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Photocycloaddition in Solid Poly(vinyl cinnamate). The Photoreactive Polymer Matrix as an Ensemble of Chromophore Sites

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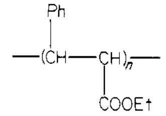
ABSTRACT: The nature of photogenerated cross-links in solid poly(vinyl cinnamate) is investigated. Hydrolysis of irradiated films and subsequent chromatography of the hydrolysis products show that the principal matrix reaction is cycloaddition between polymer-bound cinnamoyl groups. The overall quantum yield of the cross-linking reaction decreases during irradiation and the reaction virtually stops while half of the potentially reactive chromophores are still intact. Since all cinnamoyl groups are identical in structure, the lack of reactivity of some must be attributed to their environment. This suggests a description of the matrix in terms of chromophore sites, where the reactive groups are considered together with their immediate surroundings. Sites are characterized by their reaction probability and by geometry. The distribution of site reactivities in the ensemble may be derived from the dependence of the quantum yield of the photoreaction on chromophore conversion. The distribution of chromophore configurations at the sites is inferred from the distribution of cyclic isomers in the final products. Product analysis after cycloaddition may thus be used as a probe into the micromorphology of the polymer matrix.

Poly(vinyl cinnamate) is the earliest synthetic photopolymer.[1] Its design, a polyvinyl backbone with cinnamoyl side chains, was conceived in the hope that photocycloaddition between polymer-bound cinnamoyl groups[2,3] would cross-link adjacent macromolecules. The practical aims of the inventors have been realized and a whole range of successful photopolymers has developed from the original idea,[4-6] but the actual mechanism of cross-link formation in these systems is still uncertain. Attempts to identify cyclobutane derivatives in irradiated films of poly(vinyl cinnamate) have repeatedly failed[7] and only in the very early stages of irradiation could Sonntag and Srinivasan[8] detect traces of α-truxillic acid in the hydrolyzed material. The very possibility of cycloaddition in amorphous polymer matrices was seriously questioned by Schmidt,[9] because of the stringent steric requirements of the cyclization process, and several further observations seemed to support this view: Krönert[10] had found only traces of cyclic products in the photolysis of neat liquid ethyl cinnamate, and Nakamura and Kikuchi[11] had detected the ESR signals of well-defined radicals in irradiated films of poly(vinyl cinnamate), suggesting a radical-based mechanism for the cross-linking process.

The aim of this paper is to establish the nature of the photogenerated cross-links and to investigate the effect of the solid matrix on the cross-linking process. Direct proof for or against the occurrence of cycloaddition may be obtained by hydrolyzing the cross-linked films and searching for cyclobutane derivatives in the hydrolysate. Sonntag and Srinivasan[8] have used this method on very lightly irradiated poly(vinyl cinnamate). We have now found that with the use of phase-transfer agents it is possible to hydrolyze even heavily cross-linked materials, in conditions which leave the cyclobutane rings intact and preserve their stereochemistry (see Table II).

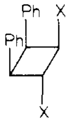
The principal outcome of these experiments is the finding that in poly(vinyl cinnamate) at least 65% of the photoproducts are cyclodimers. The remaining part of the photoproducts are oligomers which have not been fully characterized. Their elemental analysis and their NMR and IR spectra are compatible with the general structure



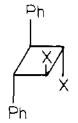
$$-(\overset{\mathrm{Ph}}{\mathrm{CH}}-\underset{\mathrm{COOEt}}{\mathrm{CH}})_n-$$

This material, which is less abundant in low-temperature photolysis (see the last column in Table I), may have been formed by a radical polymerization mechanism, in agreement with early suggestions by Schmidt.[12] Such a mechanism would also explain the presence of side-chain and main-chain radicals observed by Nakamura and Kikuchi.[11]

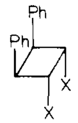
The product distribution of the more important dimer fraction is indicated in the chromatogram of Figure 1. Four of the eleven stereoisomers, which in principle may be formed from two cinnamoyl groups, are observed. The identity of the chromatographic peaks was established by calibration with authentic materials (see the Experimental Section and ref 13). They correspond, in order of retention time, to the structures shown below.



