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Reactant Preordering in Solid Polymer Matrices. 2. Effect of Decoupling the Reactant Groups from the Polymer Backbone

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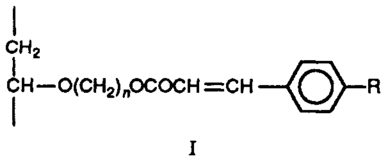
ABSTRACT: In blends of electron donor and electron acceptor substituted poly(vinyl cinnamates) a significant enhancement of photosensitivity over the mean of the sensitivities of the pure components was reported earlier.[1] In this paper the effect of decoupling the cinnamoyl groups from the polyvinyl backbone is investigated. It is found that the dilution of the reactive moieties that accompanies the introduction of spacers has a stronger effect on photosensitivity than the decoupling of the side-chain reactants. This is interpreted as a lowering of the probability of pair formation between groups belonging to different polymer chains. The shape of the quantum yield vs composition curves and other observations indicate a partial persistence of the coil structure of the individual components in the blends and the imperfect intermingling of the side chains of different backbones. The stabilization energies of the polymer-bound donor-acceptor complexes that are the source of enhanced photosensitivity were found from the effect of casting temperature on the quantum yield of cross-link formation. For blends of Cl- and CH_3O-substituted polymers these stabilization energies are 3.2 and 7.7 kcal/mol for nonspacer and spacer polymers, respectively.

In an earlier paper[1] we described the effect of electron donor-acceptor interactions on the photosensitivity of blends of substituted poly(vinyl cinnamates). In approximately equimolar mixtures of donor-substituted with acceptor-substituted poly(vinyl cinnamates) a significant enhancement of the quantum yield of intermolecular cross-link formation was observed, while the overall quantum yield of the photoreaction, which measures the formation of intermolecular as well as intramolecular links, was not increased. This means that, contrary to expectation, the photoreactivity of the blends is enhanced not by an increase in the overall number of reactive sites but by the exchange of intramolecular links for intermolecular cross-links between groups belonging to different polymer chains.

In the individual polymers as distinct from blends, intramolecular links account on average for 80% of all photoproducts, the balance between inter- and intramolecular links being determined by the equilibrium distribution of backbone conformations in the system. We have taken this to mean that the polymer backbone is the dominant factor that determines the number of side-chain pairings in these systems.

In light of these observations it was thought of interest to investigate polymers where the functional groups are mechanically decoupled from the backbone. To explore this point, polymers of the type I were prepared, their absorption spectra were measured, and their photosensitivity was determined.[5] In I *n* is either 3 or 6 and R stands for the donor or acceptor substituents CH_3O, CH_3, H, Cl, and NC.



I

Experimental Section

Polymers where the reactant groups are decoupled from the backbone by aliphatic spacers were prepared as follows.[3,4] A 159-g sample of a grade of poly(vinyl alcohol) obtained from Eastman Kodak (MW = 66 000) was dissolved in anhydrous DMSO and treated with methylsulfinyl carbanions in the absence of oxygen (nitrogen atmosphere) under anhydrous conditions.[5] The carbanion solution was prepared by reacting sodium hydride (NaH, 8.4 g) with anhydrous DMSO. This solution was added dropwise to the solution of poly(vinyl alcohol) mentioned earlier. After the reaction was complete, 0.30 mol of the spacer unit, either 3-bromo-1-propanol or 6-bromo-1-hexanol, was poured quickly into the metalated poly(vinyl alcohol) solution. A precipitate was formed which redissolved after a while to a clear viscous dope. The polymer was precipitated into acetone, dried under vacuum overnight at 50 °C, and redissolved in solvent (distilled water for the 3-bromo-1-propanol system, DMF for the 6-bromo-1-hexanol system). The polymer was again precipitated and finally vacuum-dried at 50 °C. The degree of alkylation was determined by ^{13}C NMR spectroscopy with 2,4-pentanediol and dipropylene glycol as model compounds for calibration. It was found that 72.2% of the OH groups are substituted with spacers, leaving 27.8% of the hydroxyl groups of poly(vinyl alcohol) unsubstituted. Figure 1 shows the ^{13}C NMR spectrum of the spacer-substituted polymer from which these data were obtained.[8]

The vacuum-dried polymers were finally reacted in dry pyridine with an excess of the corresponding cinnamoyl chloride. The overall synthetic route is indicated in Scheme I. The average degree of substitution of both the spacer and the nonspacer positions on the backbone was found from the UV absorption spectrum of the polymer, calibrated with the ethyl esters of the appropriate substituted cinnamic acids.[1] The data are listed for all polymers of this study in Table I.

