prediction of conformational features in the anhydrous state. In the hydrated state, however, it is not unexpected that such a single-helix conformation can be stabilized by hydrogen-bonding interaction with water molecules.
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(39) It is reasonable, on the basis of our finding as to the extent of branching points, to treat the laminaran sample used in this study as a linear glucan as far as the local secondary structure as deduced by ^{13}C NMR spectroscopy is concerned.

Reactant Preordering in Solid Polymer Matrices: Photo-Cross-Linking in Blends of Donor- and Acceptor-Substituted Poly(vinyl cinnamates)

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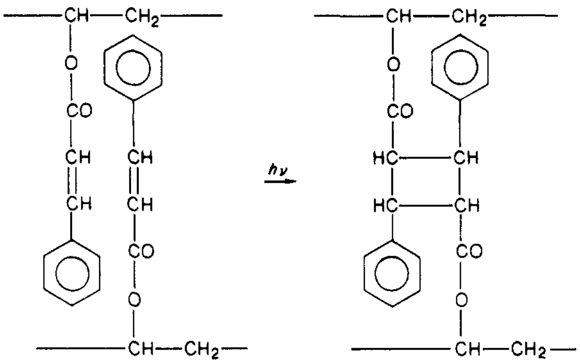
ABSTRACT: In blends of electron-donor- and electron-acceptor-substituted poly(vinyl cinnamates) a significant enhancement of photosensitivity is observed, compared to the sensitivity of the individual component polymers. The increase in cross-linking efficiency, which is the basis of the effect, is caused by reactant preordering in the solid polymer matrix. Donor–acceptor interactions between the functional cinnamoyl groups lead to a change from intramolecular to intermolecular pair formation. The magnitude of the effect is a function of the donor–acceptor interaction energy of the functional groups as measured by the difference in their Hammett substituent constants.

The performance of radiation-sensitive polymers depends not only on the inherent photoreactivity of their functional groups but also on the spatial arrangement of these groups in the solid matrix.[1] In conventional photopolymers the mutual geometries of reactants are a matter of chance and in these conditions the fraction of reactive configurations is low. It has been suggested that the number of reactive configurations or sites could be increased by reactant preordering. This is borne out by the solid-state chemistry of diacetylenes[2-4] and by the behavior of liquid-crystalline polymers.[5-8] We recall also the recent studies of Weiss et al.[9,10] on the effects of liquid-crystalline solvents on a number of photochemical probes. This paper is concerned with the partial preordering of photoreactive groups in amorphous polymer matrices. The idea of group preordering in solid polymers is of general interest since the ability of organizing the components of a polymeric system opens up a host of applications: Loosely ordered chromophore arrays may serve as pathways for the transport of photonic excitation, for the conduction of charge, and for the progression of chemical reactions.[11-13]

We have made an attempt at preordering photoreactive groups by means of electron-donor–acceptor interactions. The general aim was to attach electron donor or electron acceptor groups to the photoreactive moieties of a polymer and blend an electron-donor polymer and an electron-acceptor polymer together in a fluid medium (melt or solution), so that reactant pairs may be formed by electron-donor–acceptor interactions. The reactive configurations are then preserved in the solid state by cooling the melt or evaporating the solvent.

Poly(vinyl cinnamate) was chosen as a model system. It is a classical negative working photoresist where cross-links are formed by photocycloaddition between polymer-bound cinnamoyl groups.



Batches of poly(vinyl cinnamate) substituted with either electron-donor or electron-acceptor groups were prepared and it was hoped that blends of the donor and acceptor polymers coated from solution in the form of thin films would have a higher photosensitivity than either of the polymeric components. Watanabe and Ichimura[14] have reported interesting preliminary experiments on these lines and have indeed found increased photosensitivity. In the present paper preordering was to be detected not only by an increase in the photosensitivity of the films but also by the change in the number and in the nature of the reactive configurations.

The electron-donor or electron-acceptor groups substituted in the para position of the phenyl ring of the cinnamic acid moiety were, respectively, OCH_3, CH_3, Cl, $OCOCH_3$, and CN. In order to compare polymers of identical degree of polymerization and molecular weight distribution, the samples were prepared by polymer modification from the same batch of poly(vinyl alcohol).

The photosensitivity of the polymers was measured by determining their gel dose (E_G), that is, the quantum ex-

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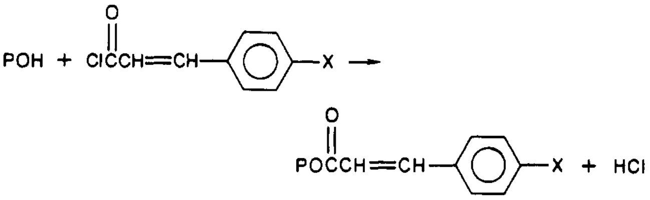
posure corresponding to just-incipient gel formation. From the gel dose, the quantum yield (Φ) of intermolecular cross-link formation was calculated. The overall efficiency of the photoreaction was determined as the quantum yield of reactant conversion (ϕ) by monitoring the dissappearance of cinnamoyl groups in the matrix by spectrometry. The overall quantum yield measures the formation efficiency of intermolecular *and* intramolecular links. The fraction of intermolecular cross-links formed in the system is therefore given by the ratio Φ/ϕ_0 and the fraction of intramolecular links similarly by the expression $(1 - \Phi/\phi_0)$. By comparing the overall quantum yield with the quantum yield of intermolecular cross-link formation, intermolecular and intramolecular links (and pair sites) in the system can be distinguished.

