solution onto Pyrex plates and, after drying, were exposed through the Pyrex glass (2.5 mm) to a Hanovia medium-pressure mercury lamp (500 W). After irradiation, the films were scraped off the glass with a blade and transferred to a 25-mL round-bottom flask for further treatment.

Hydrolysis of the material was carried out by refluxing with alcoholic KOH in the presence of a phase-transfer agent. The polymer (25 mg) was added to a mixture of 1 mL of 1 M KOH in ethanol, 1 mL of dimethylformamide, and 10 mg of benzyltriethylammonium chloride. The solution was refluxed for 30 min at 60 °C. During that time the polymer first dissolved and then gradually a precipitate was formed. The mixture was stirred without heating overnight and then filtered to remove the precipitate of poly(vinyl alcohol), and the filtrate was evaporated to dryness. The residue was taken up in 1 mL of H_2O and the acids were precipitated by a few drops of HCl. The precipitate was separated by centrifuging, redissolved in 1 M KOH, reprecipitated, washed in water, and dried.

For the esterification of the acids, the dry precipitate was added to 2 mL of dry thionyl chloride and 3 drops of dimethylformamide in a reaction flask, protected from atmospheric water vapor by a drying tube. The stirred mixture was refluxed for 30 min at 80 °C. After that, thionyl chloride was removed under reduced pressure from the reaction mixture, and the acid chlorides formed were dissolved in 5 mL of ethanol. The resulting mixture of ethyl esters was dried and later chromatographed.

Gas Chromatography. Samples for gas chromatography were evaporated to dryness and then mixed with chloroform to give a concentration of approximately 1 mg/mL. For quantitative work, *n*-dodecane was also added as an internal standard. A 0.1-μL aliquot of each sample was injected into a Hewlett-Packard 5840 gas chromatograph, fitted with an all-glass capillary inlet system. Separation was achieved on a 14-m WCOT glass capillary column coated with OV-1. The samples were injected in the splitless mode with the column temperature at 50 °C. After 30 s the column temperature was raised to 180 °C at a rate of 30°/min and held at that temperature for 20 min. In these conditions the retention times shown in Table I were found for the main components of the reaction mixture. The chromatographic peaks were identified by comparison with authentic samples of the cyclic isomers. For their preparation see ref 13.

Quantum Yield of the Photoreaction. The photoreaction of the polymer-bound cinnamoyl groups was monitored by the disappearance of the C=C absorption at 1640 cm^{-1} in the IR spectrum or by following the decrease in the UV absorption band with a maximum at 275 nm. In both cases the quantum yield was derived from the ratio of the optical densities after and before irradiation, which is a direct measure of the degree of conversion (x) of the chromophores, ($D/D_0 = 1 - x$). The quantum yield was obtained from the slope of a plot of conversion against irradiation time

$$\phi = \frac{n_0}{I_0 A}\frac{\mathrm{d}x}{\mathrm{d}t}$$

Here n_0 is the number of moles of chromophores in 1 cm^2 of the coating, I_0 is the photon flux (einstein cm^{-2} s^{-1}), and A is the fraction of photons absorbed by the chromophores.

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Photocycloaddition at Excimer Sites in a Solid Polyester of *p*-Phenylenediacrylic Acid

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ABSTRACT: In a polyester of *p*-phenylenediacrylic acid and 1,4-bis(2-hydroxyethoxy)cyclohexane, cross-links are photogenerated by a cycloaddition reaction between acryloyl groups in adjacent polymer chains. Three of the possible four all-trans cyclodimers of the phenylacrylic chromophore are observed in the photoproducts. A derivative of β-truxinic acid is the most important cyclodimer and is formed in the matrix via an excimer, the emission of which is readily observed. This affords an opportunity to monitor the photokinetics of the reaction at a well-defined matrix site in some detail. The lifetime of the excited chromophore at an excimer site, its reaction probability, and the activation energy of the cyclization step have been determined.

