Triplet Energy Migration in Solid Films of Photoreactive Polymers

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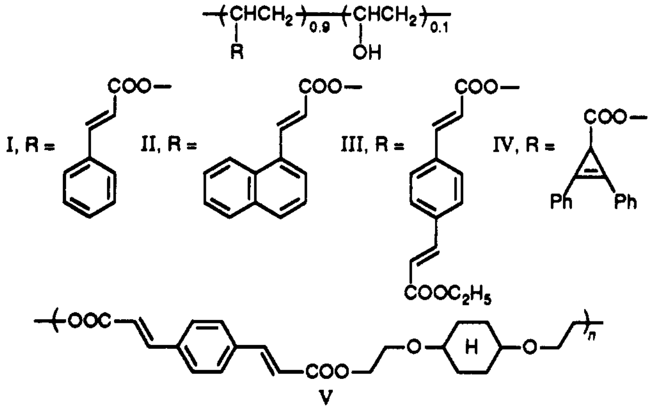
ABSTRACT: Triplet energy migration in photoreactive cross-linkable polymer matrices is investigated. By viewing the solid polymer as an ensemble of reactant sites, the encounter statistics of the excitation quanta with reactive sites can be derived. The migration range of the quanta in the solid matrix is estimated from the effect of triplet quenchers on the photosensitivity of the material. This migration range is strongly dependent on the structure of the photosensitive moiety. In the polymers investigated, the average number of jumps varies from less than 10 to over 100. The role of triplet migration in determining the sensitivity of photoreactive polymer films is discussed.

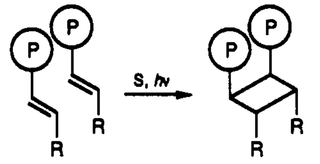
Introduction

In many applications, photoreactive polymers are used in the form of thin solid films.[1] One of the factors that determine their performance in these circumstances is the mobility of the excitation energy. The role of singlet energy migration was briefly considered in an earlier paper.[2] Triplet migration is of greater practical significance since photoreactive polymers are generally used in conjunction with spectral sensitizers, which directly populate the excited triplet state of the reactive chromophores. In this paper the occurrence of triplet energy migration in photoreactive polymers is demonstrated and the range of triplet migration is estimated from quenching experiments.

Five representative polymers (I–V) were investigated. In polymers I–IV the chromophores are attached as side chains to a polyvinyl backbone. In polymer V the photoreactive chromophore is incorporated into the main chain of a polyester. In all cases, the cross-link-producing reaction is cycloaddition of an excited C=C double bond to a similar double bond in the ground state.[3–7]

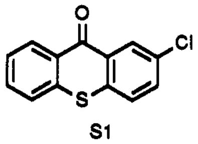


V

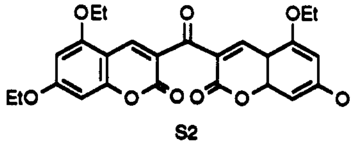


Energy migration in amorphous organic solids occurs by a series of energy-transfer steps or "jumps" between identical molecules or groups.[8,9] In this situation, the migration range can be defined as the mean number of transfer jumps that the excitation quantum executes before causing reaction or being deactivated in some other way. In photoreactive solids the range of energy migration can be estimated from the effect of quenchers (energy traps) on the quantum yield of the photoreaction.[10] In the case of triplet migration, any guest molecule with a triplet level lower than that of the reactive chromophore can act as quencher.

In the present experiments a small quantity of a triplet sensitizer was added to the reactive polymer, and the effect of adding increasing quantities of a quencher on the photosensitivity of the polymer films was monitored. 2-Chlorothioxanthen-9-one (S1) with a triplet level of E_T = 65 kcal/mol and a carbonylbiscoumarin derivative[11] (S2) with a triplet level of E_T = 56.2 kcal/mol were used as triplet sensitizers. The triplet levels of the reactive chromophores of the five photopolymers are in the range between 49 and 55 kcal/mol[12,13] as noted in Table I. Me-



