	p^a	$p/\Sigma p^b$	$\Pi \sigma^c$	$\Pi \omega^d$
2	$g^+g^-g^+$	0.0001	1.00	2.0	0.0012
3	$g^+g^+g^-t$	0.0743	0.80	2.0	0.51
	$g^+g^+g^-g^-$	0.0189	0.20	1.0	0.51
4	$g^+g^+tg^+g^+$	0.0169	0.52	0.51	1
	$g^+g^+g^-g^-t$	0.0112	0.35	0.43	0.39
5	$g^+g^+tg^+g^+t$	0.0169	0.36	0.43	1
	$g^+g^+ttg^-g^-$	0.0100	0.21	0.51	1
	$g^+g^+tg^+g^+g^+$	0.0086	0.18	0.22	1
6	$g^+g^+ttg^-g^-t$	0.0100	0.13–0.15	0.31	1
	$tg^+g^-ttg^-t$	0.0076	0.10–0.11	0.84	0.39
	$tg^+g^-ttg^+t$	0.0076	0.10–0.11	0.84	0.39

^aSum of the probabilities for the indicated conformation and its mirror image, as well as the reversed sequences if the sequences are not palindromic

^bFraction of the excimer-forming population

^cProduct of the σ_i in the statistical weight

^dProduct of the ω_i in the statistical weight

m, but the probabilities depicted in Figure 6 do not propagate the odd–even effect at *m*=6. The largest probability occurs at *m*=6 when the criteria are those of set A.

Realistic weights

The solid lines in Figure 6 connect the probabilities for occupancy of the conformational energy wells conducive to excimer formation when these probabilities are evaluated using the statistical weights in Table 1. Utilization of the realistic weighting scheme produces a reduction in the values of the probabilities at all values of *m*. The fragment with *m*=3 has the highest probability when the criteria are those of set A or set B, and the odd–even effect persists at *m*=2, ..., 5. However, the odd–even effect still does not propagate to *m*=6 because the calculated probability is too large.

Since a similar dependence of probability on *m* is seen in Figure 6 in both the dashed lines (calculated with the assumption that all conformations are weighted equally) and the solid lines (calculated using the realistic set of statistical weights collected in Table 1), it is obvious that the odd–even effect at *m*=2, ..., 5 in this polyester series is not sensitive to the precise values of the statistical weights. Imposition of the realistic set of statistical weights increases the agreement between the calculated probabilities and the measured I_D/I_M only by unambiguously assigning the largest probability to *m*=3. In the series in which the flexible spacer is provided by ethylene oxide units⁹, qualitative agreement between computed probabilities and measured I_D/I_M was obtained only when the probabilities were evaluated using realistic values of the statistical weights.

Dominant excimers

Table 3 summarizes the dominant excimer-forming conformations when the rotational isomers are weighted with the parameters in Table 1. The second-order interactions denoted by the ω_i severely penalize the excimer-forming conformation in the fragment with *m*=2, but they play a lesser role at larger *m*. The conformations listed for *m*=2, ..., 5 account for most of the excimer-forming population. When *m*=6, many distinguishable conformations contribute to the excimer-forming population. The most prevalent excimer accounts for roughly 1/2 of the total excimer population when *m*=4, and only about 1/7 of the population when