Films of the polymers were cast on quartz plates from solutions in 1,2-dichloroethane or 3:7 1,2-dichloroethane/1-methyl-2-pyrrolidone, prebaked at ca. 90 °C for 30 min and then exposed to radiation from a high-intensity monochromator. Development was in 1,2-dichloroethane/hexane mixtures. The compatibility of the component polymers in the films was tested by DSC. Those systems where a single glass transition was observed (such as the system P-Cl/P-CH_3 in Figure 2) were considered compatible true blends. Systems where two separate glass transitions persisted, e.g., the system P-OCH_3/P-3-CN shown on the right-hand side of Figure 2, were not investigated further. A detailed account of the glass transition behavior of these blends and mixtures can be found in ref 2.

The overall quantum yield ϕ_0 of the photoreaction and the quantum yield Φ of intermolecular cross-link formation in the solid films were determined respectively by monitoring the evolution of the absorption spectrum during irradiation and from the gel point radiation dose. The films were exposed to 300-

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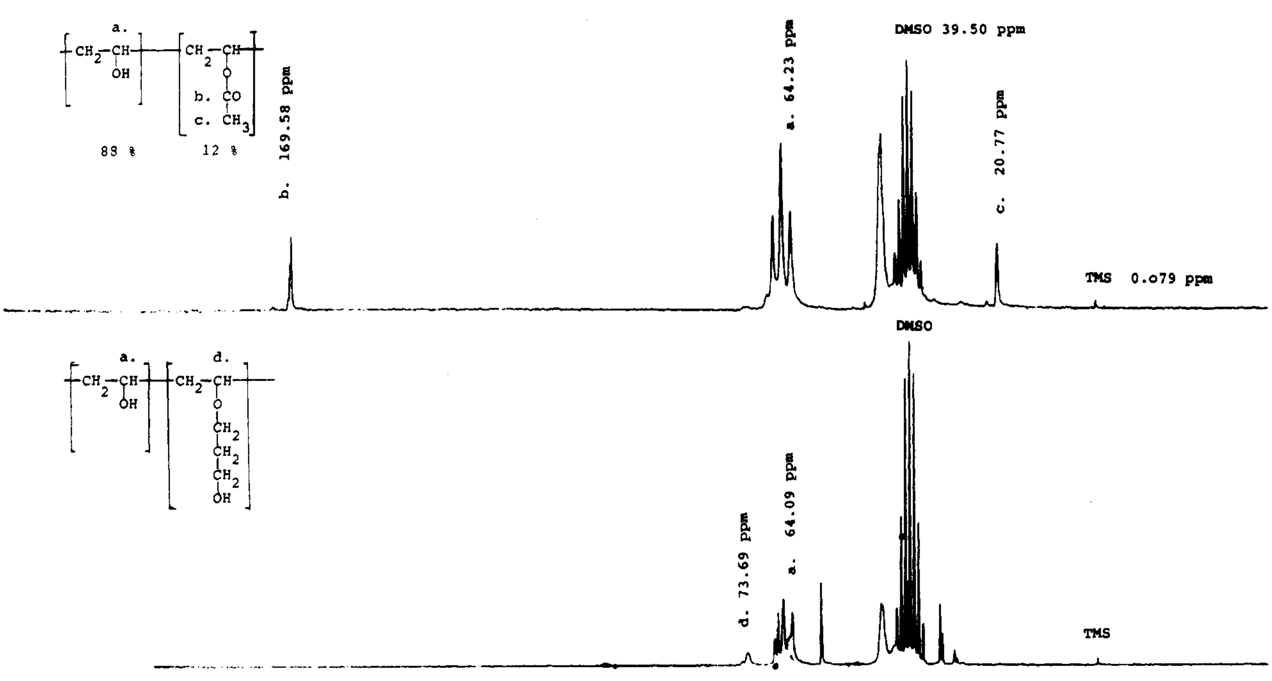


Figure 1. Carbon-13 NMR spectra of vinyl alcohol (88%)–vinyl acetate (12%) copolymer and of this polymer substituted (72%) with $(CH_2)_3OH$. DMSO-d_6 solvent external TMS, room temperature, concentration 10%. Single pulse, 25 μs, repetition 10 000 s, acquisition time 0.679 s, spectral width 6024 Hz. Chemical shifts in ppm.