S1



S2

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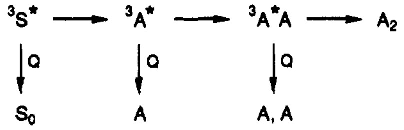
Table I
Triplet Energy and Lifetime, Rate, and Efficiency of Dimerization of Methyl or Ethyl Esters of the Reactive Monomeric Chromophores in Toluene Solution[a]

$$^3A^* + A \xrightarrow{k_A} A_2(\alpha) + 2A(1-\alpha)$$

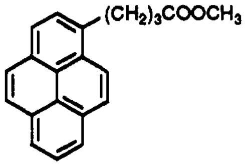
polymer	E_T, kcal/mol	τ_0, μs	k_A, L/(mol s)	α
I	54.8	0.01	8.8×10^6	0.5
II	48.5	10	8.9×10^5	0.18
III	49.3	6.9	2.4×10^6	0.35
IV	51.0	360	3.8×10^7	0.8
V	49.3	6.9	2.4×10^6	0.35

[a] Data from ref 12.

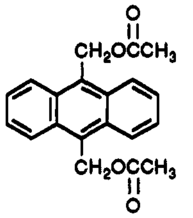
Scheme I



thyl pyrenebutyrate (Q1) with a triplet level similar to that of pyrene, E_T = 48 kcal/mol, and 9,10-bis(acetoxymethyl)anthracene (Q2) with a triplet level similar to that of anthracene, E_T = 42 kcal/mol, were used as quenchers.



Q1



Q2

Sensitizers and quenchers had to be chosen so as to ensure irreversible energy transfer from the sensitizer to the reactive chromophores and from the reactive chromophores to the quencher. The cross-link-forming reaction sequence and the quenching processes are given in Scheme I.

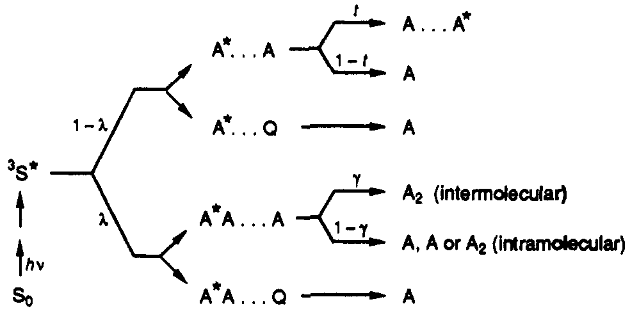
Here $^3S^*$ is a triplet excited sensitizer molecule, $^3A^*$ is an excited chromophore, $^3A^*A$ denotes an excited chromophore pair at a reactive site, A_2 is the dimeric reaction product, which in the polymer embodies a cross-link, and Q is the quencher.

The quencher can intervene in the reaction chain at three points: it can directly deactivate the excited sensitizer, it can quench an isolated reactant (which is not located at a reactive site), and it can quench a reactant that is part of a reactive site. Systems where long-range energy migration occurs will be more sensitive to quenchers than others. The migration range of the excitation may thus be inferred from the effect of quencher concentration on the quantum yield of the solid-state reaction. To draw this inference in a quantitative way, the statistics of energy migration in the solid polymer have to be considered.

Statistics of Energy Migration

Photopolymer films are molecular ensembles comprised of reactive pair sites (A^*A) and of nonreactive sites ($A^*...A$). In the latter sites the reactants are not suitably positioned for cross-link formation to take place. Triplet energy transfer, which is the mechanism of energy migration in these systems, depends on direct orbital overlap between donor and acceptor and occurs only between nearest neighbors in the matrix. The behavior of the excitation in the neighborhood of any site is therefore determined by the distribution of reactants and quenchers in this neighborhood. We shall characterize the neighborhood of a molecule by its mean coordination number, this being the average number of molecules or groups directly in contact with the central molecule. The mean coordination number of a reactant A is labeled m; that of a quencher molecule Q is labeled n.

Scheme II



The various possible destinations of an excitation quantum in a sensitized photoreactive polymer matrix are shown in Scheme II.

Here $A^*A...Q$ is a reactive pair site with at least one molecule of Q in its immediate vicinity; $A^*A...A$ is such a site without a quencher in its immediate surroundings. To determine the quantum yield of the solid-state photoreaction, one has to find the probability that the quantum proceeds by the pathway that eventually leads to intermolecular formation of A_2 (i.e., a cross-link) in competition with all the other possibilities. We shall now investigate the probabilities of the individual routes.

