Macromolecules 1991, *24*, 4600–4604

Reactant Preordering in Solid Polymer Matrices. 3. Triplet Sensitized Blends of Donor–Acceptor Substituted Poly(vinyl cinnamates)

Wei-Yu Huang, Anshyang A. Lin, and Arnost Reiser*

Institute of Imaging Sciences, Polytechnic University, Brooklyn, New York 11201

Received November 9, 1990; Revised Manuscript Received March 13, 1991

ABSTRACT: In blends of electron donor- and electron acceptor-substituted poly(vinyl cinnamates) triplet sensitization brings about a substantial increase in reaction efficiency. This effect is shown to be caused by triplet energy migration in the solid polymer films, which increases the encounter probability between excitation quanta and reactive sites. The migration range of triplet excitation correlates quite accurately with the increase in the effective quantum yield of the photoreaction. The migration range of the triplet excitation in the blends is smaller than in the component polymers, because in the blends the reactive sites are donor–acceptor complexes, which have lower excitation energies than the isolated reactants and which, therefore, act as energy traps. In the pure component polymers the reactive sites have the same energy as the isolated (unreactive) cinnamoyl groups and do not trap the excitation on its migration path.

In two earlier papers[1,2] we reported on the photoreactivity of electron donor- and electron acceptor-substituted poly(vinyl cinnamates). It was found that in those systems where the interaction between the reactant groups is sufficiently strong, the photosensitivity of donor–acceptor blends is significantly higher than that of the individual components. We have now measured the photoreactivity of these materials in the presence of triplet sensitizers and find that triplet sensitization enhances the photoreactivity of the blends even further. (This phenomenon was also noted, without comment, by Watanabe and Ichimura[10] in 1982.) The reasons for this behavior are investigated in the present article.

In systems with strong electron donor–electron acceptor interactions the sensitivity enhancement brought about by triplet sensitization is rather striking. Figures 1 and 2 show representative examples. They refer, respectively, to blends of *p*-chloro- and *p*-methoxy-substituted poly(vinyl cinnamates) (P-Cl/P-OCH$_3$) and to the corresponding blends P-3-Cl/P-3-OCH$_3$ where the cinnamoyl groups have been decoupled from the polyvinyl backbone by the intercalation of (CH$_2$)$_3$ spacers. The extend of the effect can be judged from the quantum yield data listed in Table I. The phenomenon is caused by differences in the singlet and in the triplet pathways of cross-link formation and can be traced in particular to the occurrence of energy migration in the sensitized systems.

Triplet vs Singlet Pathways of Cross-Link Formation

In unsensitized poly(vinyl cinnamate) films radiation is directly absorbed in the cinnamoyl groups, and it is known from earlier work[3,4] that in these circumstances the photoreaction originates in the singlet excited state of the reactant groups. In contrast, when sensitized films are exposed to 400-nm radiation, only the triplet excited state of the cinnamoyl groups is populated and the reaction follows a triplet pathway.

Cross-link formation by the singlet and by the triplet path differs in two respects:

(a) Photocycloaddition between a singlet excited cinnamoyl group and a similar group in the ground state occurs in a single (Woodward–Hoffman allowed) reaction step, while cycloaddition of a triplet excited molecule to a ground-state molecule is a two-step process. We have dealt with this aspect of photocycloaddition in ref 3.