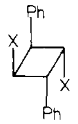
neotruxinate



δ-truxinate



β-truxinate



α-truxillate

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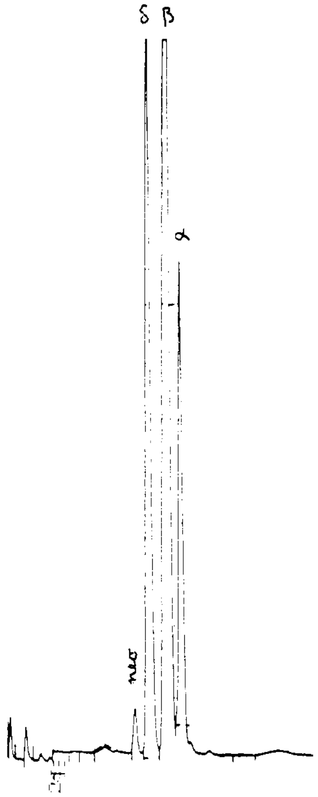

Figure 1. Gas chromatogram of the dimer fraction in the hydrolysis products of an irradiated poly(vinyl cinnamate) film.

The quantitative analysis of the dimer fraction is given in Table I. Several points are of interest: (i) the distribution of isomers is very nonuniform, β-truxinate being the majority product, (ii) there is a preponderance of truxinates (head-to-head dimers) over truxillates (head-to-tail dimers), (iii) the starting material is *all-trans*-poly(vinyl cinnamate), yet a mixed trans–cis dimer, neotruxinate, is found in the products. We reserve discussion of these points to a later stage.

Effect of the Matrix on Reaction Efficiency. The effect of the solid matrix on the efficiency of the cycloaddition process is illustrated in Figure 2, which refers to the photoreaction between cinnamoyl groups in three different states of aggregation: a crystal of cinnamic acid (A), a solid film of poly(vinyl cinnamate) (B), and a solution of poly(vinyl cinnamate) in dichloroethane (C). In the figure, the quantum yield of the photoreaction is plotted as a function of the degree of conversion of cinnamoyl groups. The differences in the behavior of the three systems are striking. The dominant feature of the quantum yield function of the solid film is the sharp decrease of ϕ with increasing conversion. In the solid matrix the photoreaction comes to a virtual standstill ($\phi = 0$) at a point where about half of the potentially reactive chromophores are still intact. Since all chromophores in the system have the same structure, the lack of reactivity in some must be attributed to their environment.

This suggests a description of the photoreactive matrix as an ensemble of chromophore sites. The sites so defined are related to the "reaction cavity" introduced by Schmidt and Cohen into the photochemistry of organic crystals.[14,15] However, while all reaction cavities of a crystal are identical, and the crystal is therefore either photoreactive or photostable, the matrix contains, side by side, reactive as well as nonreactive sites. As the matrix reaction proceeds, the reactive sites will be gradually depleted, more and more quanta will be captured by nonreactive sites, and the quantum yield of the system will decrease. In contrast, the photoreactive crystal does not contain nonreactive sites, and the photoreaction proceeds there at a constant rate (curve A, Figure 2), until the continuity of the lattice is destroyed by the chemical transformation.

Table I
Distribution of Isomers in the Dimer Fraction of the Photoproducts

	t_r,[a] min	25 °C	77 K
neotruxinate	21.9	5	2
δ-truxinate	23.4	19	21
β-truxinate	24.5	61	64
α-truxillate	25.1	15	13
dimer fraction %		65	80

[a] Retention time.