In an earlier paper we reported on photocycloaddition between cinnamoyl groups in solid films of poly(vinyl cinnamate).[1] From the results there emerged a view of the matrix as an ensemble of chromophore sites, and some

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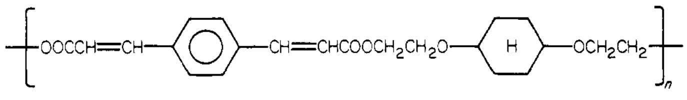
conclusions about the molecular morphology of the polymeric solid were suggested. In poly(vinyl cinnamate) the photoreactive cinnamoly groups are pendent from a hydrocarbon backbone; it seemed of interest to investigate a system where the reactive chromophores form part of the main chain of the polymer.

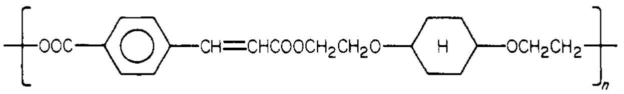
A polyester of *p*-phenylenediacrylic acid (PDA) and 1,4-bis(2-hydroxyethoxy)cyclohexane was chosen for this work. Its structure is shown below.



PPDA

This material is particularly suitable for such a study because the photochemistry of PDA has been thoroughly elucidated by Hasegawa and others[2-8] and also because PDA is the active component of a group of successful photopolymers.[9] The polyester PPDA, in particular, is used on a large scale in the manufacture of printing plates; its photochemical behavior is therefore of practical interest. We have measured the quantum yield of the photoreaction as a function of chromophore conversion over a range of temperatures, we have observed the fluorescence emission of the matrix, and we have identified the principal products of the matrix reaction. From the results, the photokinetics of the reaction at certain well-defined matrix sites can be derived and some conclusions relating to the molecular morphology of the matrix may be drawn.

PDA is a bifunctional chromophore and undergoes two consecutive cycloaddition steps on irradiation. This complicates the spectrophotometry of the primary process; we have therefore in some instances used a monofunctional analogue of PPDA. This is a polyester of 4-carboxycinnamic acid with the same glycol component as that used in PPDA. Its structure is indicated below.



PCCA

The Matrix as an Ensemble of Chromophore Sites. The results of earlier work suggested[1] that the photoreactive polymer matrix behaves like an ensemble of chromophore sites. This view was based on the relationship between the quantum yield of the cycloaddition reaction (ϕ_r) and the degree of conversion (x) of the chromophores: in poly(vinyl cinnamate) the quantum yield decreases rapidly during irradiation and tends to zero while a large fraction of potentially reactive chromophores still remains intact. Films of the polyesters PPDA and PCCA behave qualitatively in the same way. Figure 1 shows the quantum yield as a function of the degree of conversion of the chromophores in PPDA and in PCCA. In both cases the quantum yield decreases and extrapolates to $\phi_r = 0$ at conversions well below unity. This is clearly evident in the case of PCCA, where the spectrophotometric determination of ϕ_r over the whole conversion range is more reliable than in PPDA.

We note at this point the virtual absence of cis–trans isomerization in the polyester films. This is illustrated in Figure 2, which shows the evolution, under irradiation, of the absorption spectrum of PCCA. The sharp isosbestic point at 256 nm indicates that a single process occurs in the system, namely, the disappearance of the 4-carboxycinnamic group.

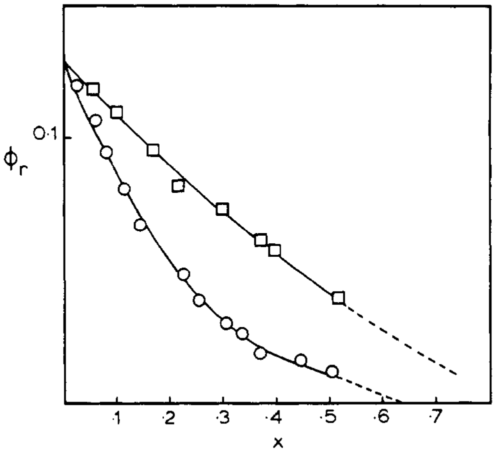


Figure 1. Quantum yield, ϕ_r, as a function of chromophore conversion x: (□) in PPDA; (○) in PCCA.