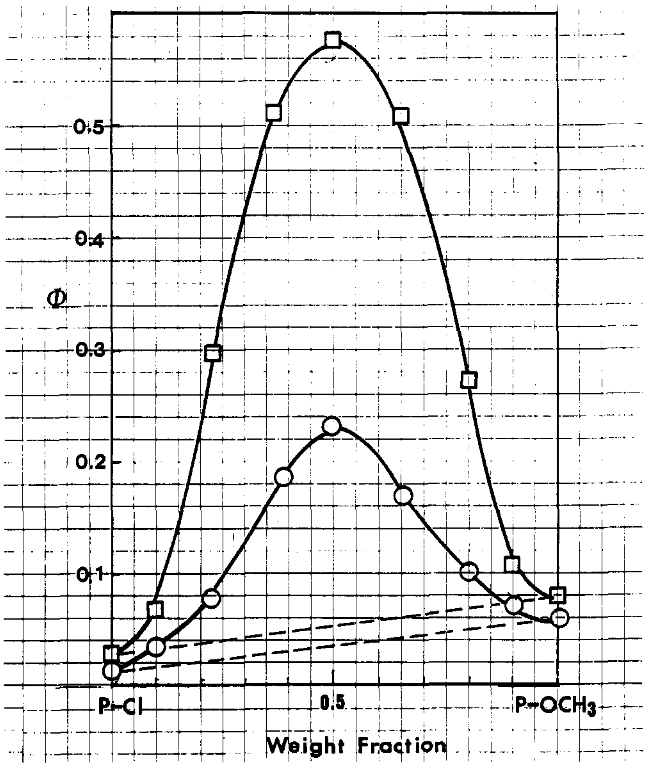


Figure 1. Quantum yield of cross-link formation in blends of *p*-chloro- and *p*-methoxy-substituted poly(vinyl cinnamates) P-Cl/P-OCH$_3$. ○, unsensitized, irradiated at 300 nm. □, sensitized with 6% 3,3′-carbonylbis(coumarin), irradiated at 400 nm.

(b) The triplet excited state of the cinnamoyl groups in common with that of most other chromophores has a longer lifetime than the singlet excited state. In model experiments with ethyl cinnamate, the lifetime of the triplet[12] was found to be τ_T = 10.3 ns in benzene solution, while the lifetime of the excited singlet state is shorter than 1 ns. The longer lifetime opens the possibility of triplet energy migration in the solid matrix, which increases the encounter probability between excitation quanta and reactive sites. Quite generally, energy migration tends to enhance the sensitivity of photoreactive systems. To assess the role of triplet migration in the sensitivity enhancement of poly(vinyl cinnamate) blends we have tried to demonstrate triplet migration in these systems by estimating

0024-9297/91/2224-4600$02.50/0

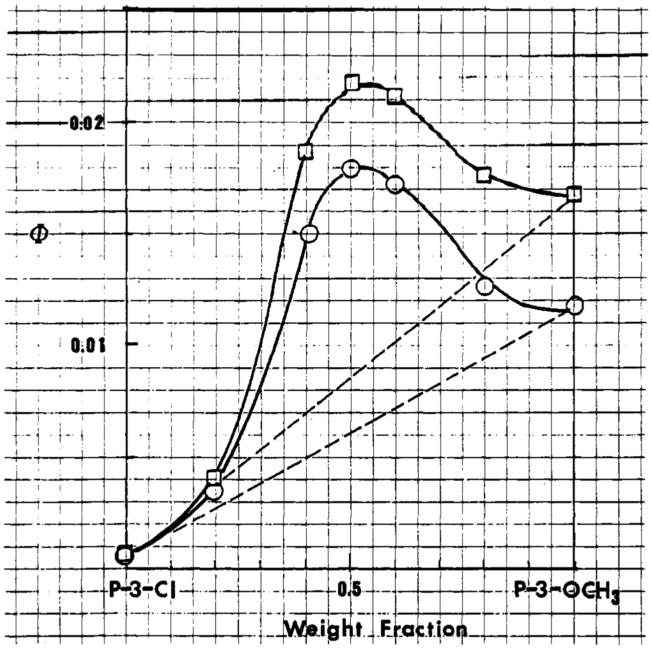


Figure 2. Quantum yield of cross-link formation in blends of two polymers having *p*-chloro- or *p*-methoxy-substituted cinnamoyl groups attached to a polyvinyl backbone by $(CH_2)_3$ spacers. ○, unsensitized, irradiated at 300 nm. □, sensitized with 6% 3,3'-carbonylbis(coumarin), irradiated at 400 nm.