The probability of energy transfer from the excited sensitizer to a reactant molecule, rather than directly to a quencher, is given by eq 1 where [A] and [Q] are the

$$\frac{[A]}{[A]+[Q]} = \frac{1}{1+[Q]/[A]} \tag{1}$$

molar concentrations of reactant and quencher in the matrix. If the fraction of reactant molecules that are part of a potentially reactive pair is λ, then the probability that the excitation reaches such a site is given by the fraction

$$\frac{1}{1+[Q]/[A]}\lambda \tag{2}$$

The probability that the excited reactive site so formed is *not* quenched is the probability that there are exclusively A molecules in all the m sites that surround the potentially reactive pair A^*A. The number m is the mean coordination number of A in the matrix, i.e., the average number of molecules (either A or Q) in contact with one molecule of A. The probability that there is an A molecule at any site of the system, picked at random, is

$$\frac{1}{1+[Q]/[A]}$$

The probability that there is an A molecule in *every one* of the m sites surrounding the reactive site is

$$\left(\frac{1}{1+[\mathrm{Q}]/[\mathrm{A}]}\right)^{m} \tag{3}$$

One has now to consider the probability that the excitation does not find a reactive site on its first try but transfers to a nearby site. The probability that a quantum has reached a nonreactive site (A*) and is not quenched there is the probability of *not* having a Q molecule around A*. That probability is approximately[14]

$$\left(1 - n\frac{[\mathrm{Q}]}{[\mathrm{A}]}\right) \tag{4}$$

Whether this excitation quantum (that has *not* been quenched) will decay to the ground state or transfer to a neighboring site depends on the relative values of the rate of decay and the rate of energy transfer. The fraction of quanta taking the transfer route is given by

$$t = \frac{k_t}{k_t + k_d} = \frac{1}{1 + k_d/k_t} \tag{5}$$

The fraction decaying is

$$1 - t = \frac{k_d/k_t}{1 + k_d/k_t} \tag{5a}$$

where k_d and k_t are the rate constants for the two processes.

An equation for the quantum yield of cross-link formation in terms of the probabilities determined in eqs 1–5 can now be written. Consider first the case of a film where no quencher has been added and where therefore $[\mathrm{Q}] = 0$, $[\mathrm{Q}]/[\mathrm{A}] = 0$, and $\phi = \phi_0$. In these conditions the quantum yield ϕ_0 of the photoreaction is

$$\phi_0 = \lambda\gamma(1 + y + y^2 + y^3 + ...) \tag{6}$$

where γ is the mean reactivity of the reactive sites, i.e., the probability that an excited reactive site will produce a cross-link (an intermolecular dimer). The symbol y stands here for

$$y = (1 - \lambda)t$$

and eq 6 can be expressed in the more compact form[15]

$$\phi_0 = \frac{\lambda\gamma}{1 - (1 - \lambda)t} \tag{7}$$

Following the same argument and using the probabilities determined before, the quantum yield of cross-linking in the presence of a quencher Q becomes

$$\phi = \left(\frac{1}{1 + [\mathrm{Q}]/[\mathrm{A}]}\right)^{1+m} \frac{\lambda\gamma}{1 - (1 - \lambda)(1 - n[\mathrm{Q}]/[\mathrm{A}])t} \tag{8}$$

The ratio of quantum yields ϕ_0/ϕ can finally be written in the form of eq 9 or eq 9a

$$\frac{\phi_0}{\phi} = (1 + [\mathrm{Q}]/[\mathrm{A}])^{1+m}\left[1 + n\frac{1-\lambda}{\lambda + k_d/k_t}\frac{[\mathrm{Q}]}{[\mathrm{A}]}\right] \tag{9}$$

$$\frac{\phi_0}{\phi}(1 + [\mathrm{Q}]/[\mathrm{A}])^{-(1+m)} = 1 + nJ[\mathrm{Q}]/[\mathrm{A}] \tag{9a}$$

where J

$$J = \frac{1 - \lambda}{\lambda + k_d/k_t} \tag{10}$$

is the jump number. Equation 9a makes it possible to find the jump number J, i.e., the migration range, from the effect of the quencher concentration on the quantum yield ratio ϕ_0/ϕ.

Experimental Section

Materials. Polymers I–IV were prepared by the reaction of a single batch of poly(vinyl alcohol) (Elvanol 71-30, molecular weight M_w = 138 400–146 500; average 142 000) with various acid chlorides of the reactive chromophores. The amount of the acid chloride used led to 90% esterification of the hydroxyl groups. Pyridine was the reaction medium in all cases. The photopolymer was isolated by precipitation into water. All of the preparations were quite similar. An example follows.