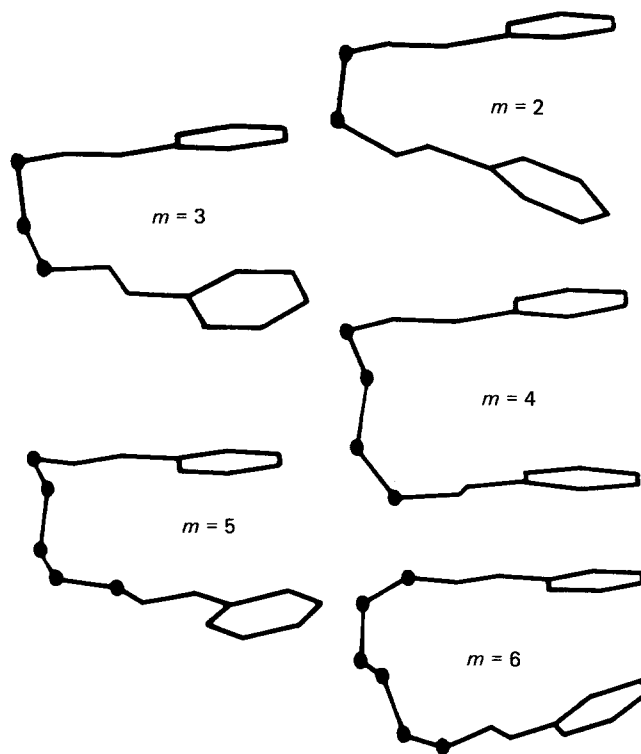


Figure 7 Excimer-forming conformations of highest probability in the ensembles for *m*=2, ..., 6. ●, Carbon atoms in the methylene units. Carbonyl oxygen atoms are omitted. The statistical weights are taken from Table 1, and the conformation depicted is the first one listed for each *m* in Table 3. The view is from an angle of 10° with respect to the plane of the top ring. The dihedral angles for the rotatable bonds are –80, 40, –60° for *m*=2; –60, –40, 80, –160° for *m*=3; –40, –80, 160, –80, –40° for *m*=4; –40, –80, 180, –80, –40, 160° for *m*=5; and –160, 80, 40, –160, 160, –80, –40° for *m*=6

m=6. The first entry for each value of *m* in Table 3 is depicted in Figure 7. The view for each fragment in Figure 7 is from an angle of 10° with respect to the top ring.

One factor that is not included in the present analysis is the rate at which non-excimer forming rotational isomers are converted to excimer-forming rotational isomers through the process by which a dihedral angle passes over a conformational energy barrier. The present model only allows for the oscillation of the dihedral angles that can be achieved without crossing over a conformational energy barrier. The degree of success enjoyed by this approach is undoubtedly related to the fact that we are dealing with extremely fast photophysical processes. The fluorescence lifetime for the model compound, dimethyl terephthalate, is significantly smaller than 1 ns in the solvents used¹⁹. This time scale is slow compared to the rate of oscillation within wells, but it is not slow compared with the rate of crossing over the potential barriers that separate wells. The agreement between calculation and measured values of I_D/I_M might be improved by incorporation of the rates at which one rotational isomer is converted into another by crossing a conformational energy barrier. This objective has been made feasible by recent extensions²⁰ of the formalism introduced by Jernigan²¹.

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REFERENCES

- 1 Yanari, S. S., Bovey, F. A. and Lumry, R. *Nature* 1963, 200, 242
- 2 Hirayama, F. *J. Chem. Phys.* 1965, 42, 3163
- 3 Longworth, J. W. and Bovey, F. A. *Biopolymers* 1966, 4, 1115
- 4 de Schryver, F. C., Collart, P., Vandendriessche, J., Goedeweck, R., Swinnen, A. and Van der Auweraer, M. *Acct. Chem. Res.* 1987, 20, 159
- 5 Winnik, M. A. *Acct. Chem. Res.* 1985, 18, 73
- 6 Jacobson, H. and Stockmayer, W. H. *J. Chem. Phys.* 1950, 18, 1600
- 7 Flory, P. J., Suter, U. W. and Mutter, M. *J. Am. Chem. Soc.* 1976, 98, 5733
- 8 Zachariasse, K. and Kuhnle, W. Z. *Phys. Chem.* 1976, 101, 267
- 9 Mendicuti, F., Viswanadhan, V. N. and Mattice, W. L. *Polymer* 1988, 29, 875
- 10 Mendicuti, F., Patel, B., Viswanadhan, V. N. and Mattice, W. L. *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* 1988, 29, 505
- 11 Morgan, P. W. 'Condensation Polymerization', Interscience, New York, 1965, p. 502
- 12 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', 2nd Edn., Wiley, New York, 1975, pp. iv-25
- 13 Ignatov, V. N., Vasnev, V. A., Korshak, V. V. and Vinogradova, S. V. *Vysokomol. Soedin.* 1985, B27, 487
- 14 Lakowicz, J. 'Principles of Fluorescence Spectroscopy', Plenum, New York, 1983, p. 131
- 15 Abe, W., Jernigan, R. L. and Flory, P. J. *J. Am. Chem. Soc.* 1966, 88, 631
- 16 Riande, E. and Guzman, J. *J. Polym. Sci., Polym. Phys. Edn.* 1985, 23, 1235
- 17 Abe, A. and Mark, J. E. *J. Am. Chem. Soc.* 1976, 98, 6468
- 18 Flory, P. J. *Macromolecules* 1974, 7, 381
- 19 Mendicuti, F. and Mattice, W. L., unpublished
- 20 Bahar, I. and Erman, B. *Macromolecules* 1987, 20, 1368
- 21 Jernigan, R. L. in 'Dielectric Properties of Polymers', (Ed. F. E. Karasz), Plenum, New York, 1972, p. 99