Table I
Quantum Yields of Cross-Link Formation and Related Data[a]

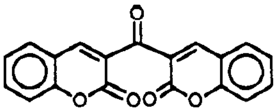
	ϵ	m	M_w	t_G, s	Φ
with 6% Sensitizer, Exposed at 400 nm					
$P\text{-}OCH_3/P\text{-}Cl$					
100:0	16 510	0.168	347 000	15.2	0.079
50:50	16 510	0.168	300 900	2.39	0.58
0:100	16 510	0.168	254 800	30.3	0.025
$P\text{-}3\text{-}OCH_3/P\text{-}3\text{-}Cl$					
100:0	16 510	0.168	334 800	35.1	0.017
50:50	16 510	0.168	319 600	28.5	0.022
0:100	16 510	0.168	304 400	780	0.0008
without Sensitizer, Exposed at 300 nm					
$P\text{-}OCH_3/P\text{-}Cl$					
100:0	23 150	4.95	347 000	2.55	0.080
50:50	21 260	4.88	300 900	1.08	0.23
0:100	19 380	4.80	254 800	16.2	0.020
$P\text{-}3\text{-}OCH_3/P\text{-}3\text{-}Cl$					
100:0	19 480	3.80	334 800	5.6	0.012
50:50	16 400	3.78	319 600	4.5	0.018
0:100	13 330	3.75	304 400	104.8	0.001

[a] ϵ and m are the molar extinction coefficient and the molarity of sensitizer. M_w is the weight-average molecular weight of the polymer. t_G is the gel point exposure time.

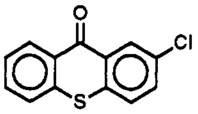
the migration range of the excitation.

Triplet Energy Migration

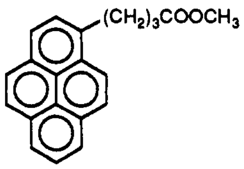
A method was described recently[13] whereby the range of energy migration in a photoreactive polymer can be estimated from the effect of triplet quenchers (energy scavengers) on the quantum yield of the photoreaction. The migration range of the excitation can be defined as the number, J, of transfer steps (jumps) that the excitation quanta undergo on average during their lifetime. The "jump number" J is obtained experimentally by adding increasing quantities of a triplet quencher to a triplet sensitized polymer film and monitoring the effect of the quencher concentration on the quantum yield of the photoreaction. Such experiments were carried out on substituted poly(vinyl cinnamate) blends by exposing solid films of these materials to 400-nm radiation which is only absorbed by the sensitizer. A bis(ketocoumarin),[5] 3,3'-carbonylbis(coumarin), E_T = 57.9 kcal/mol



and 2-chlorothioxanthone were used as sensitizers. The triplet energy of 2-chlorothioxanthone is assumed to be similar to that of thioxanthone, E_T = 65 kcal/mol.



Methyl 4-pyrenebutyrate, with a triplet level similar to that of pyrene,[6] E_T = 48 kcal/mol, was chosen as triplet quencher.



It was shown in ref 13 that the effect of the triplet quencher on the quantum yield of the photoreaction can be described quantitatively by the following expression.

$$\frac{\Phi_0}{\Phi} = \left(1 + \frac{[Q]}{[A]}\right)^{m+1}\left[1 + nJ\frac{[Q]}{[A]}\right] \qquad (1)$$

Here Φ_0 and Φ are, respectively, the quantum yield of the photoreaction in the absence and in the presence of quencher, [Q] and [A] are the molar concentrations of the quencher and of the reactant (cinnamoyl group) in the film, and m is the mean coordination number of the reactant groups in the matrix, i.e., the average number of molecules, reactants or quenchers, surrounding a reactant as nearest neighbors. The constant n is the corresponding average coordination number of the quencher in the system. The derivation of eq 1 can be found in ref 13.

To extract the jump number J from the experimental data, the expression

$$(\Phi_0/\Phi)(1 + [Q]/[A])^{-(m+1)}$$

is plotted as a function of the molar ratio of quencher and reactant, [Q]/[A]. The resulting plot is linear, and the jump number J is obtained from the slope of the straight line together with a knowledge of the coordination number n. Figure 3 shows such linear plots for the *p*-chloro- and the *p*-methoxy-substituted poly(vinyl cinnamates), P-Cl and $P\text{-}OCH_3$, and their 50:50 blend $P\text{-}Cl/P\text{-}OCH_3$; Figure 4 refers to the spacer polymers P-3-Cl and $P\text{-}3\text{-}OCH_3$ and their 50:50 blend $P\text{-}3\text{-}Cl/P\text{-}3\text{-}OCH_3$. The jump numbers obtained from these data are listed in Table II.