Poly[vinyl 3-(1-naphthyl)acrylate]. Dry poly(vinyl alcohol) (PVA; 11 g, 100% hydrolyzed, 0.25 mol of OH) was suspended with stirring in 500 mL of dry pyridine. The reaction mixture was kept overnight under nitrogen at 70 °C. Prior to the addition of the acid chloride, the temperature was dropped to 50 °C. The reactions are quite exothermic, and if the temperature of the reacting solution rises much above 80 °C, it would lead to discoloration of the polymer.

1-Naphthylacryloyl chloride (19 g, 0.26 mol) was added to the reaction mixture as rapidly as the stirrer could mix it into the solution. The complex of pyridine with the acid chloride precipitated immediately but dissolved again with stirring. After stirring for 16 h at 60 °C, the contents were cooled to room temperature. Some of the pyridinium hydrochloride precipitated out and was removed by filtration. The color of the polymer can be lightened by diluting the pyridine solution with acetone before precipitation into water. This, however, was rarely needed if the temperature had been controlled during the reaction. Precipitation into highly sheared water gave a stringy, filmy precipitate, which eventually broke up into large flakes.

The water was removed and replaced several times in order to minimize traces of pyridine. A final rinse with methanol and water (1:1) gave a light-colored polymer, which was dried under reduced pressure with a nitrogen bleed at 45 °C. Except for mechanical losses, yields were quantitative.

3-(1-Naphthyl)acryloyl Chloride. A solution of 84 g of 1-naphthaldehyde and 130 g of malonic acid in 250 mL of dry pyridine was prepared. A total of 4 mL of piperidine was added as catalyst, and the reaction mixture was heated under reflux for 6 h. The product was isolated by pouring the reaction mixture onto 2 kg of an ice/water mixture containing 250 mL of HCl. The precipitate was collected, washed with water, and recrystallized from ethanol. The yield was 90 g (95%). The acid was converted to the acid chloride by treatment with thionyl chloride and DMF.

4-Ethyl(3-acryoyloxy)cinnamoyl Chloride. A total of 250 g of diethyl-1,4-bis(acryoyloxy)benzene was dissolved in 2500 mL of ethanol and the reaction mixture brought to reflux. Over an 8-h period 375 mL of a 10% solution of NaOH was added dropwise. The monoacid precipitated. When the addition was complete, the mixture was allowed to cool. The solid product was then collected and dried. It was dissolved in 8 L of distilled water, and any unreacted starting material was removed by filtration. The solution was acidified with HCl, whereupon the acid precipitated. The solid precipitate was washed with water and dried. Final purification was by Soxhlet extraction with toluene. The yield was 210 g (90%). The acid was converted to the acid chloride by treatment with thionyl chloride and dimethylformamide.

1,2-Diphenylcyclopropene-3-carbonyl Chloride. A total of 1 g of copper powder was added to 50 g (0.28 mol) of diphenylacetylene, and the mixture was heated in a reactor to 135 °C. Ethyl diazoacetate (16 g, 0.14 mol) was added slowly to the hot reactor contents. After the addition was complete, the mixture was heated for another 30 min and then allowed to cool. A solution of 30 g of KOH in 250 mL of methanol was added to the solid reaction mixture, and that was brought to reflux and kept there for another 30 min. After that, 500 mL of water was added and the aqueous mix extracted with cyclohexane. The brownish acid product was isolated by adding dilute HCl to the aqueous solution. Recrystallization from acetone/water produced 21.8 g (yield 65%) of the cyclopropenecarboxylic acid, which was converted to the acid chloride by treatment with thionyl chloride.

9,10-Bis(acetoxymethyl)anthracene (Q2). In a three-necked round-bottom flask 2.5 g (0.085 mol) of $NaBH_4$ was dissolved in 200 mL of methanol containing 5 mL of 5% aqueous NaOH. After that, 10 mL of dioxane was added to the warm solution. Subsequently, 5 g (0.021 mol) of anthracenedicarboxaldehyde was dissolved in 150 mL of dioxane. This was added to the first solution over a period of 45 min, and the solution was refluxed for another 1 h. After cooling, the solvent was distilled off and the residue digested in 1% aqueous NH_4Cl and filtered. The NMR spectrum of an aliquot showed complete conversion to the diol. The yield was 4.77 g (95%).