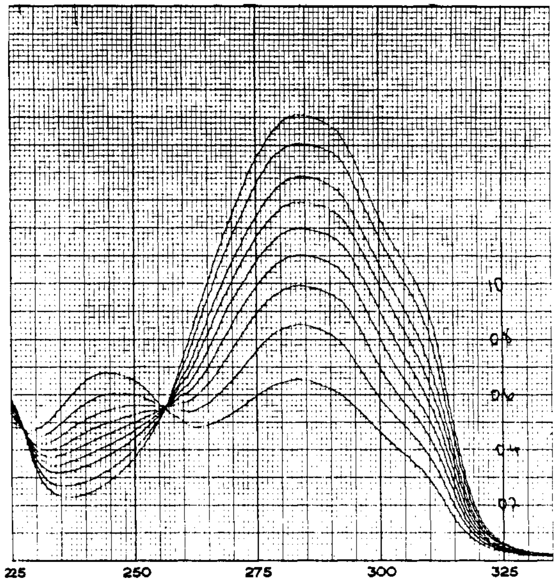


Figure 2. Change in the absorption spectrum of PCCA film on irradiation.

The polyester PPDA differs from poly(vinyl cinnamate) in another respect: the singlet excited state of the PDA chromophore is sufficiently long-lived to emit fluorescence. The fluorescence yield of a 10^{-5} M solution of Et_2PDA in dichloroethane is $\phi_f = 0.023$. As Nakanishi et al.[5] have observed, in concentrated solutions the fluorescence emission is shifted to longer wavelength, indicating the presence of an excimer. Monomer as well as excimer fluorescence is observed in solutions of the polyester PPDA (see Figure 3), the relative importance of the two components depending on concentration. Solid films of PPDA emit only excimer fluorescence;[25] the quantum yield of emission is here $\phi_f = 0.085$. Since the energy of the excimer is lower than that of the excited monomer, the high quantum yield of excimer fluorescence and the absence of monomer emission are direct evidence for energy migration and trapping in the solid matrix.

Further evidence for the mobility of excitation quanta in PPDA (and to a lesser extent in PCCA) is provided by the depolarization of the sensitized emission of fluorescent probes in the irradiated films.[12]

In PPDA films energy migration is sufficient to collect in the early stages of irradiation all incident quanta in excimer traps. At that stage, therefore, the quantum yield of the system is determined only by the reactivity of the excimer sites. Since these sites also fluoresce, there arises an opportunity to monitor the photokinetics of the matrix reaction in some detail.

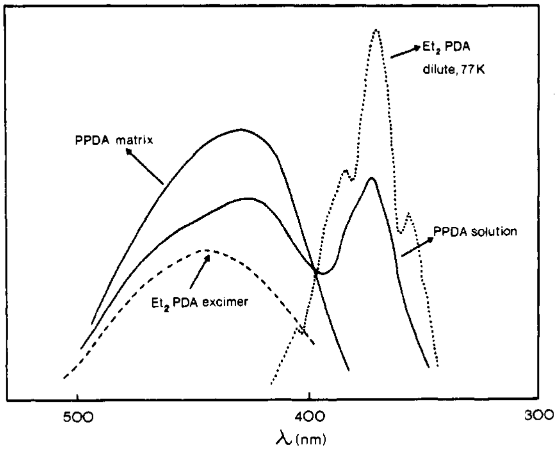


Figure 3. Fluorescence spectra of Et_2PDA solutions, PPDA solution, and PPDA matrix.