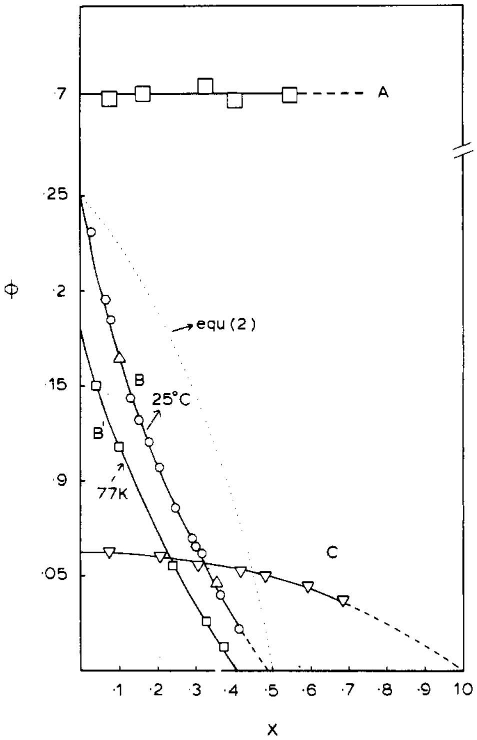

Figure 2. Quantum yield of cycloaddition between cinnamoyl groups as a function of reactant conversion, in three states of aggregation: (A) crystalline cinnamic acid, α form; (B) solid film of poly(vinyl cinnamate); (C) solution of poly(vinyl cinnamate) in dichloroethane.

A third type of behavior is observed in fluid media, e.g., in a solution of poly(vinyl cinnamate) in dichloroethane (curve C, Figure 2). Here the quantum yield of the photoreaction steadily decreases with a falling concentration of cinnamoyl groups because the encounter probability between chromophores decreases. However, at any stage of the process all reactant groups have the same finite chance of finding a reaction partner, and the quantum yield function $\phi(x)$ extrapolates to the point $\phi = 0$, $x = 1$.

It could be argued that the distinction between the matrix and the fluid solution is not fundamental but only a difference of degree, the polymer film behaving as a very viscous fluid. This point is disproved by experiment. Cooling the matrix to 77 K in liquid nitrogen and increasing in this way the internal viscosity have only a small effect on the overall reaction efficiency (see Figure 2, curve B′). The permanence of the reaction sites is furthermore demonstrated by changing the time scale of the exposure experiments. The points in curve B, Figure 2, marked by a circle refer to an experiment where the quantum yield was measured semicontinuously during irradiation; for the hexagonal points the quantum yield was measured 2 h after a "depleting" exposure of the film, and the triangles in curve B refer to a similar experiment where the waiting period between the bulk exposure and the measurement of the quantum yield was 2 days. All the experiments produce quantum yield values which fall on the same $\phi(x)$ curve. This means that the reactive sites have not been replenished in the time interval between exposure and quantum yield measurement, that the number of reactive sites does not change with time, and that in effect the number of reactive sites is decided when the matrix is cast. Evidently, the chromophore sites are not transient entities but are the permanent constituents of the photoreactive matrix, in the same way in which the unit cells of a lattice constitute the organic crystal. This view agrees with the work of Guillet et al.[16] on the immobilization of luminescent probes in polystyrene and with the observations of Frank and Harrah[17] on the permanence of excimer sites in poly(vinylnaphthalene) and is, in general, supported by a variety of results collected in a recent review by Williams and Daly.[18]

From the point of view of the efficiency of the matrix reaction the most important characteristic of a chromophore site is its reactivity. The observable macroscopic quantum yield of the system is the average site reactivity, if the nonreactive sites are included in the count. For a system comprising only nonreactive and a single type of reactive sites, the quantum yield function $\phi(x)$, which corresponds to curve B in Figure 2, is easily derived. In the absence of energy migration (and we have shown earlier that energy migration is unimportant in poly(vinyl cinnamate),[6] the quantum yield of the system is proportional to the product of the fraction of reactive sites (c_r) and the site reactivity (q)

$$\phi = 2qc_r \tag{1}$$

If the degree of reactant conversion (x) is defined as the fraction of the initial number of chromophores which has reacted, eq 1 may be expanded in the form

$$\phi(x) = 2q\frac{c_r^0 - x}{1 - x} = \frac{\phi_r^0}{c_r^0}\,\frac{c_r^0 - x}{1 - x} \tag{2}$$

where c_r^0 is the initial fraction of reactive sites and ϕ_r^0 the initial quantum yield. The factor 2 takes account of the stoichiometry of the dimerization reaction. The broken curve in Figure 2 corresponds to eq 2 as applied to a film of poly(vinyl cinnamate). Comparison with the experimental curve shows that the quantum yield decreases much faster than can be accounted for by the disappearance of a single type of reactive sites: the sites of the matrix cover a whole range of reactivities.