The diol, 4.71 g (0.02 mol), was dissolved in dry pyridine and cooled in an ice/water bath. After that, 15.7 (0.02 mol) of acetyl chloride was slowly added over a period of 15 min. The solvent was removed by distillation and the residue digested with 10% aqueous $NaCO_3$ and toluene. The toluene layer was then separated, washed with water, dried over $MgSO_4$, and filtered. Toluene was distilled off. The yield was 2.25 g (31%).

The polyester of *p*-phenylenediacrylic acid (polymer V) and the two sensitizers are commercial materials and were supplied by Eastman Kodak. Methyl pyrenebutyrate (Q1) was prepared by simple esterification of the commercially available acid (Aldrich).

Testing Procedures. Film casting: A total of 2 g of the polymer was dissolved in 100 mL of a 0.003 M cyclohexanone solution of the sensitizer. Varying amounts of the quencher were added to 10-mL aliquots of this mixture. The casting solution was then spin-coated (200 rpm for 1 min and then increasing gradually to 2000 rpm for 3 min) on anodized aluminum sheets (12 × 18 cm). The coatings were dried for 3 min in a stream of hot air (60 °C).

Exposures: Small pieces (1 × 2 cm) of the dry films were exposed to the radiation of a highly defocused superhigh-pressure mercury lamp (PEK). Balzer interference filters were used to isolate either the 405-nm or the 436-nm line of the mercury spectrum. The exposures were made through a step tablet (2-mm step width) with density increments of 0.15 units. A set of timed exposures was given to the films, and the exposed films were then tray developed in cyclohexanone for 1 min. The relative sensitivities of the quenched and the unquenched films were determined by matching the last three steps of the tablet. The ratio ϕ_0/ϕ is equal to the ratio of the exposure times required for films with and without added quencher to give the same number of developed steps.

Results and Discussion

The sensitizers and quenchers used in these experiments had to be chosen not only with the appropriate triplet levels but also with the correct absorption range so that the two would not compete for the incident radiation. Also, it was necessary that neither sensitizer nor quencher interact chemically with the reactive groups of the polymer. In preliminary experiments a range of sensitizers and quenchers was tried and eventually two sensitizers and two quenchers were selected for the final experiments. The biscoumarin sensitizer S2 with a triplet energy level of $E_T = 56.2$ kcal/mol was adequate for polymers II–V but not for polymer I where its triplet level was not quite high enough to ensure irreversible energy transfer to the cinnamoyl chromophores. The chlorothioxanthenone sensitizer S1 with a triplet energy of about 65 kcal/mol was effective with all our polymers. Regarding the quenchers used in this study, it was found that methyl pyrenebutyrate,[17] quencher Q1 with a triplet level of $E_T = 48$ kcal/mol, was well suited for polyvinyl cinnamate (polymer I), which has a triplet energy of 54.8 kcal/mol. As expected, Q1 did not act as an efficient quencher for the polymer II, since quencher and chromophore have approximately the same triplet energy. The anthracene derivative Q2, with a triplet energy similar to that of anthracene (42 kcal/mol)[18] was used for the other polymers (II–V). With polymer IV equal quenching efficiencies were achieved by using unsubstituted anthracene or Q2. However, anthracene reacted with the chromophore of the other polymers, being consumed during exposure by a Diels–Alder addition of the olefinic chromophore to triplet excited anthracene. This resulted in low apparent quenching efficiencies. In the case of the 9,10-disubstituted anthracene quencher Q2, the unwanted addition reaction is essentially suppressed.