Scheme I

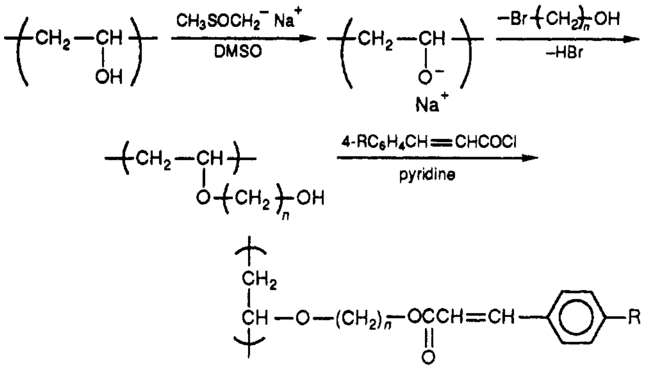


Table I
Average Degree of Substitution by Cinnamoyl Groups

polymer	deg of subst by cinnamoyl groups, %	free OH, %
P-3-OCH_3	85.6	14.4
P-3-CH_3	94.9	5.1
P-3-H	96.9	3.1
P-3-Cl	76.4	23.3
P-3-CN	99.0	1.0

Table II
Overall Quantum Yield ϕ_0, Quantum Yield of Intermolecular Cross-Link Formation Φ, and Fraction of Intramolecular Links Formed by the Photoreaction

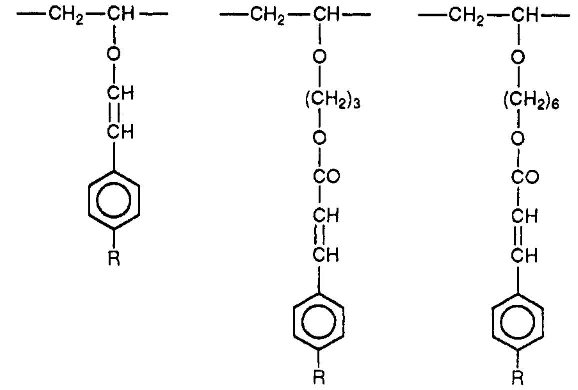
subst	ϕ_0		Φ		$1-\Phi/\phi_0$	
	$n = 0$	$n = 3$	$n = 0$	$n = 3$	$n = 0$	$n = 3$
CH_3O	0.39	0.24	0.08	0.010	0.79	0.96
CH_3	0.31	0.17	0.21	0.031	0.32	0.82
H	0.28	0.14	0.18	0.012	0.35	0.92
Cl	0.25	0.064	0.020	0.0010	0.92	0.99
NC	0.30	0.19	0.031	0.0023	0.89	0.99

nm radiation from a Bausch and Lomb xenon lamp and monochromator combination. The procedures have been described earlier[1] in some detail.

Results and Discussion

Effect of Spacers on the Reactivity of the Component Polymers. The overall quantum yield of the photoreaction between cinnamoyl groups in the system and the quantum yield of intermolecular cross-link formation are listed for the pure components in Table II both for the polymers without spacers ($n = 0$) and for the polymers with spacers ($n = 3$). Two features are immediately apparent: The quantum yields in the spacer polymers are substantially lower, and the fraction of intramolecular links is substantially higher.

The lowering of the values of ϕ_0 is not unexpected since the introduction of spacers dilutes the concentration of reactive moieties in the system and lowers the probability of encounter between the two reactants (cinnamoyl groups) that are needed for the formation of a cross-link. One can estimate the degree of dilution brought about by the introduction of spacers by considering the relative volume of the reactive moiety in the monomer unit, as indicated below.



