

Photophysical models of aromatic polyesters: excited state interactions in bis(phenalkyl)terephthalates

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Summary

The nature of the excited state interactions in poly(ethylene terephthalate) is still subject to debate. We study a new series of model compounds composed of a central terephthaloyl group condensed with α -hydroxy- ω -phenyl- n -alkanes. Although the molecular architecture prevents these molecules from achieving symmetric ring-ring overlap, the steady-state fluorescence spectra are remarkably similar to those of other models studied earlier, where such overlap was expected. The solvent polarity dependence suggests that the excited state complex is an exciplex and not an excimer.

Introduction

The luminescence arising from the singlet excimer and exciplex states of interacting aromatic molecules has been well established (1,2), and the former is often used as a probe of chain conformation in polymers containing aromatic units (3). Since the geometric requirements for the excimer and exciplex can differ, it is important to determine the nature of excited state interaction before using it to infer the local conformational properties of polymer chains. The excimer and the exciplex differ in the source of the stabilization, which may be illustrated by the equation due to Mataga and Kubota (2). Ignoring the ground state interaction, the wavefunction of the complex, Ψ , is

$$\Psi \approx \sum_i a_i \Phi_i(M_1^* M_2) + \sum_i b_i \Phi_i(M_1 M_2^*) + \sum_i c_i \Phi_i(M_1^- M_2^+) + \sum_i d_i \Phi_i(M_1^+ M_2^-) \quad (1)$$

The Φ_i 's are the one-electron molecular orbitals which contribute to Ψ with i indexing the electrons in the complex. Specific interactions occur between species M_1 and M_2 with their so-called locally excited, or exciton, states (denoted by the *, with coefficients a_i and b_i) and excited charge resonance states (denoted by + and -, with coefficients c_i and d_i). When the two interacting species are identical, ($M_1 \equiv M_2$), $a_i = b_i$ and $c_i = d_i$ while when they are different ($M_1 \neq M_2$), $a_i \neq b_i$ and $c_i \neq d_i$.

If the interacting species are identical and can achieve a geometry in which the aromatic planes are parallel and co-facially separated by $\sim 3 - 4 \text{ \AA}$, then the exciton resonance term may dominate the charge resonance term. The resulting excited state

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complex is an excimer (1) with the high symmetry of the complex required to maximize the exciton resonance interaction. If the two species are connected by a propylene bridge, a sequence of g^+g^- torsion placements in the bridge brings the rings into such a symmetric, face to face arrangement (4). There is little effect of solvent polarity on the fluorescence of this complex. On the other hand, if the charge resonance states dominate, the complex is an exciplex (2). In general, the interacting species need not be identical, the high symmetry requirements are relaxed versus the excimer, and geometries other than the parallel, co-facial one may be seen depending on the participating species. Since it is coulombic interactions which are now important, solvent effects on the fluorescence of the exciplex, in contrast to the excimer, are quite pronounced. Some species may exhibit characteristics of both the excimer and the exciplex.

The nature of the excited state interaction in poly(ethylene terephthalate) (PET) has not yet been firmly established (5-10). Since PET has low solubility in most solvents, the photophysics of small molecule model compounds consisting of benzoate groups connected by a series of methylene units of increasing length has been studied (11). One may consider the addition of an ester group to benzene to be a perturbation of the aromatic ring, but yet be somewhat separable from it (10). In this spirit, we have studied a series of model compounds, $C_6H_5-(CH_2)_x-OOC-p-C_6H_4-COO-(CH_2)_x-C_6H_5$, $x = 1, 2, 3, 4$, with a central terephthalate unit and two phenyl groups each connected to the central chromophore by a bridge of 1-4 methylene groups. These model compounds are abbreviated as X1, X2, X3, and X4, according to the number of methylene groups in the bridge. Although such compounds are incapable of forming intramolecular complexes in which the aromatic rings form a symmetric sandwich overlapping pair, the fluid solution steady state fluorescence characteristics of these models are nevertheless directly comparable to those of the dibenzoylalkane model compounds and PET itself.

Experimental

The model compounds were synthesized by standard condensation procedures (11) from terephthaloyl chloride and the appropriate α -phenyl- ω -hydroxy- n -alkane. All model compounds, including dimethylterephthalate (DMT), were purified by repeated recrystallization from methanol. All solvents were monitored for fluorescent impurities. The 1,4-dioxane and methanol were distilled over sodium metal just prior to use.