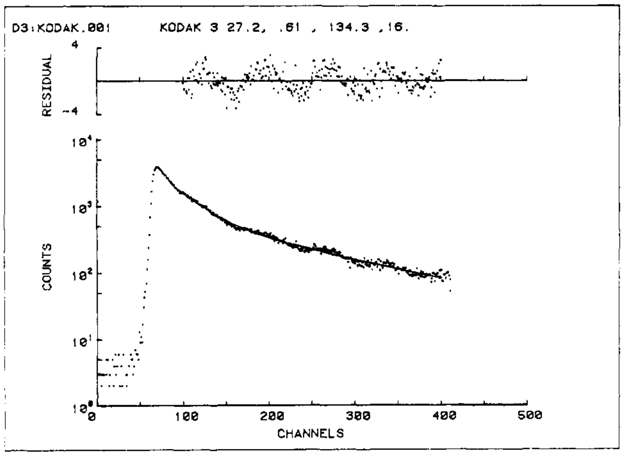


Figure 4. Fluorescence decay of a film of PPDA after excitation by a laser pulse.

Photokinetics of the Matrix Reaction at Excimer Sites. When an excitation quantum is trapped at an excimer site, it can cause the site to emit or to decay to the ground state of a reactant pair, or it may bring about a photoreaction. In terms of the probabilities of these three competing processes the macroscopic quantum yield of the photoreaction may be expressed in the form

$$\phi_r = k_r/(k_r + k_f + k_d) \qquad (1)$$

The subscripts r, f, and d refer to the reaction, to fluorescence, and to nonradiative decay, respectively, and k stands for the average probability of occurrence of the event in the ensemble of sites. The quantum yield of fluorescence may be written in a similar way

$$\phi_f = k_f/(k_r + k_f + k_d) \qquad (2)$$

The common denominator in (1) and (2) is the reciprocal of the fluorescence lifetime

$$\tau_f = 1/(k_r + k_f + k_d) \qquad (3)$$

The individual probabilities can therefore be derived from measurements of ϕ_r, ϕ_f, and τ_f. Figure 4 shows the time decay of the fluorescence of a film of PPDA following excitation by a laser pulse. It can be seen that the decay is nonexponential, indicating a range of lifetimes in the ensemble of excimer states. The main component, however, has a fluorescence decay time of about 1.9×10^{-9} s. This, together with the fluorescence yield in the matrix of $\phi_f = 0.085$ and a reaction quantum yield of $\phi_r = 0.13$ leads to the k values listed in Table I, which are compared there with the corresponding data for the excimer sites in solid polystyrene and poly(vinylcarbazole)[13] as well as the anthracene excimer in toluene solution.[14] The high radiative emission rate of the PDA chromophore in the matrix is caused by the comparatively large transition dipole moment. The cyclization reaction at the excimer sites of PPDA is remarkably efficient, since its probability is the same as that of the classic 1,4-cycloaddition of anthracene. However, the salient feature of the PDA system is the high rate of nonradiative deactivation, which is chiefly responsible for the short lifetime of the excited species. We believe this is related to the presence of the ethylenic double bond, which tends to assume a perpendicular configuration in the excited state.[15] Even if such a configurational change cannot fully develop in the solid matrix, incipient nonplanarity of the system is enough to reduce the energy gap between adjoining states and promote the nonradiative transition to the ground state.

Table I
Photokinetic Parameters of Excimer Sites in Polymer Matrices

	$\tau_f \times 10^{-9}$ s	$k_f \times 10^7$ s^{-1}	$k_d \times 10^7$ s^{-1}	$k_r \times 10^7$ s^{-1}
polystyrene	19	0.2	5	
poly(vinylcarbazole)	40	0.75	2.5	
PPDA	2	4.5	41	6.8
anthracene[a]	2.5	0.16	(33)	6.4

[a] Solution in toluene.