Distribution of Reactivities over Sites. At any stage of the matrix reaction the macroscopic quantum yield is determined by the reactivities of the ensemble of surviving sites. By definition, the more reactive ones are consumed earlier in the process than the less reactive ones, and this is reflected in the observed decrease in quantum yield as the photoreaction progresses. As a consequence, the distribution of site reactivities in the matrix is implicit in the quantum yield function $\phi(x)$. It is not possible to extract the distribution of reactivities directly from these data, but it is possible to calculate the quantum yield function $\phi(x)$ which corresponds to any given reactivity distribution. The true reactivity distribution in the matrix may be found by exploring a range of assumed distributions and comparing their $\phi(x)$ functions with the experimental results. This approach is now briefly presented.

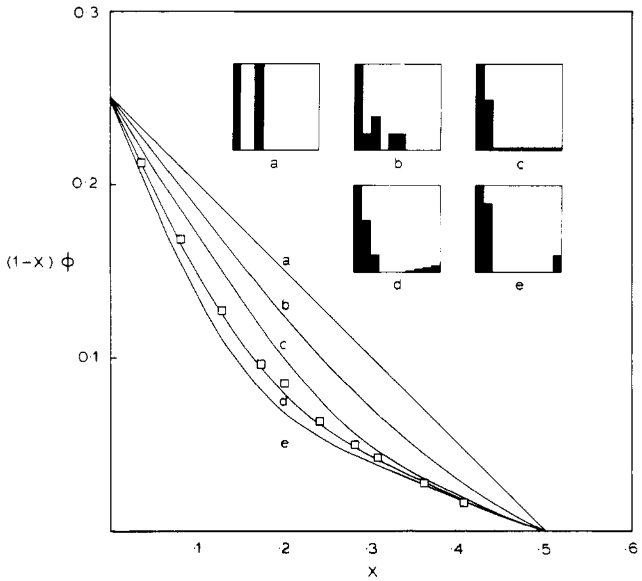

Figure 3. Quantum yield function $\phi(x)$ for five representative reactivity distributions. The experimental points were obtained with an irradiated film of poly(vinyl cinnamate).

Consider a system of N potentially reactive chromophores. The distribution of reactivities in this ensemble may be described by dividing the chromophores into groups according to reactivity and indicating the population of the groups. If at the very beginning of irradiation n_i^0 chromophores have the reactivity q_i, the initial quantum yield of the system is

$$\phi^0 = \frac{2}{N}\sum q_i n_i^0 \tag{3}$$

The factor 2 in eq 3 indicates that two chromophores disappear simultaneously in every successful reaction event. At a time t after the onset of irradiation, the population in the various groups changes to $n_i(t)$. The overall fraction of chromophores reacted at that time (i.e., the conversion $x(t)$) is given by

$$1 - x(t) = \frac{1}{N}\sum n_i(t) \tag{4}$$

and the quantum yield of the matrix reaction at that stage of the process is

$$\phi(t) = 2\frac{\sum q_i n_i(t)}{N(1 - x)} \tag{5}$$

To find the relation between ϕ and x, n_i must be established as a function of time. The probability of reaction of a chromophore in group i is proportional to the fraction of the sites in this group (i.e., $n_i/[N(1 - x)]$) times the reactivity (q_i). If the rate at which photons are absorbed in the system is Q, the change in the population of reactivity group i is given by