In an earlier paper[15] a method was developed by which the distribution of site reactivities can be derived from the dependence of the overall quantum yield of the photoreaction on reactant conversion. It is based on the fact that at any stage of the photoprocess the macroscopic quantum yield of reactant consumption reflects the average reactivity of the sites, taken over the ensemble of sites that have survived to this stage. The quantum yield as a function of the degree of chromophore conversion samples progressively more and more depleted versions of the original ensemble of reactivities; it contains therefore information on the initial distribution of site reactivities. This makes it possible to determine the fraction of reactive sites in the system. The degree of preordering achieved in the substituted materials can be judged by the change in the number and in the nature of the reactive sites.

Experimental Section

Materials. The polymer samples were prepared by functionalizing a single grade of poly(vinyl alcohol), obtained from Eastman Kodak (M_w 780 000), with para-substituted cinnamoyl chlorides.[16]



The *acid chlorides* were prepared by dissolving 1 mol of the substituted cinnamic acid and 0.01 mol of BHT (2,6-di-*tert*-butyl-4-hydroxytoluene) in benzene, refluxing under nitrogen, and dropwise adding of 1.5 mol of thionyl chloride. After the reaction had ceased, the mixture was cooled and excess $SOCl_2$ removed under reduced pressure. The remaining acid chloride was used without further purification.

Methoxy-, methyl-, and chloro-substituted cinnamic acids are commercially available (Aldrich); the cyano- and the aceto-substituted acids were prepared from the corresponding benzaldehydes and malonic acid.[17,18]

The functionalization of poly(vinyl alcohol) was carried out as follows: 7.5 g (0.15 mol of OH) of poly(vinyl alcohol) was dried under vacuum at 50 °C for 24 h and suspended in 300 mL of anhydrous pyridine containing 5 mg of BHT. The system was kept in a dry nitrogen atmosphere and 0.3 mol of the corresponding cinnamoyl chloride was added with stirring. The reaction was conducted for about 4 h at 50–60 °C. The resulting viscous dope was diluted either with acetone or more pyridine, filtered through glass fibers, and poured into an aqueous solution of sodium bicarbonate to precipitate the polymer. After vacuum drying overnight at 50 °C, the polymer was redissolved in THF or acetone, (DMSO for the cyano-substituted polymer), reprecipitated into distilled water, and finally dried under the same conditions as before. The polymers were characterized by T_g and by their UV and IR absorption spectra. These data are listed in Table I.

Table I
Molecular Weight, T_g, and Absorption Maximum of Individual Polymers

substituent	M_w	T_g, °C	λ_{max}, nm
CH_3O	249 000	88.4	306
CH_3	232 000	83.7	281
H	260 000	74.0	272
Cl	268 000	92.5	275
CH_3COO	299 000	98.5	274
NC	271 000	129.0	278

Table II
Absorption Maxima and Extinction Coefficients of Model Compounds

substituent	λ_{max}, nm	ϵ_{max} $1/M$, cm
CH_3O	310	22 500
CH_3	280	25 200
H	271	22 300
Cl	280	25 600
CH_3COO	280	21 600
NC	279	30 500

Ethyl esters of the substituted cinnamic acids were prepared for use as model compounds in estimating the degree of substitution of poly(vinyl alcohol) by cinnamoyl groups. Substituted acid chlorides of cinnamic acid were added to a mixture of anhydrous benzene, absolute alcohol (excess), and a stoichiometric quantity of pyridine. The reaction was started at room temperature (30 min) and continued for about 4 h at 60 °C. After the solvent was removed at reduced pressure, the residue was dissolved in chloroform or benzene and washed with 2% aqueous HCl, 2% sodium bicarbonate solution, and finally with distilled water. The organic solution was dried with anhydrous $MgSO_4$ and filtered and the solvent removed by distillation. The crude product was either purified by vacuum distillation or by recrystallization from petroleum ether/ethanol or from chloroform. The characteristics of the UV spectrum of the model compounds are listed in Table II.

The Gel Dose. The polymers were coated from 1,2-dichloroethane or its mixtures with hexane onto quartz plates. The dried films were irradiated through the transparent support with monochromatic radiation from a Bausch and Lomb high intensity monochromator and lamp combination. After the films were developed in 1,2-dichloroethane/hexane mixtures (or *N,N*-dimethylacetamide for the cyano-substituted polymer) and dried, the remaining film thickness in the exposed areas was measured with an interference microscope. The gel dose was found by extrapolating the gel curve to zero film thickness.