If the grouping COCH=CHC is identified as the reactive moiety, its volume fraction in the system is approximately 4/10 in poly(vinyl cinnamate), 4/14 in the polymer with a three-membered spacer, and 4/17 in the polymer with a six-membered spacer. From the volume fraction, v, of the reactive moieties the probabilities of pair formation are obtained in a crude approximation as the square of the volume fraction, v^2. Volume fractions, pair formation probabilities, and overall quantum yields ϕ_0 are listed in

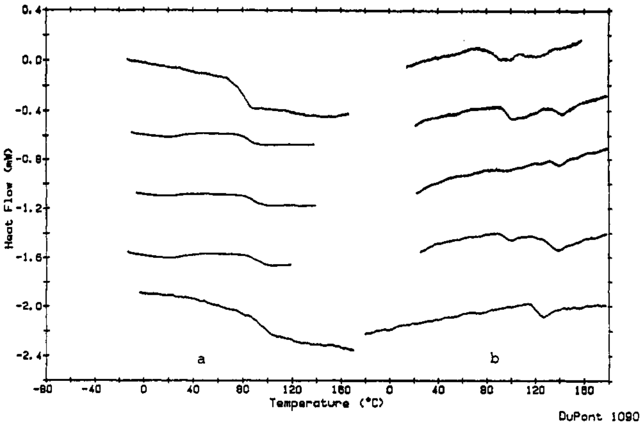


Figure 2. DSC curves for the systems P-CH_3/P-Cl (a) and P-OCH_3/P-3-CN (b). Mixture compositions from top to bottom: P-CH_3/P-Cl and P-OCH_3/P-3-CH, 100/0, 70/30, 50/50, 30/70, 0/100.

Table III for three *p*-methoxy-substituted polymers that differ only in the size of the spacers. It can be seen in the data of Table III that the decrease in the overall quantum yield of the bimolecular photoreaction can be accounted for almost quantitatively by the dilution effect of the spacers. Thus, decoupling of the reactants groups from the polymer backbone does not produce the hoped for overall increase in the reaction probability between cinnamoyl groups.

The high fraction of intramolecular links in the spacer polymers (Table II) reflects a large decrease in the number of intermolecular pairings. In fact, the probability of pair formation between two groups belonging to different chains is significantly lower than expected on the basis of a simple dilution effect. This indicates a persistence in the intramolecular interaction of the functional groups of individual chains and a less than random intermingling of the side chains of different backbones. This lack of complete dispersion of the two species in each other is reflected also in other observations described later in this paper.

Effect of Spacers on the Reactivity of Blends. The overall quantum yield ϕ_0 of the photoreaction in the blends is in all cases a linear function of blend composition. This means that on introduction of spacers the overall quantum yield ϕ_0 decreases in accordance with the above-mentioned dilution effect of the spacers. In contrast, the quantum yield of intermolecular cross-link formation Φ is affected more significantly. This is illustrated in Figure 3, where the quantum yields ϕ_0 and Φ are plotted as a function of blend composition for the blends P-OCH_3/P-Cl and P-3-OCH_3/P-3-Cl. While in the blends of nonspacer polymers over 80% of all links are intramolecular at the sensitivity maximum, in the corresponding blends of spacer polymers the fraction of intramolecular links is increased to over 90% (Table II). We believe that this is again an indication of the partial persistence of the secondary structure of the individual polymer coils, which leads to imperfect intermingling of the side chains of different backbones.

The quantum yield of intermolecular cross-link formation, Φ, which determines the efficiency of photoinsolubilization, is plotted as a function of blend composition in Figure 4. It has a maximum (or minimum) near a composition where both components are present in similar quantities.

The change $\Delta\Phi$ is a measure of the enhancement in photographic sensitivity brought about by donor-acceptor interactions in the system. The degree of enhancement depends on the strength of the donor-

Table III
Volume Fraction of Reactive Moieties and Overall Quantum Yield of the Photoreaction of Methoxy-Substituted Polymers with Different Spacer Groups

n	v_r	v_r^2	ϕ_0	ϕ_0/v_r^2
0	0.40	0.16	0.392	2.5
3	0.286	0.082	0.238	2.9
6	0.235	0.055	0.142	2.6

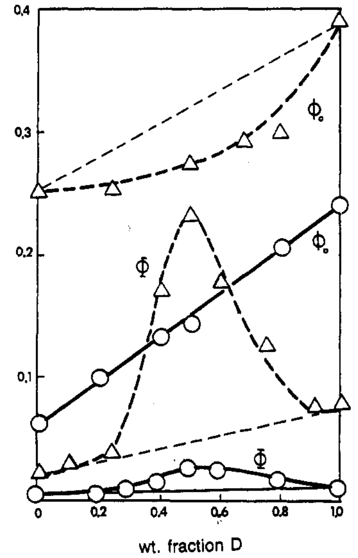


Figure 3. Plot of the overall quantum yield ϕ_0 and of the quantum yield Φ of intermolecular cross-link formation as a function of blend composition for blends of *p*-Cl- and *p*-CH_3O-substituted poly(vinyl cinnamate). Triangles refer to the polymers without spacers, and circles refer to the polymers carrying the three-membered spacers -$(CH_2)_3$- in the side chain.