All steady state fluorescence spectra were measured at 20° using a SLM 8000 fluorimeter equipped with a 450 W cw argon lamp, double grating excitation monochromator, single grating emission monochromator, and 1P28 photomultiplier tube detector, which was thermo-electrically cooled and operated in single-photon counting mode. Fluorescence spectra were normalized to the intensity of the excitation source to compensate for intensity fluctuations of the lamp, but were uncorrected for detector response. Excitation was at 296 nm for all emission spectra. The monochromator bandwidths used for the emission spectra were 16 nm for excitation and 4 nm for emission. The spectra were each normalized individually to the greatest value on that particular curve.

For the preparation of films, methyl methacrylate monomer (Aldrich) was distilled under vacuum to remove inhibitor, and then polymerized at 90°C with thermally induced decomposition of the monomer serving to initiate the polymerization. The resulting poly(methyl methacrylate) (PMMA) was repeatedly dissolved in Optima grade

dichloromethane and precipitated with purified methanol to remove any unreacted monomer, and then dried in air at 60°C for 4 hours. The PMMA and appropriate model compound were dissolved in dichloromethane, the solution was applied to a quartz slide, and the solvent was allowed to evaporate slowly to yield a film estimated to be of order 10^{-4} m in thickness which appeared optically clear and smooth to the unaided eye. The sample was illuminated through the quartz slide to minimize the scattering from the polymer surface. The scattered light was removed by subtraction of the spectra of the model compounds in the film from that of a blank PMMA film, i. e., with no model compound added.

Results

The solution absorption spectra for the four model compounds showed no new absorption bands red-shifted relative to those of the DMT-like absorption, and the fluorescence excitation spectra for all new emission bands showed no difference from that of dilute DMT at 330 nm emission.

The steady state fluorescence spectra of the model compounds in dichloromethane and acetonitrile are shown in Figures 1 and 2, respectively. The DMT has no methylene bridged phenyl group attached and exhibits only monomer emission at approximately 330 nm (monomer emission refers to the 330 nm fluorescence band of isolated DMT). The spectrum of X1 is similar to that of DMT. However, if the number of methylene units in the bridge is increased to two, a new low intensity emission is observed at 400 nm. With X3, the fluorescence characteristics are markedly different. Two or three new emission bands are observed red-shifted relative to the DMT type monomer emission in these solvents. These new bands occur at 375, 400, and, perhaps, at 450 nm. For the solutions of X4 in these solvents, the spectra resemble those of X2, with slightly higher intensity of the new bands relative to X2.

In addition to a dependence on the number of methylene units in the bridge, there is a strong solvent polarity effect on the emission of the model compounds with $x > 1$. The extremes for the spectra of X3 are seen in 2,2,4-trimethylpentane and acetonitrile. In 2,2,4-trimethylpentane ($\epsilon = 1.94$), the solvent of lowest polarity used, the fluorescence is nearly the same as that of DMT, with so little emission at 400 nm that only a very small shoulder appears (Figure 3). For solutions in solvents of increasing polarity (1,4-dioxane, ethyl acetate, dichloromethane), the new bands emerge and change in intensity relative to the monomer peak. Finally, in acetonitrile ($\epsilon = 37.4$), the 400 nm band is dominant with the 450 nm band now being evident but manifested only as a shoulder (Figure 2). In solvents of relatively low dielectric constant, both the 375 nm and 400 nm emission bands are easily observed, but in solvents of high dielectric constant, only the 400 nm band is favored with the 450 nm band appearing as a shoulder.

For each solution of X3 over the concentration range studied, approximately 1×10^{-3} to 1×10^{-4} M, the ratio of the intensity of the new emission (400 nm) to that of the monomer band (330 nm) remains constant. Since no concentration dependence of this ratio exists, the new bands must arise from *intra*- and not *inter*molecular interactions. These new emission bands must be due to intramolecular interactions of the phenyl and terephthalate rings.