Experimental Section

The synthesis of the substituted poly(vinyl cinnamates) was described earlier.[1,2] The sensitizers and the quencher were supplied by the Kodak Research Laboratories and were used as received. Triplet sensitizer, 3–6% by weight of the polymer, was added to the 0.3% coating solutions in dichlorethane, and films were coated onto quartz plates. The dry films were prebaked at 90 °C for 45 min and then exposed through the quartz support[7] to 400-nm radiation from a Bausch and Lomb high-intensity monochromator coupled to a xenon lamp. The intensity of the

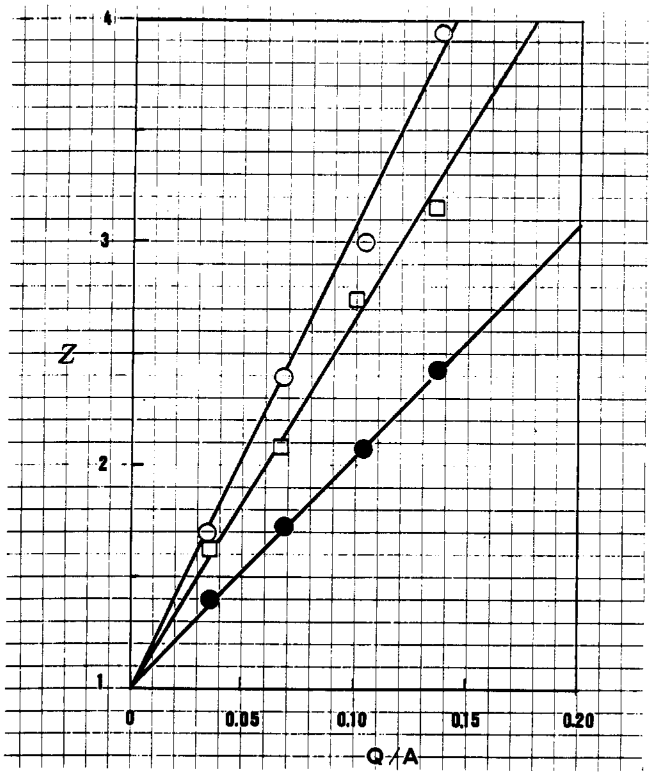


Figure 3. Plot of the corrected quantum yield ratio $Z = (\Phi_0/\Phi)(1 + [Q]/[A])^{-(m+1)}$ against the quencher-to-reactant ratio [Q]/[A]. ○, *p*-chloro-substituted poly(vinyl cinnamate). □, *p*-methoxy-substituted poly(vinyl cinnamate). ●, 50:50 blend of P-Cl/P-OCH$_3$.

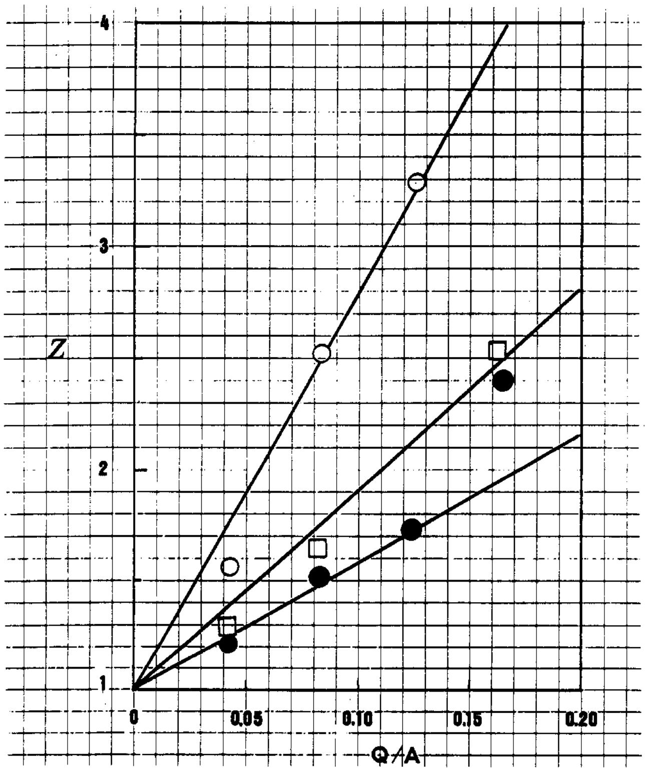


Figure 4. Plot of the corrected quantum yield ratio $Z = (\Phi_0/\Phi)(1 + [Q]/[A])^{-(m+1)}$ against the quencher-to-reactant ratio [Q]/[A]. ○, polymer with *p*-chloro-substituted cinnamoyl groups attached to a polyvinyl backbone by (CH$_2$)$_3$ spacers. □, polymer with *p*-methoxy-substituted cinnamoyl groups attached to a polyvinyl backbone by (CH$_2$)$_3$ spacers. ●, 50:50 blend of P-3-Cl/P-3-OCH$_3$.