$$dn_i = -2q_i Q\frac{n_i}{N(1 - x)}\,dt \tag{6}$$

This expression can be integrated to give

$$n_i(t) = n_i^0 \exp[-q_i\alpha(t)] \tag{7}$$

where $\alpha(t)$ is an abbreviation for the integral

$$\alpha(t) = \frac{2Q}{N}\int_0^t \frac{dt}{1 - x} \tag{8}$$

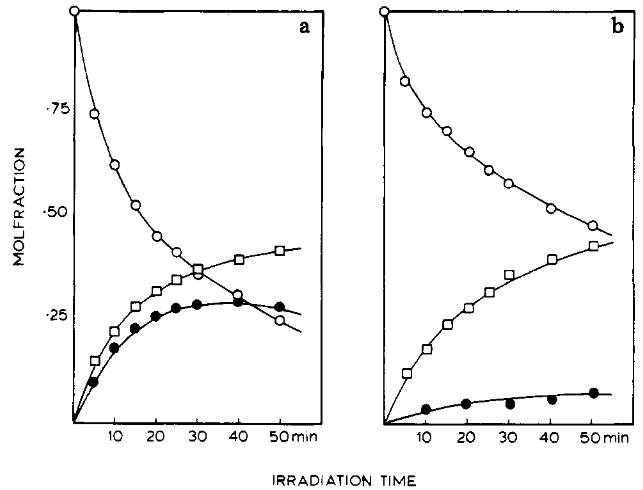

Figure 4. Simultaneous progress of cycloaddition and of cis-trans isomerization in (a) a solution of poly(vinyl cinnamate) in dichloroethane and (b) a solid film of the polymer.

To implement the practical calculation of x and ϕ, the chromophores are divided into a set of 10 groups with reactivities 0, 0.1, 0.2, ..., 0.8, 0.9. In terms of this set, the overall degree of conversion and the quantum yield can be written in the form

$$1 - x = \sum_{0}^{9} f_i r^i \qquad (9)$$

and

$$\phi = \frac{2}{1 - x} \sum_{0}^{9} q_i f_i r^i \qquad (10)$$

where f_i is the mole fraction of group i in the initial distribution

$$f_i = n_i/N \qquad (11)$$

and r is given by

$$r = \exp(-0.1\alpha) \qquad (12)$$

It can be seen that in eq 9 and 10 r acts merely as a parameter. Thus, by choosing values of r between 0 and 1, x and ϕ can be calculated for any given set of f_i, that is, for any initial distribution of reactivities. The values of f_i chosen to represent a distribution must of course satisfy the two conditions

$$\sum f_i = 1 \qquad (13)$$

and

$$\phi(0) = 2\sum q_i f_i \qquad (14)$$

Using this procedure, we calculated the quantum yield functions $\phi(x)$ for a number of representative distributions. The result is shown in Figure 3, where the product $(1 - x)\phi$ is plotted as a function of x. Distribution a consists only of unreactive and a single group of reactive sites and leads to a linear relation between $(1 - x)\phi$ and x, as predicted by eq 2. In distributions b–e increasingly higher reactivity groups are populated. It can be seen from a comparison with the experimental points that the photokinetic behavior of poly(vinyl cinnamate) is best represented by distribution d, where the majority of sites are unreactive or barely reactive and only a small fraction of sites have maximum or near-maximum reactivity. This is a significant result which provides new insight into the makeup of the matrix. It shows that the steric requirements of cycloaddition are exacting and that only a small fraction of chromophores is located at sites with a truly favorable reaction geometry. Yet it is this small minority of sites which determines the chemical, and photographic, behavior of the matrix.

Cis–Trans Isomerization. Cycloaddition need not be the only photoprocess occurring in poly(vinyl cinnamate). Unsaturated chromophores which are capable of cycloaddition often undergo cis–trans isomerization about the reactive double bond.[19] In solid polymer matrices isomerization is inhibited, but Morawetz et al.[20,21] and more recently Eisenbach[22] have shown that photoisomerization of polymer-bound azobenzene groups does proceed even below the glass transition, although to a smaller extent and with a lower quantum yield than in fluid solution. Conditions are similar in poly(vinyl cinnamate) matrices and here too isomerization may compete with cyclization. The extent of this competition was estimated from spectrophotometric measurements as follows: Where isomerization is the only photoprocess, such as in dilute solutions of ethyl cinnamate, the spectral curves obtained on progressive irradiation intersect at an isosbestic point at 250 nm. If a second reaction of a different kinetic order competes with isomerization, the isosbestic point is lost and the changes of optical density at that wavelength (250 nm) may be used to measure the extent of the competing photoreaction. Thus, spectrophotometry at two wavelengths, one of which coincides with the isosbestic point of cis–trans isomerization, makes it possible to monitor cyclization and isomerization simultaneously. The progress of both reactions may be estimated from the experimental data via the following set of equations, which are obtained directly from a material balance:

$$\frac{n_a}{n_0} = \frac{\epsilon_a}{\epsilon_a - \epsilon_b}\left[\frac{D_2}{D_2{}^0} - \frac{\epsilon_b}{\epsilon_a}\frac{D_1}{D_1{}^0}\right]$$

$$\frac{n_b}{n_0} = \frac{\epsilon_a}{\epsilon_a - \epsilon_b}\left[\frac{D_1}{D_1{}^0} - \frac{D_2}{D_2{}^0}\right]$$

$$\frac{n_c}{n_0} = 1 - \frac{D_1}{D_1{}^0}$$

Here a, b, and c denote the trans form, the cis form, and the bimolecular (cyclic) product, respectively, n_a, n_b, and n_c are the numbers of moles of the components at time t, n_0 is the initial (total) number of moles of chromophore D_1 and D_2 are the optical densities at the two wavelengths (D_1 refers to the isosbestic point (at 250 nm) and D_2, e.g., to the absorption maximum at 275 nm), and ϵ_a and ϵ_b are the molar extinction coefficients of the trans and of the cis forms at the second wavelength.

Using these equations on the spectra of a solution of poly(vinyl cinnamate) in dichloroethane and on those of a solid film of poly(vinyl cinnamate) and taking the required extinction coefficients from Rennert et al.[23] yields the results shown in Figure 4. It can be seen that in the polymer solution isomerization competes quite effectively with cycloaddition and that here a quasi-photostationary state is established between the geometric isomers from which the cyclization reaction proceeds. In the polymer film, however, isomerization plays only a minor role and does not seriously interfere with cyclization or any other bimolecular photoprocess. This finding is of interest in connection with some of the arguments of the following section.

Geometry of the Reaction Site. So far, we have characterized chromophore sites by their reactivity and have in effect presented the matrix as an ensemble of reactivities. However, the primary attribute of a site is its geometric configuration. In a crystalline solid, information on site geometry may be gained from diffraction experiments. Using this method, Schmidt and Cohen[15,24] have

Table II
Distribution of Cyclodimers in Irradiated Ethyl Cinnamate before and after Hydrolysis and Reesterification

peak no.	% before	% after
1 (neotruxinate)	6.2	8.5
2	2.6	2.6
3	2.2	0.9
4 (δ-truxinate)	53.3	56.4
5 (β-truxinate)	17.8	17.0
6 (α-truxillate)	11.3	11.2
7 (ζ-truxinate)	6.5	3.3

established a direct correlation between the geometric configuration of the unit cell and the stereochemistry of the reaction products. If we may assume a similar correlation between site geometry and product structure in the amorphous solid, the distribution of site configurations may be inferred from the isomer distribution in the products: the photoreaction may be said to act here as a probe into the micromorphology of the solid.

In order that the above argument may hold, it must of course be assumed (i) that the chemical operations which intervene between the conclusion of the photoprocess and the final product analysis do not alter the stereochemistry of the products, (ii) that the photoreactive groups represent a substantial part of the material, and (iii) that cis–trans isomerization does not sever the link between the original site configurations in the unirradiated matrix and the final photoproducts. The first and second conditions hold in poly(vinyl cinnamate). Having applied the hydrolysis and reesterification procedures to irradiated ethyl cinnamate, we find that the distribution of cyclodimers is not substantially affected by these operations (see Table II). Furthermore, it can be seen from Figure 4 that only at a small number of sites does cis–trans inversion occur and that the majority of chromophores in the matrix has but one configurational option. In these conditions, the product distribution obtained in the photolysis of poly(vinyl cinnamate) films can be taken to represent in a first approximation the distribution of the original site geometries in the unirradiated matrix.

From the data in Table I it follows that most of the cyclic products in the photolysis of solid poly(vinyl cinnamate) are head-to-head dimers. These could have been formed by the interaction of nearest neighbors on the same chain, in analogy with the behavior of propane-1,3-dicinnamate in solution[25,26] and in agreement with Hirayama's rule.[27] However, it has been shown by gel-point determinations that in solid poly(vinyl cinnamate) intrachain interaction is negligible.[28] This finding is also supported by the very low concentration of excimer sites in solid films of poly(vinylnaphthalene)[17] and of poly(vinylcarbazole)[29] as well as by recent work of Tanaka and Honda on the behavior of dicinnamylidene acetate in organic glasses.[30] Since, therefore, the cyclic products arise in large part through the dimerization of cinnamoyl groups belonging to different chains, the predominance of truxinates over truxillates (the ratio is about 10:1) must be caused by the relative configuration of the chains.