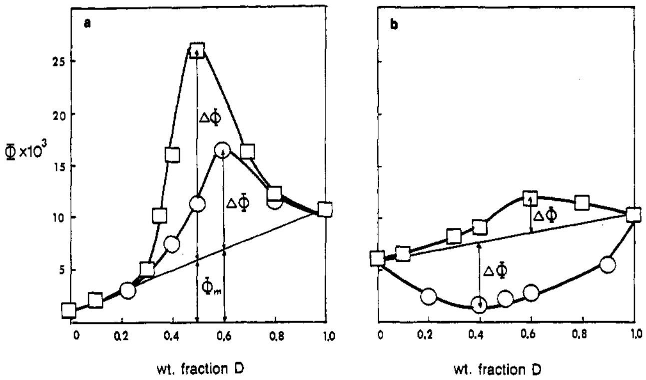


Figure 4. Quantum yield Φ of intermolecular cross-link formation plotted as a function of blend composition for the following polymer pairs, all of them with three-membered spacers -$(CH_2)_3$-: (a) (□) P-3-Cl/P-3-OCH_3, (○) P-3-Cl/P-3-CH_3; (b) (□) P-3-H/P-3-OCH_3, (○) P-3-H/P-3-CH_3.

acceptor interactions between the components. At the sensitivity maximum, the excess of the quantum yield Φ over the weighted mean, Φ_m, of the quantum yields of the pure components is a linear function of the donor-acceptor interaction energy. This energy is measured here by the difference in the Hammett constants, $\Delta\sigma$, of the substituents (Figure 5a). It is noted that the points of the nonspacer blends and those of the spacer blends fall on two straight lines with different slopes. However, if the excess quantum yield $\Delta\Phi$ is divided by the weighted mean Φ_m, the image points of all polymer pairs fall on the same straight line when plotted as a function of $\Delta\sigma$ (see Figure 5b).

Molecular Mechanism of Film Casting. The fact that electron donor-acceptor interactions of a given

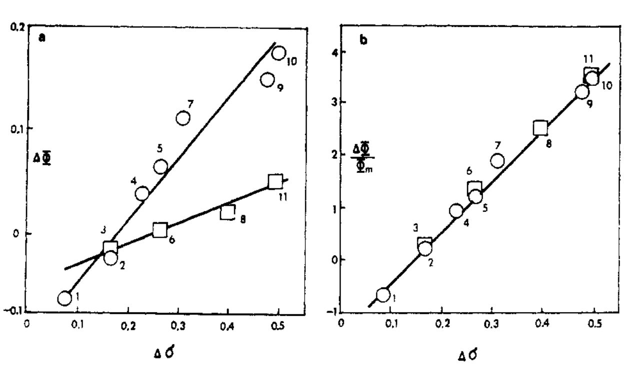


Figure 5. (a) Maximum excess quantum yield $\Delta\Phi$ and (b) maximum relative excess quantum yield $\Delta\Phi/\Phi_m$ for 11 pairs of polymers plotted as a function of the difference ($\Delta\sigma$) of the Hammett σ constants of donor and acceptor substituents: (1) P–Cl/P–OAc, (2) P–CH_3/P–H, (3) P-3-CH_3/P-3-H, (4) P–H/P–Cl, (5) P–OCH_3/P–H, (6) P-3-OCH_3/P-3-H, (7) P–H/P–OAc, (8) P-3-CH_3/P-3-Cl, (9) P–CH_3/P–OAc, (10) P–OCH_3/P–Cl, (11) P-3-OCH_3/P-3-Cl.