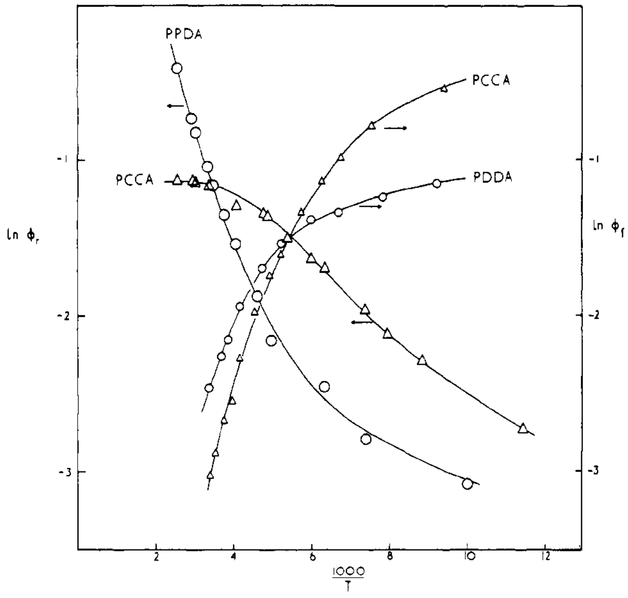


Figure 5. Effect of temperature on the initial reaction yield (ϕ_r^0) and on the fluorescence yield (ϕ_f^0).

The effect of temperature on the initial reaction yield (ϕ_r^0) and on the fluorescence yield (ϕ_f^0) of PPDA and PCCA is shown in Figure 5. While ϕ_r^0 decreases with falling temperature, ϕ_f^0 increases and levels off when the competing processes have either ceased or become temperature independent. Cohen et al.[16] have observed a similar complementary behavior of fluorescence and cycloaddition in crystalline diphenylbutadienes. The nonlinear shape of the Arrhenius plot is caused, at least in part, by the temperature dependence of k_d. This effect can be eliminated by plotting the ratio ϕ_r^0/ϕ_f^0 against reciprocal temperature (Figure 6). If the probability of the radiative step, k_f, is temperature independent, the quantum yield

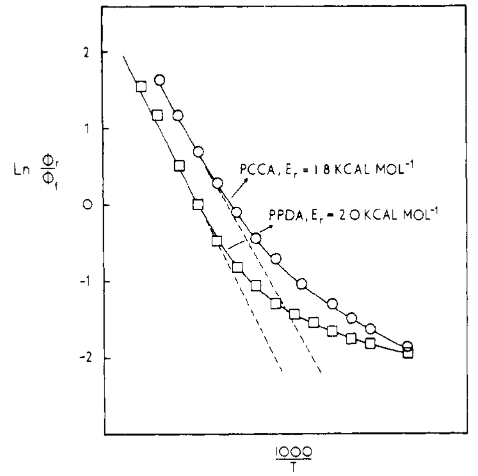


Figure 6. Determination of the activation energy of the cyclization reaction in PPDA and in PCCA.

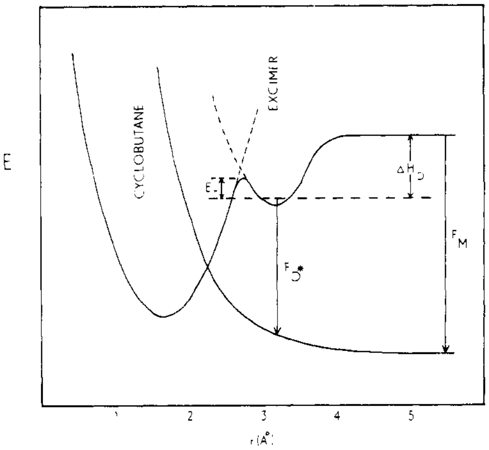


Figure 7. Potential energy curve for photocycloaddition via an excimer intermediate.

ratio is determined only by the activation energy of the cyclization step

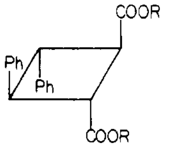
$$\frac{\phi_r^0}{\phi_f^0} = \frac{k_r^0}{k_f^0} e^{-E_r/RT} \tag{4}$$