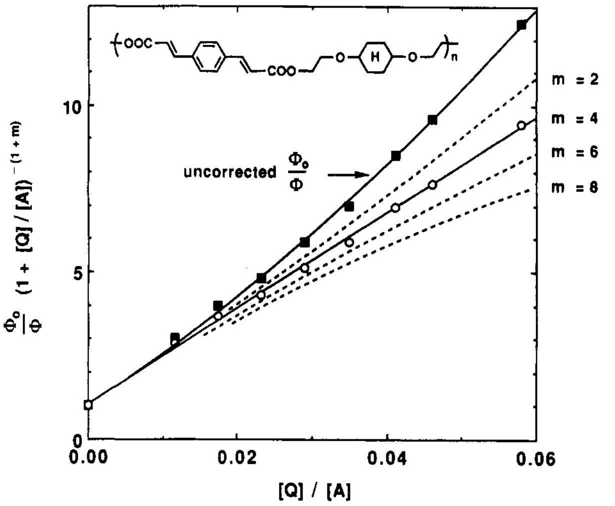


Figure 1. Plot of the quenching efficiency vs quencher to chromophore molar ratio [Q]/[A] for polymer V. The squares are the measured values of Φ_0/Φ; the circles are the corresponding values multiplied by $(1 + [Q]/[A])^{-(1+m)}$, where $m = 4$, which is the optimum value for a linear relationship (see text). The straight line is the least-square fit for the latter with an intercept of 1. The dashed lines correspond to least-square fits according to a quadratic equation using other values of m. The corresponding calculated points are not shown.

The immediate results of the quenching experiments are plots of the ratio ϕ_0/ϕ vs the quencher-to-chromophore ratio [Q]/[A], which show an upward curvature, as predicted by eq 9. To obtain values of J following eq 9a, a correction of the measured values of ϕ_0/ϕ is needed, and that requires knowledge of the coordination number m. On the basis of the molecular dimensions of the chromophores, m should lie between 2 and 6. An estimate of m can be obtained by plotting ϕ_0/ϕ values "corrected" according to eq 9a with various assumed values of m. As m increases, the upward curvature of the plots gradually decreases and eventually changes to a downward curvature. The value of m that yields a linear plot in this procedure is used as the average coordination number of the reactive chromophore. It can be seen in Figure 1 that the appropriate value of m for polymer V is 4, which also happens to be the correct number for polymers I–III. For the somewhat larger cyclopropene derivative IV, the value of m required to obtain a linear plot is 5 (see Figure 2).

The linear plots for the side-chain polymers I–IV, using $m = 4$, are shown in Figure 3. According to eq 9a, the slope of these plots is the product of the jump number, J, and the quencher coordination number, n. The latter is the number of chromophore moieties that on average surround a quencher molecule. Accordingly, the values of n should increase with increasing molecular dimensions of the quencher and with decreasing size of the photoreactive moiety A. Although n cannot be determined by direct experiment, an estimate of n can be obtained on the basis of the molecular dimensions of the components (cf. Table II) together with the values of m mentioned before. We realize that there is a probable error margin of about 20% associated with the estimate of n, which will lead to a similar error margin in the energy migration range. The

Table II
Triplet Migration Data for Solid Films of the Photoreactive Polymers I–V

polymer[a]	S_{rel}[b]	M_w[c]	Φ_0[d]	nJ[e]	n[f]	J[g]	λ[h]
I	(1.00)	150 000	(0.045)	23	4	6	~0.06–0.1
II	3.3	192 000	0.12	200	4	50	0.02
III	2.5	232 000	0.073	101	3.5	29	0.033
IV	17.5	223 000	0.53	345	3	115	0.0086
V	0.68	~21 000	• ~0.22	144	3.5	41	0.024

[a] In polymers I–IV poly(vinyl alcohol) was esterified to 90% with the acid chloride of the photoactive chromophore; 10% of the OH groups of the alcohol were left free. [b] S_{rel} is the photosensitivity of the polymers relative to that of polymer I. [c] Polystyrene-equivalent weight-average molecular weights of polymers I and V were determined by using size-exclusion chromatography in THF. The corresponding M_w for polymers II–IV were calculated from that of polymer I by correcting for differences in molecular weight of the reactive moieties. Accordingly, the ratio of the molecular weights of I–IV is much more accurate than the molecular weight ratios of the condensation polymer V to these side-chain-substituted polymers. [d] The absolute quantum yield for cross-linking of polymer I (0.045) has been determined earlier.[16] Absolute quantum yields for the other polymers were obtained from their sensitivities relative to polymer I (S_{rel}) and from their molecular weights: $(\Phi_0)_j = 0.045(S_{rel})_j(M_w)_I/(M_w)_j$. [e] nJ is the slope of the linear plots in Figures 1–3. [f] n is the estimate of the average coordination number of the quencher (see text). [g] J is the jump number of the excitation (migration range). [h] λ is the fraction of reactive sites in the matrix. For polymers II–V, $\lambda \approx 1/(1 + J)$, eq 10b. For polymer I, eq 10 was used to estimate λ; see text.