Table IV
Excess Quantum Yield $\Delta\Phi$ and Relative Excess Quantum Yield $\Delta\Phi/\Phi_m$ of Intermolecular Cross-Link Formation in Blends of Spacer-Containing Polymers

		$\Delta\Phi$		$\Delta\Phi/\Phi_m$	
substit	$\Delta\sigma$	$n = 0$	$n = 3$	$n = 0$	$n = 3$
Cl/AcO	0.04	–0.07		–0.70	
CH_3/H	0.17	–0.02	–0.015	+0.21	0.24
H/Cl	0.23	$+0.03_2$		0.94	
CH_3O/H	0.27	0.07_3	0.002	1.25	1.43
H/AcO	0.31	0.125		1.90	
CH_3/Cl	0.40		0.040		2.54
CH_3/AcO	0.48	0.14		3.20	
CH_3O/Cl	0.50	0.18	0.050	3.50	3.58

strength will increase the population of reactive sites in both nonspacer and spacer systems by the same factor allows some insight into the molecular events during film casting. The preordering of reactants observed in the form of a sensitivity enhancement must be established in the last phase of the casting process when the system is still fluid. The system solidifies in a state where each reactant is surrounded by a set of potential reaction partners. In the absence of (donor–acceptor) interactions, the probability of reacting with any of these partners and furthermore the probability that this partner belongs to another chain are reflected in the value of Φ_m. This value depends on the dilution of reactants and it characterizes their statistical environment. When the donor–acceptor interactions are "switched on", they act on the given environment and enhance the probability of intermolecular reaction in that environment by a factor that is solely a function of the interaction energy.

It may be concluded from this that the weak donor–acceptor interactions considered in these experiments do not fundamentally change the statistics of pair formation. These are basically determined by the structure of the polymers, by the volume fraction of the reactants, and by the distribution of backbone configurations in the system. The donor–acceptor interactions are only able to bias the pairing probabilities in favor of intermolecular pairings, at the expense of the formation of intramolecular reactant pairs which predominate in the pure component polymers.

We have calculated the stabilization energies of the donor–acceptor pairs from the effect of the casting temperature on the quantum yield Φ of cross-link formation. These data are plotted as a function of the reciprocal temperature in Figure 6. From the slope of the curves (at the low-temperature end) the stabilization enthalpy is calculated as 3.2 and 7.7 kcal/mol for the nonspacer and the spacer blends of the pair of Cl- and CH_3O-substituted polymers, respectively.

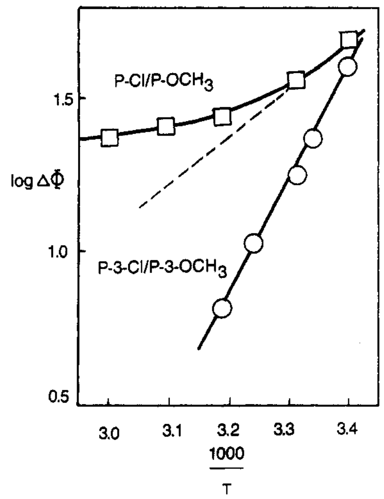


Figure 6. Excess quantum yield of cross-link formation plotted as a function of reciprocal casting temperature for 50:50 blends of the systems P–Cl/P–OCH_3 and P-3-Cl/P-3-OCH_3. The stabilization enthalpies of the donor–acceptor complexes derived from the slopes as indicated are 3.2 and 7.7 kcal/mol, respectively.

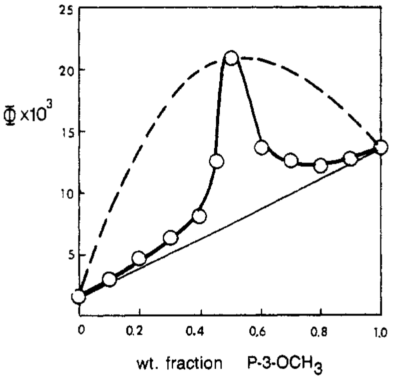


Figure 7. Quantum yield of cross-link formation in the system P-3-Cl/P-3-OCH_3 plotted as a function of blend composition. The broken line corresponds to the quantum yield function for a completely random distribution of donor- and acceptor-substituted reactants.