Table II
Triplet Migration Data

polymer system	slope of plot from eq 1	*J*
P-OCH$_3$	17	4.3
P-Cl	21	5.3
P-Cl/P-OCH$_3$, 50:50	10.5	2.6
P-3-OCH$_3$	9	2.25
P-3-Cl	18	4.5
P-3-Cl/P-3-OCH$_3$, 50:50	5.9	1.5

irradiating beam was determined by ferrioxalate actinometry.[8] After exposure, the films were postbaked at 90 °C for 20 min and developed by immersion in a 7:3 mixture of dichlorethane and heptane. This mixture dissolves those parts of the film that have not been cross-linked in the photoreaction. The critical gel point exposure, E_G, which is a measure of the sensitivity of the system, is defined as that exposure dose producing the first clearly visible image on the exposed and developed plates. The quantum yield of cross-link formation, Φ, can be calculated from the gel point exposure by the expression[9]

$$\Phi = 1/(2.303\epsilon m M_w E_G) \qquad (2)$$

where M_w is the weight-average molecular weight of the polymer before cross-linking, ϵ and m are the molar extinction coefficient and the molarity of the sensitizer in the solid polymer film, and E_G is the gel point exposure dose (gel dose) in einstein per centimeter squared.

Results and Discussion

The results of quantum yield determinations on blends of the polymer pairs P-Cl/P-OCH$_3$ and P-3-Cl/P-3-OCH$_3$ are shown in Figures 1 and 2. The spacer polymers have in general lower sensitivities than the simple poly(vinyl cinnamates) and that aspect has been dealt with in ref 2. It can be seen from the summary in Table II, that in neither system is triplet migration wide-ranging, but from the point of view of the photographic sensitivity of the materials it is nontheless significant.

It may be assumed that the jump number *J* is the factor by which the reaction probability is increased in systems where energy migration does occur. The migration range is indeed quite accurately reflected in the ratio of the quantum yields of sensitized and unsensitized systems. For the chloro- and methoxy-substituted polymers the ratio of the quantum yields of the sensitized and the unsensitized 50:50 blend is

$$\Phi_T/\Phi_S = 0.58/0.23 = 2.52$$

while the migration range (jump number) for this system is $J = 2.6$.

The quantum yield ratio for the 50:50 blend of the corresponding spacer polymers is

$$\Phi_T/\Phi_S = 0.022/0.018 = 1.22$$

and the migration range for this system is $J = 1.45$.

Two further aspects of the data in Table II require comment:

(a) The migration range in the spacer polymers and their blend is lower than in the nonspacer system. That, we believe, is the result of the dilution of cinnamoyl groups brought about by the presence of the spacers. Triplet transfer requires the close proximity of the groups between which energy is to be exchanged, and the probability of this decreases in the more dilute systems.

(b) The migration range measured in the blends is in both systems significantly lower than in the individual polymeric components. In the search for a distinction between the blends and the component polymers it is noted (see ref 1) that in the blends most reactive sites are pairs of one donor-substituted group and one acceptor-substituted cinnamoyl group, while in the component polymers the reactive sites are pairs of identical reactants. The mixed pairs are by their nature electron donor–electron acceptor complexes and as such have lower excitation energies than single cinnamoyl groups. The reactive sites represent therefore energy traps in the ensemble of sites. When the excitation quantum encounters a trapping site, its migration ends then and there, irrespective of whether the reaction actually occurs at the site or not. At the nontrapping reactive sites of the component polymers the situation is different; here the excitation can either induce the reaction or be thermally deactivated, but it may also continue on its migration path by transferring to a neighboring cinnamoyl group. As a result, the migration statistics in trapping and in nontrapping systems are slightly different.