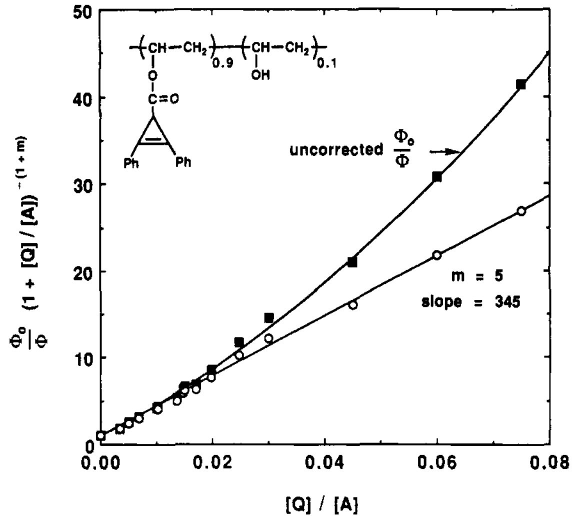


Figure 2. Plot of the quenching efficiency vs quencher to chromophore molar ratio [Q]/[A] for polymer IV. The squares are the measured values of Φ_0/Φ; the circles are the corresponding values multiplied by $(1 + [Q]/[A])^{-(1+m)}$, where $m = 5$, which is the optimum value for a linear relationship (see text). The straight line is the least-square fit for the latter with an intercept of 1.

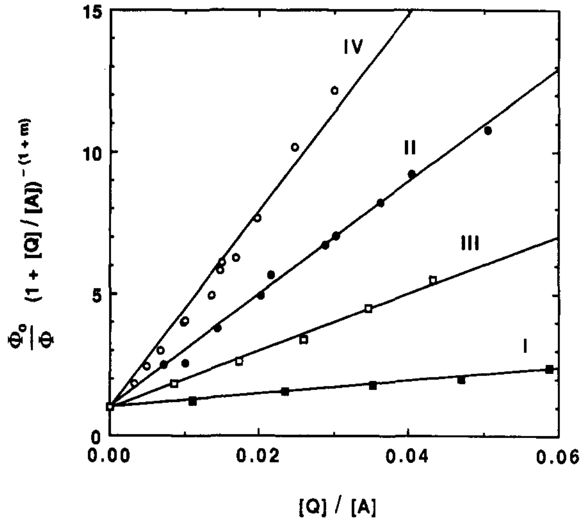


Figure 3. Plots of the quenching efficiency Φ_0/Φ multiplied by $(1 + [Q]/[A])^{-(1+m)}$, where $m = 4$ for polymers I–III and 5 for polymer IV (see text), vs quencher to chromophore molar ratio [Q]/[A]. The straight lines are the least-square fits with an intercept of 1. Points at [Q]/[A] higher than 0.04 for polymer IV (see Figure 2) are not shown here but were included in the determination of the linear fit.

J values derived in this way from the quenching data are listed in Table II together with other pertinent information on the solid polymer films, such as the quantum yield of cross-link formation and the weight-average molecular weight of the polymers.

According to eq 10, the jump number, J, is a function of the fraction of reactive sites, λ, and of the ratio of the rate constants for excitation decay and for transfer, k_d/k_t. When the latter term is very small compared to λ, eq 10 simplifies to eq 10a, and under these conditions the migration range J is controlled by the concentration of reactive sites.

$$J = (1 - \lambda)/\lambda \qquad (10a)$$

The reorganization energy associated with the hopping process (isoenergetic triplet excitation transfer) increases with increasing differences in nuclear configuration between the ground state and the triplet states of the chromophore A. As this reorganization energy increases, the rate constant of energy transfer, k_t, decreases. On the basis of the reorganization energies[12,13] of the chromophores used in the present work, the rate constants k_t are likely to be on the order of 10^9–$>10^{10}$ s^{-1}. For the chromophores of the polymers II–V, the values of k_d are on the order of 10^6–10^4 s^{-1} (see Table I). As a consequence, in these cases the ratio k_d/k_t is very small (0.001) compared to λ, and eq 10a is a valid approximation.