The concentration of donor–acceptor pairs as a function of blend composition deserves comment. In solutions of small donor and acceptor molecules the concentration of complexes is proportional to the product of the concentrations of donors and acceptors, c_Dc_A. If the total number of reactant molecules is kept constant, this is proportional to the product $c_D(1 - c_D)$, and in that case the concentration of complexes as a function of blend composition would have the form indicated by a broken line in Figure 7, while the experimental results are represented by the full line. The deviations of the real systems from the idealized random behavior are significant. They indicate that at low concentrations of either the donor or the acceptor intermolecular pairings are less frequent than predicted by random statistics but that the concentration of intermolecular pairs increases steeply as the numbers of donors and acceptors in the system become comparable. We believe that this is one more indication of the structural persistence of the coils of the individual components in the mixture. For example, when the donor polymer is a guest in the acceptor polymer, its secondary structure is being kept intact in preference to intermingling with the coils of the host polymer. This is a subtle kind of phase separation where cooperative forces between the side chains of the pure guest component act as a barrier to interaction with the side chains of the host. When donors and acceptors are present in approximately equal numbers and guest and host are not anymore clearly distinguishable, this intraspecies cooperativity is broken and donor–acceptor pairs can be formed with less restriction. It will be noted that the effect is more pronounced in blends of spacer polymers where side-chain interaction in the homopolymer can express itself more freely. It will also be recalled that *p*-methoxycinnamic acid, which is the reactant moiety in P-3-OCH_3, is a well-known mesogen where dipole forces between cinnamoyl groups can lead to liquid crystalline organization.[6]

Conclusions

The decoupling of the functional groups from the polymer backbone does not effectively enhance the photosensitivity of blends of electron donor or acceptor substituted poly(vinyl cinnamates). The dilution effect that accompanies the introduction of spacers into the polymers is more important in determining the concentration of reactive sites than the effect of separating the cinnamoyl groups from the polyvinyl chain. As a result the photoreactivity of the spacer blends is reduced below that of the corresponding nonspacer systems.

The decrease in the number of intermolecular pair sites in blends of spacer polymers is larger than expected for randomly distributed reactants, and this is interpreted as an indication of the partial persistence of the coil structure of the individual polymeric components. This view is also supported by the dependence of the quantum yield of cross-linking on the composition of the blends shown in Figure 7.

In spite of this, the effect of donor–acceptor interactions in the spacer-carrying systems is undeniable. In Figure 4 the quantum yield of cross-linking of the blends is, with one exception, higher than the weighted mean of the quantum yields of the pure components. The fact that donor–acceptor interactions between the reactants are the source of enhanced photosensitivity is further indicated by the effect of casting temperature on quantum yield. The stabilization energy of the donor–acceptor complexes can be derived from these experiments. It is found to be 3.2 and 7.7 kcal/mol, respectively, for the nonspacer and the spacer blends of the Cl- and CH_3O-substituted polymers.

References and Notes

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Triplet-State Reactivity of α-Sulfonyloxy Ketones Used as Polymerization Photoinitiators

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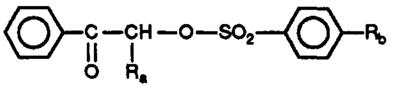
ABSTRACT: Three α-sulfonyloxy ketones have been investigated by laser flash photolysis. The decay kinetics of their triplet states and the radicals formed through β-cleavage and photoreduction were studied, and quenching rate constants by amine, monomer, and hydrogen donor were determined. These data are of interest when these compounds are used as radical or UV-deblockable photoinitiators. A general discussion of the processes involved is presented.

I. Introduction

The present paper is part of a series concerned with the excited-state processes in polymerization photoinitiators[1-7] and the working out of structure–reactivity relationships. Its purpose is to discuss the primary steps involved in the photolysis of α-sulfonyloxy ketones:



1, $R_a = H$; $R_b = CH_3$
2, $R_a = CH_3$; $R_b = CH_3$
3, $R_a = C_6H_5$; $R_b = C_{12}H_{25}$

These compounds[8] as well as α-sulfonylacetophenone **4**,[9] sulfonic acid derivatives of α-hydroxymethylbenzoin **5**,[10] β-sulfonyloxy ketone **6**,[11] *N*-hydroxyimide sulfonates **7**,[12] or quinolinium sulfonates **8**[13] can work as usual radical photoinitiators (except **7** and **8**), but they have been proposed primarily as UV-deblockable and acid-releasing molecules, e.g., for the cross-linking of aminoplast resins[8]

$$\text{blocked photoinitiator in the resin} \xrightarrow{h\nu} \text{acid species} \xrightarrow{\Delta} \text{cross-linking}$$

or the simultaneous activation of radical and acidic cross-linking mechanisms in hybrid systems. In the present investigation, the behavior of **1**–**3** was investigated by time-

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