Energy Migration in Systems of Trapping and Nontrapping Sites. It was shown in ref 13 that in systems where energy migration does occur, the quantum yield of a solid-state photoreaction can be described by the expression

$$\Phi_0 = \lambda\gamma/(1-y) \tag{3}$$

Here λ is the fraction of reactive sites in the ensemble and γ is the probability that the reaction takes place on excitation of the reactive site. The quantity y is defined (see ref 13) as

$$y = (1-\gamma)t \tag{4}$$

where t, the probability of energy transfer between sites, is determined by the average rate of energy transfer, k_t, and the rate, k_d, of deactivation of the excited state.

$$t = k_t/(k_t + k_d) \tag{5}$$

In these terms, the ratio of the quantum yields in the absence and in the presence of a triplet quencher Q may be expressed in the form

$$\frac{\Phi_0}{\Phi} = \left(1 + \frac{[Q]}{[A]}\right)^{m+1}\left[1 + \frac{y}{1-y}n\frac{[Q]}{[A]}\right] \tag{6}$$

A comparison of (6) with (1) shows that the ratio $y/(1-y)$ represents the jump number (migration range) of the excitation.

$$J = y/(1-y) \tag{7}$$

The difference between trapping and nontrapping systems is that in the former energy transfer can occur only from unreactive (isolated) sites, but not from reactive (trapping) sites. However, if the reactive sites are nontrapping, there is a finite transfer probability even from the reactive sites to nonreactive sites. This transfer probability is given by

$$t' = k_t/(k_t + k_d + k_r) \tag{8}$$

where k_r is the rate constant of the reaction at the reactive site.

The quantity y in a trapping system counts the chances that an excitation quantum arrives at a reactive site from a nonreactive site. In a system with nontrapping reactive sites, excitation quanta can also be transferred into the migration network from reactive sites. The total probability of furnishing an excitation quantum to a reactive site is now given by the expanded expression

$$y' = (1-\lambda)t + \lambda t' \tag{9}$$

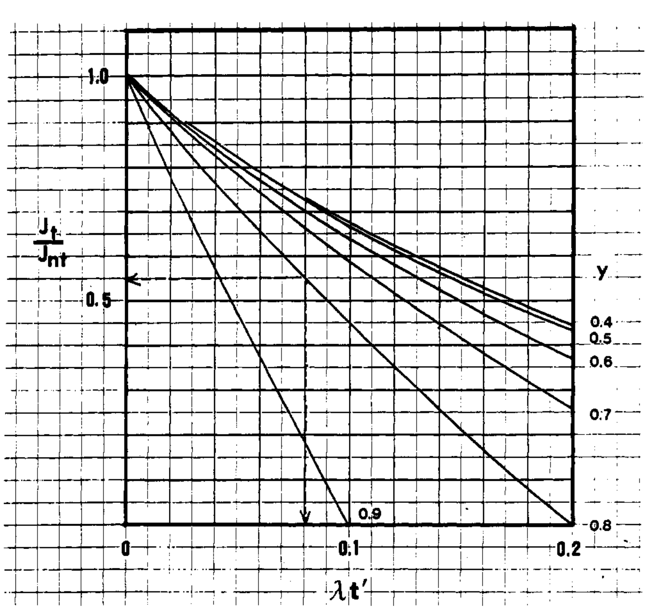


Figure 5. Ratio of migration ranges between systems with trapping and with nontrapping reactive sites, J_t/J_{nt}, plotted for a few values of $y = (1-\lambda)t$ and a range of values of $\lambda t'$. Here λ is the fraction of reactive sites, t is the probability of energy transfer between nonreactive sites, and t' is the probability of energy transfer from a nontrapping reactive site to any other site.

As a result, the ratio of the jump numbers in two systems, one with trapping and the other with nontrapping reactive sites, but which in all other respects are identical, takes the form

$$\frac{J_t}{J_{nt}} = \frac{y}{y'}\frac{1-y'}{1-y} = \frac{y}{y+\lambda t'}\frac{1-y-\lambda t'}{1-y} \tag{10}$$

Since by definition $\lambda t'$ is positive, the ratio of the jump numbers in trapping and nontrapping systems is always smaller than unity.