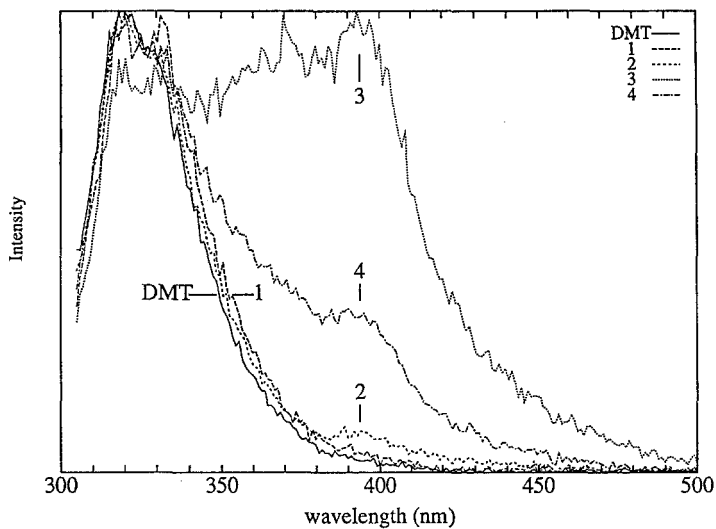


Figure 1. Fluorescence of DMT and the four model compounds in dichloromethane. The numerals identify the number of methylene groups in the bridge.

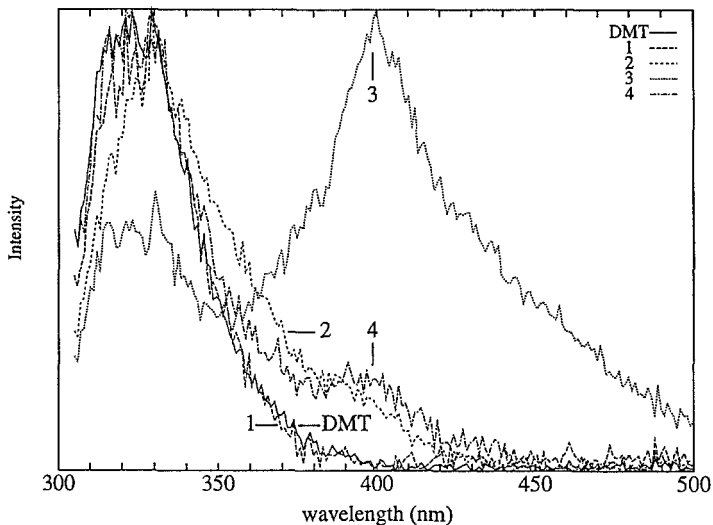


Figure 2. Fluorescence of DMT and the four model compounds in acetonitrile.

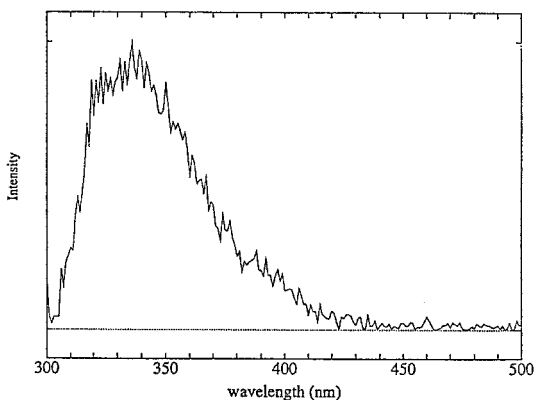


Figure 3. Fluorescence of X3 in 2,2,4-trimethylpentane.

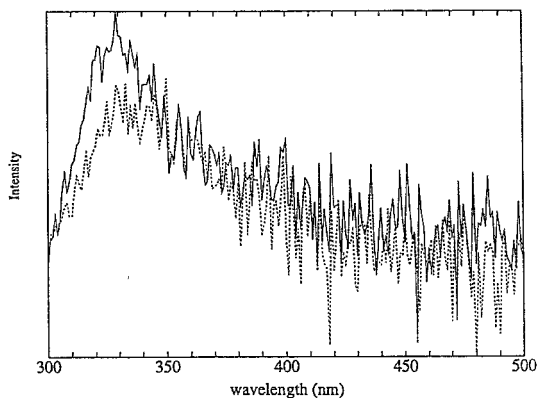


Figure 4. Fluorescence of DMT (—) and X3 (- -) in PMMA solid film.

Figure 4 shows the emission of DMT and X3 in the rigid PMMA film, which serves as a photophysically neutral matrix. Although the spectra are quite noisy, the new emission seen from X3 in fluid solution is absent, and the fluorescence of X3 in the film is indistinguishable from that of DMT.