From the slope of the linear part of the plot of Figure 6 the activation energy, E_r, is found to be 2.0 and 1.8 kcal mol^{-1} for PPDA and for PCCA, respectively. These values are too low to be associated with the rotational motion of chain fragments in the matrix.[17,18] We believe E_r measures a low-energy barrier at the intersection of the potential energy surfaces of the excimer and of the cyclobutane (Figure 7). An activation energy of 2 kcal mol^{-1} appears reasonable at this point, in view of an excimer binding energy[19] of the order of 6–8 kcal mol^{-1}. The value of E_r agrees quite well with the activation energy of 1.6 ± 0.3 kcal mol^{-1} which Gerasimov et al.[8] found for Et_2PDA crystals in the temperature range between 100 and 200 K. The interpretation of E_r as an excimer-related activation energy is also supported by the fact that photocyclization is temperature independent in systems where the chromophores do not form an excimer (poly(vinyl cinnamate) and poly(vinylcinnamylidene acetate)[12]). Photocyclization via the excimer may thus be regarded as the thermal reaction of a photoexcited species.

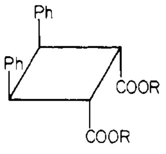
Product Analysis and Its Implications. The practical usefulness of PPDA is based on the formation of cross-links between polyester chains on exposure to radiation. The nature of the cross-linking reaction can be established by careful hydrolysis of irradiated films.[1] This leads to fragmentation of the polyester chains and isolates individual cross-links in the form of small molecules which can be identified by conventional methods. In the presence of phase-transfer agents hydrolysis is achieved under sufficiently mild conditions to preserve the stereochemical identity of the fragments. Results obtained in this way for heavily and moderately irradiated films of PPDA are listed in Table II. The fraction of cyclodimers in the products is high. The oligomers which make up the rest of the photoproducts result from the reaction of both acryloyl groups in the PDA chromophore and also contain cyclobutane rings: photocycloaddition is clearly the principal photoprocess in the polymer. The three cyclodimers which are found in quantity are derivatives of β-truxinic, δ-truxinic, and α-truxillic acid.

Table II
Product Distribution in the Photolysis of PPDA Films

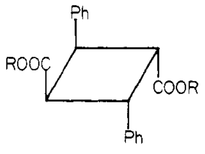
	overall conversion	
	0.85	0.15
dimer fraction	0.52	0.8
δ-truxinate	0.35	0.23
β-truxinate	0.48	0.68
α-truxillate	0.18	0.09



δ



β



α

The head-to-head syn dimer, β-truxinate, makes the largest contribution to the cyclobutane fraction. It corresponds to a ground-state pair configuration in which there is maximum overlap of the π systems of the reactants and is therefore the structure associated with the excimer sites in the matrix. Since the proportion of excimer sites in the ensemble is high, moderate energy delocalization in the matrix is sufficient to populate preferentially the excimer sites in the early stages of irradiation. The effect is illustrated in the last column of Table II by the higher proportion of β-truxinate in the products at low conversion (at 15% chromophore conversion over 80% of the products are cyclodimers, two-thirds of which are β-truxinate). Thus, at the start of irradiation excitation quanta are quantitatively collected at excimer sites, and the efficiency of cross-link formation in the system is limited only by the successful conclusion of the cyclization step. This in turn is determined by the activation barrier separating the excimer from the cyclobutane.

In the high-conversion experiment quoted in Table II most of the chromophore sites have reacted; the product distribution after hydrolysis is therefore representative of the distribution of ground-state pair configurations in the matrix. The high proportion of cyclic products thus points to a preferential grouping together of the aromatic and the aliphatic components, respectively, and the predominance of head-to-head dimers (truxinates) over head-to-tail dimers (truxillates) (in the ratio 5:1) indicates that more often than not the chromophores of adjacent polyester chains are "in phase", i.e., overlap in pairs over a large part of their aromatic systems.