The exceptionally short lifetime of the triplet state of the cinnamoyl moiety makes polymer I a borderline case. Here k_d/k_t is comparable with the fraction of reactive sites λ, and eq 10 applies in its original form. The hopping frequency (k_t) in polymer I is estimated between 1×10^9 and 3×10^9 s^{-1}. The decay rate constant k_d ($=1/\tau$) is 10^8 s^{-1}, and consequently the ratio k_d/k_t lies between 0.1 and 0.033. From this and the value of the jump number, 6 (Table II), λ is estimated to be between 0.06 and 0.11. These values are similar to the fraction of reactive sites (0.1) found earlier in singlet-state experiments.

Quite generally, the data derived from triplet quenching are consistent with data from singlet-state excitation experiments. For example, in IV the fraction of reactive sites, λ, derived from the dependence of the singlet-state quantum yield on the degree of chromophore conversion (see ref 16 for details) is about 0.01. This value is very close to the fraction of reactive sites ($\lambda = 0.0086$) obtained from the triplet migration experiments of this work (Table II).

If the quantum yield, ϕ_0, of the photoreaction and the fraction of reactive sites, λ, are known, it is possible to estimate the average reactivity, γ, of the reactive sites from eq 7. In the absence of energy migration ($t = 0$), the quantum yield is the product of the fraction of reactive sites and the average site reactivity.

$$\phi_0 = \lambda\gamma \ (t = 0)$$

If, however, there is even a moderate degree of migration, t will tend to unity, and eq 7 will simplify to

$$\phi_0 = \gamma \ (t = 1)$$

Thus, for polymer IV the value of t approximates unity to better than 0.0001, and the values of t for polymers II–IV are greater than 0.993. Consequently, in these materials $\gamma = \phi_0$.

The value of γ measures the probability that a reactive site will form an intermolecular dimer on excitation (i.e., a cross-link in this case). There are conceivably three sources of energy wastage in the dimerization step.

(1) Certain sites may act as traps by virtue of the formation of low-energy excimers, which nonetheless are incapable of bond formation because of an unfavorable topography of the double bonds. The trapped quanta are excluded from further migration and yet do not lead to a cross-link.

(2) If topography permits, the reactive site will form a biradical on excitation. This may lead to cycloaddition, but the biradical may also fragment into two olefins and thus again waste the excitation energy.

(3) A reactive site may involve two chromophores on the same polymer chain. Reaction at this site would lead to an intramolecular dimer, which does not constitute a cross-link.

It is interesting to note that polymer IV, which has the lowest fraction of reactive sites λ, has the highest value of γ. The monomeric chromophore of this polymer has also a very high dimerization efficiency in a nonpolar fluid medium ($\alpha = 0.8$; see Table I). In general, the efficiency of cross-link formation in the polymeric matrix (γ) is lower than the dimerization efficiency in a fluid medium (α). This difference may be attributed to the restricted mobility in the matrix, which inhibits the proper orientation of the chromophores required for 2 + 2 cycloaddition. A further consideration is the formation of intramolecular dimers in the solid matrix. The latter process may be significant in polymer I where singlet-state experiments indicate the presence of a considerable fraction of intramolecular reactive pair sites.[19]

Summary

The data in Figures 1–3 and in Table II demonstrate the effect of triplet energy migration in photoreactive polymer films. The importance of the effect is clearly illustrated in polymer IV, which has the highest quantum yield of cross-link formation although the fraction of reactive sites in the system is less than 1%. What matters is that the excitation quantum encounters a reactive site sometime in its life and that this encounter leads to reaction. The probability of these events is maximized in systems with a large migration range.

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(14) The reason for using this approximation is to simplify the final kinetic equations.

(15) Equation 6 is the sum of all probabilities that an excitation quantum will, in one way or another, produce a cross-link. First, there is the reaction yield of those quanta that reach a reactive site directly. Their fraction is λ, and the probability that they will lead to cross-link formation is γ. Second, one has to count those quanta that reached a reactive site on their first transfer. Their fraction is $\lambda(1 - \lambda)t$, and the probability that they will lead to cross-linking is again γ. Further, one must count those quanta that reach a reactive site on their second transfer. Their fraction is $\lambda[(1 - \lambda)t]^2$, and their cross-linking probability is γ. The total probability over all quanta of producing a cross-link is the sum of all these terms up to infinity, as indicated in eq 6. The infinite sum can be represented by the well-known expression

$$1 + y + y^2 + y^3 + ... = 1/(1 - y)$$

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