Discussion

The red-shifted fluorescence bands presented here bear a striking resemblance to those observed in dilute solutions of PET and similar model compounds comprised of two benzoate groups separated by bridges of 1–5 methylene units (11). This similarity is not surprising in that through the addition of the ester groups to a phenyl ring to form a terephthalate group, there is a perturbation of the 1L_a and 1L_b benzene-like states and the main change is the addition of a low lying excited state which has

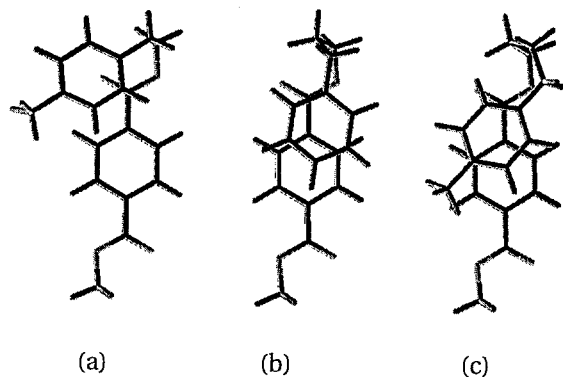


Figure 5. Closest approach of the phenyl ring to the terephthaloyl ring for three model compounds exhibiting red-shifted fluorescence, and the rotational isomeric states of the $\text{CH}_2\text{-CH}_2$ bonds in the bridge. (a) X2, g^+ (b) X3, g^+g^- (c) X4, g^+g^-t . The portion of each model compound depicted is $\text{C}_6\text{H}_5\text{-(CH}_2\text{)}_x\text{-OOC-}p\text{-C}_6\text{H}_4\text{-COO-CH}_3$.

been assigned as $\pi\pi^*$ in nature with the molecular orbital wavefunction lying primarily across the terephthaloyl $\text{C}_{\text{aromatic}}\text{-C}_{\text{carbonyl}}$ bond (10). In the models presented here, the terephthaloyl unit which has been excited to its S_1 state at 296 nm, must then interact with a phenyl ring and not another terephthaloyl, as in PET and the symmetric α,ω -dibenzoylalkane models mentioned earlier. This interaction may not be excimeric in nature. The phenyl ring in our model compounds has no such low lying electronic state to which the exciton of the terephthaloyl may transfer. Further, due to the geometric constraints imposed by the short sequences of methylene units and the lack of an ester group in these molecules, symmetric ring-ring overlap of the aromatic rings is not possible as it is in α,ω -dibenzoylpropane. Figure 5 shows the closest approach of the phenyl ring and the terephthaloyl ring for X2, X3, and X4. There is no stable conformation of the bridge which would permit direct overlap of the rings in our model compounds. However, there is the possibility of each phenyl ring simultaneously interacting with the ring-ester portion of the terephthaloyl unit.

In the folded conformation of X3 with little strain, shown in Figure 5(b), a phenyl ring sits over the terephthaloyl $\text{C}_{\text{aromatic}}\text{-C}_{\text{carbonyl}}$ bond, but reaches no further over the terephthaloyl ring. If the phenyl ring is indeed interacting with the excited terephthaloyl group in such a fashion, it is certainly an exciplex-type of interaction and not an excimer-type. This assertion is supported from the solvent polarity dependence. The ratio of the excimer to monomer emission intensity should not change very much with solvent polarity.

Solvent polarity has a strong effect on exciplex formation due to the stabilization of charge separation by the dipolar nature of the solvent. If the interacting species are free of each other, increasing solvent polarity shifts the equilibrium to favor the solvated ion-pair which results in a decrease in exciplex emission intensity. However, a covalently

bonded alkyl bridge reduces the entropy to be gained by ion-pair dissociation, because of the restricted phase space of the bridged species. Since the solvent effect is greatest for the 400 nm band and the folded conformation described affords the greatest interaction of the phenyl ring HOMO and terephthaloyl LUMO, it should have the greatest stability. This still leaves open the question of possible geometries for the species which give rise to the emissions at 375 and 450 nm. At this time, however, there is not sufficient evidence from which these geometries may be deduced.

The excited state complex is not significantly populated in the ground state as evidenced by the lack of new emission from X3 in the PMMA matrix. However, since the exciplex must form within the short fluorescence lifetime of the excited terephthalate group (< 100 ps) (12), the geometry of the ground state conformation that is the precursor must be quite close to that of the excited state complex.

Conclusions

The red-shifted fluorescence of X2, X3, and X4 in dilute fluid solution presented here is due to interactions of aromatic rings which are primarily stabilized by charge resonance forces and not by exciton resonance. No emission attributable to an excited state interaction is found from the model compounds in a rigid matrix. Thus, the intramolecular excited state complex which results must be an exciplex.

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