To visualize the size of the trapping effect, the ratio J_t/J_{nt} is plotted in Figure 5 for a few values of y and a range of values of $\lambda t'$. If the reduced migration range in the blends is caused by energy trapping, the ratio of the experimentally determined jump numbers should correlate with the ratio J_t/J_{nt} of eq 10, provided that plausible values for y and for $\lambda t'$ can be introduced. To test this hypothesis we note that the fraction of reactive sites in poly(vinyl cinnamate) was estimated earlier[1] as $\lambda = 0.1$, and that the probability of energy transfer[13] in this system was estimated as $t = 0.9$. With use of eq 4, this leads to $y = 0.8$. The probability of energy transfer in the corresponding trapping system is expected to be somewhat smaller and is estimated at $t' = 0.8$. With these values the expected reduction in migration range in going from a nontrapping to a trapping poly(vinyl cinnamate) system can be read off the curve for $y = 0.8$ at a value of $\lambda t' = 0.08$ in Figure 5. It is found as $J_t/J_{nt} = 0.55$. This value is in good agreement with the ratio between the experimentally determined migration range in the blend P-Cl/P-OCH_3 and the average migration range in the component polymers, which represents the ratio of the jump numbers in trapping and nontrapping poly(vinyl cinnamate).

$$\frac{J(\text{blend})}{J(\text{av of components})} = \frac{2.6}{4.65} = 0.56$$

In the blend of the spacer polymers P-3-Cl/P-3-OCH_3, the fraction of reactive sites is expected to be smaller than in the simple poly(vinyl cinnamates) and the transfer probability from reactive to unreactive sites somewhat lower. This increases the value of y and somewhat lowers the value of $\lambda t'$. As a result the ratio of the trapping and nontrapping migration ranges J_t/J_{nt} is expected to be lower than in blends of nonspacer polymers. That expectation is fulfilled; the experimentally determined ratio in the spacer polymers is

$$J_t/J_{nt} = 0.44$$

Conclusions

Triplet sensitization increases the photoreactivity of blends of electron donor- and electron acceptor-substituted poly(vinyl cinnamates). This effect is caused by energy migration, which increases the encounter probability between excitation quanta and reactive sites. In blends where donor–acceptor interactions between reactants are strong, the observed sensitivity increases correlate quite accurately with the migration range of triplet excitation.

The range of triplet energy migration in the blends is smaller than in the component polymers, and this effect can be traced to the fact that in donor–acceptor blends the reactive sites have the character of electron donor–electron acceptor complexes. These reactive sites have lower excitaton energies than isolated cinnamoyl groups and act therefore as energy traps in the system. In the pure components, where the reactive sites are constituted from identical groups, energy trapping does not occur. The differences in the statistics of energy migration in systems with trapping and with nontrapping reactive sites have been considered.

Acknowledgment. We are grateful to the Office of Naval Research and to the National Science Foundation for financial support of this project.

References and Notes

(1) Lin, A. A.; Reiser, A. *Macromolecules* **1989**, *22*, 3898.
(2) Lin, A. A.; Chu, C.-F.; Reiser, A. *Macromolecules* **1990**, *23*, 3611.
(3) Reiser, A.; Egerton, P. L. *Photogr. Sci. Eng.* **1979**, *23*, 144.
(4) Egerton, P. L.; Pitts, E.; Reiser, A. *Macromolecules* **1981**, *14*, 95.
(5) Specht, D. P.; Martic, P. A.; Farid, S. *Tetrahedron* **1982**, *38*, 1203.
(6) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA 1978; p 357.
(7) Parham, N. J. H.; Pitts, E.; Reiser, A. *Photogr. Sci. Eng.* **1977**, *21*, 145.
(8) Kurien, K. C. *J. Chem. Soc. B* **1971**, 2081.
(9) Reiser, A.; Pitts, E. *J. Photogr. Sci.* **1981**, *29*, 187.
(10) Watanabe, S.; Ichimura, K. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3261.
(11) Shankoff, T. A.; Trozzolo, A. M. *Photogr. Sci. Eng.* **1975**, *19*, 173.
(12) Herkstroeter, W. G.; Farid, S. *J. Photochem.* **1986**, *35*, 71.
(13) Farid, S.; Moody, R. E.; Daly, R. C.; Huang, W.-Y.; Reiser, A. *Macromolecules*, in press.