Whether such an arrangement contains an element of organization is a matter of definition. Crystallographically the matrix is amorphous: neither the precipitated polyester nor the pulverized matrix shows any signs of structure in X-ray diffraction experiments, while crystals of Et_2PDA produce a sharp diffraction pattern. At the same time, the frequency of occurrence of "pretruxinic" reactant pairs is far higher in the matrix than could be expected in a strictly random ensemble. Even without taking account of the angular distribution of reactants, the fraction of nearest neighbors which fall within the critical reaction distance of 4 Å in a random distribution of points is about 0.35; yet the fraction of cyclic structures in irradiated PPDA is larger than 0.8. There clearly is a considerable degree of intermolecular correlation between chromophores in the matrix. The driving forces for this effect are the dipolar interactions which commonly produce liquid crystalline behavior in small molecules. The structural similarities between PDA and classic mesogenic compounds are indeed striking.[20,21] Furthermore, concentrated solutions of Et_2PDA in dichloroethane are strongly birefringent and demonstrate, on a macroscopic scale, an incipient molecular organization which eventually leads to a fully crystalline precipitate. In PPDA the development of discrete chromophore domains is inhibited by the entropic requirements of the polymer chain; chromophores correlate only in pairs or in small groups, and the replication of reactant geometry in these groups is not exact. The type of molecular correlation which is established in the matrix is therefore not easily detected by physical means, yet it is this local morphology which has important chemical, and photographic, consequences.

Experimental Section

Materials. The polyester PPDA is a commercial photopolymer; the sample supplied by Eastman Organic Chemicals had a molecular weight of $\bar{M}_w = 1.5 \times 10^5$. The polyester PCCA ($M_w = 4.9 \times 10^4$) was kindly prepared for us by R. C. McConkey of Eastman Kodak Research Laboratories, Rochester.

Solvents used were reagent grade.

Procedures. Films of the polyesters were coated from solution on the inside of Pyrex flasks and irradiated through additional Pyrex filters with a medium-pressure mercury lamp (Hanovia, 500 W). After irradiation, the films were heated with 1 M ethanolic KOH in the presence of benzyltriethylammonium chloride. The cross-linked polymer dissolved within 30 min. The free acids were precipitated from solution with HCl, removed by centrifugation, washed, and dried. They were then reesterified by refluxing with dry thionyl chloride, for 30 min, removing $SOCl_2$ under vacuum, and dissolving the residue in ethanol. The mixture of ethyl esters was dried and partially separated by chromatography on silica gel.

Gas Chromatography. Samples for gas chromatography were presented in chloroform solution at concentrations of about 1 mg/mL. They were injected via an all-glass capillary inlet into a Hewlett-Packard 5840 gas chromatograph fitted with a 12-m WCOT capillary column, coated with CP^{tm}SIL-5 (Chrompack, Middelburg, The Netherlands). Injection temperature was 50 °C. After 1 min the column temperature was raised at the rate of 30 °C/min to 230 °C and was increased after 9 min to 300 °C. Retention times for the dimers of PDA in these conditions were of the order of 40 min. The identity of the fractions was established from the NMR spectra. The order of appearance of the isomers is analogous to that of the diethyl truxinates and truxillates investigated earlier.[22]

Quantum Yields. The quantum yield of the photoreaction was determined by spectrometry from the change in chromophore absorption in the film during irradiation. The experimental results were substituted into the expression

$$\frac{\mathrm{d}D}{\mathrm{d}t} = \Delta\epsilon I_0 A \cdot 10^3 \frac{D - D_\infty}{D} \phi_r$$

where D is the optical density (e.g., at the peak of the chromophore absorption), $\Delta\epsilon$ is the difference in the extinction coefficient of reactant and product at the measured wavelength, I_0 is the intensity of incident radiation (measured by ferrioxalate actinometry), and A is the fraction of photons absorbed in the film.

The quantum yield of fluorescence in the matrix was measured in a frontal irradiation geometry by comparison with dibenzoxazolylbiphenyl[23] ($\phi_f = 1.0$) dissolved in a film of poly(methyl methacrylate), due account having been taken of the spectral sensitivity of the photomultiplier detector.

Fluorescence Decay Time. The fluorescence decay time of the excimers of PPDA was measured with a single-photon-counting apparatus at the Royal Institution, London. Excitation was with a frequency-doubled jet-stream dye laser (Rhodamine G) synchronously pumped with a mode-locked argon–air laser.[24]

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