In a solid environment, head-to-head dimers are formed by groups pointing in the same direction. The predominance of such a geometry in an ensemble of polymer-bound cinnamoyl groups implies a sheetlike arrangement of the principal polymer chains, as it is rather inadequately indicated in Figure 5. The situation is reminiscent of the morphology of liquid crystalline polymers of the smectic order,[31] where the more important interactions occur between laterally adjoining chains and give rise to two-dimensional lamellar structures which extend over macroscopic domains. In poly(vinyl cinnamate) domain formation of this kind cannot develop because of the restraints imposed by the backbone.[32] However, the driving forces for incipient phase separation are clearly available in the hydrophilic–hydrophobic interactions of the components[33] (polar side chains, nonpolar backbone) and in particular in the strong dipolar interactions between cinnamoyl groups. The inherently mesogenic nature of the cinnamoyl grouping is demonstrated, for instance, by 4-methoxycinnamic acid, which forms a nematic mesophase[34] in the temperature interval between 171 and 192 °C.

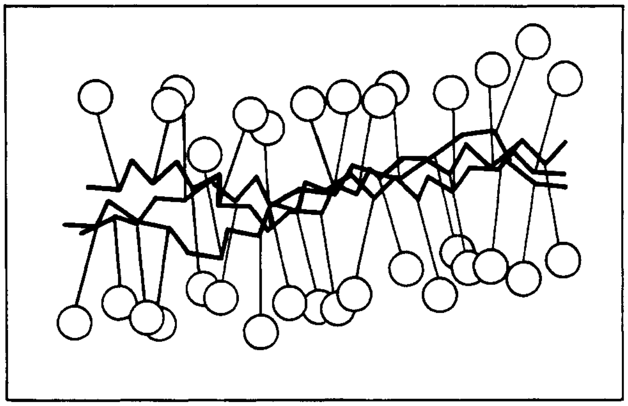

Figure 5. Schematic representation of the molecular arrangement in a poly(vinyl cinnamate) matrix.

Product analysis testifies to the presence in the matrix of a distribution of site configurations, the quantum yield function to that of a distribution of reactivities. If there was a strong correlation between site configuration and reactivity, each type of configuration would be associated with a different reactivity and the product distribution would change as the more reactive sites become preferentially depleted. We have found no evidence for this effect. The group of sites which all finally produce a particular cyclodimer must therefore contain a whole spectrum of reactivities, and their configurations deviate to a greater or lesser extent from the ideal pair geometry which exactly matches the structure of the final product. It is these exact matches which correspond to the highly reactive sites in the matrix.

We conclude that the photoreactive matrix presents itself as an ensemble of sites with a quasi-continuous range of configurations and reactivities. The pair configurations associated with a particular final product share an approximate geometry which is defined rather crudely but is nonetheless distinct from other geometries. In crystallographic terms, the degree of molecular organization in the system is therefore very low and hardly measurable by physical methods. Yet, at the same time, the arrangement of chromophores in the matrix is far from random, with certain types of pair configurations clearly preferred in the ensemble and others virtually absent. Thus, all our results point to considerable local correlation between cinnamoyl groups which produces a distinctive regional morphology in the photoreactive solid and leads to interesting chemical and photographic consequences.

Experimental Section

Materials. Poly(vinyl cinnamate) was supplied by the Eastman Kodak Research Laboratories. It was prepared by esterification of a poly(vinyl alcohol) of medium viscosity with cinnamoyl chloride, in pyridine as solvent. About 15% of the hydroxyls were substituted with acetate groups; $M_w = 2.5 \times 10^5$.

The solvents used, 1,2-dichloroethane and trichloroethylene, were reagent grade.

Procedures. Films of poly(vinyl cinnamate) were coated from 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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