The Quantum Yield of Intermolecular Cross-Link Formation. The quantum yield of intermolecular cross-link formation was calculated from the gel dose E_G (einstein/cm²) by the expression[19]

$$\Phi = 1/2.303\epsilon m M_w E_G$$

where M_w is the weight-average molecular weight, ϵ the molar extinction coefficient of the cinnamoyl chromophore, and m its molarity in the solid film.

The Quantum Yield of Overall Reactant Conversion. The progress of the photoreaction during irradiation was monitored by spectrometry with a Cary 19 UV–visible spectrophotometer. The overall quantum yield of reactant conversion was derived from the dependence of the rate of chemical conversion (dx/dt) on exposure dose, via the equation[1]

$$\phi = \frac{n_0}{I_0 A}\frac{dx}{dt}$$

Here n_0 is the number of moles of chromophore in 1 cm² of the film, I_0 is the radiation flux [einstein/(cm² s)], and A is the fraction of incident photons absorbed by the reactive chromophores.

The Distribution of Site Reactivities. The distribution of reactivities over the ensemble of chromophore (cinnamoyl group) sites in the matrix was derived from the dependence of the overall quantum yield ϕ on reactant conversion (x) by a method described

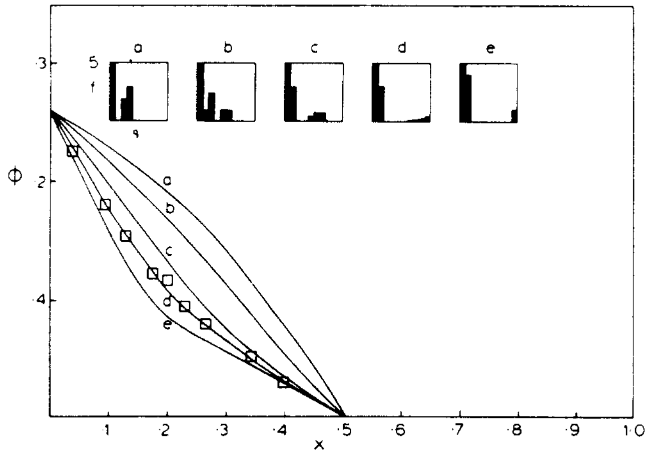


Figure 1. Plot of overall quantum yield, ϕ, as a function of reactant conversion, x. The curves correspond to the assumed reactivity distributions represented in the histograms a–e. The experimental points refer to a sample of unsensitized poly(vinyl cinnamate).

earlier.[15] It is based on a set of equations which allow the calculation of the function $\phi(x)$ for any given reactivity distribution. By starting with a plausible trial distribution and gradually modifying it until the corresponding $\phi(x)$ curve fits the experimental data, a good approximation to the site reactivity distribution in the material can be found.[15]

The method described in ref 15 applies directly to homopolymers; a modified treatment that is adapted to the analysis of blends has now been developed and will be published separately. The reactivity distributions emerge from these procedures in the form of histograms in which the frequency of occurrence in the ensemble of a given reactivity value is plotted against reactivity. Figure 1 shows assumed reactivity distributions and the corresponding $\phi(x)$ curves calculated for unsensitized poly(vinyl cinnamate). Curve d fits the experimental points quite closely, indicating that histogram d is a good approximation to the actual reactivity distribution in the polymer film.

Results and Discussion

Effect of Substitution on the Photosensitivity of the Individual Polymers. The quantum yield data on poly(vinyl cinnamate) and on five substituted poly(vinyl cinnamates) are given in Table III. In principle, substitution at the para position of the phenyl ring of the cinnamoyl group will affect the photosensitivity of the polymeric materials in two ways.

(a) The substituent will change the electron density at the reaction site proper, which is the C=C double bond of the cinnamoyl group, and may in this way alter the reaction probability, as measured by the average reactivity of the reactive sites.

Table III
Quantum Yield and Fraction of Intermolecular and Intramolecular Links for Substituted Poly(vinyl cinnamates)

substituent	ϕ_0	Φ	$\phi_0 - \Phi$	Φ/ϕ_0	$1 - \Phi/\phi_0$
CH_3O	0.39	0.08	0.31	0.21	0.79
CH_3	0.31	0.12	0.19	0.39	0.61
H	0.28	0.05	0.23	0.18	0.82
Cl	0.25	0.02	0.23	0.08	0.92
CH_3COO	0.26	0.05	0.21	0.19	0.81
NC	0.30	0.03	0.27	0.10	0.90

Table IV
Mean Site Reactivities, Fraction of Reactive Sites, and Hammett Substituent Constants

substituent	q_r	F_r	σ
CH_3O	0.95	0.18	−0.27
CH_3	0.95	0.14	−0.17
H	0.90	0.11	0
Cl	0.87	0.23	0.23
CH_3COO	0.93	0.11	0.31
NC	0.77	0.12	0.66

(b) The substituent may also affect the mutual configuration of the cinnamoyl groups in the matrix and thereby change the number (fraction) of reactive sites in the matrix.

The effect of the substituents on the average site reactivity is shown in Figure 2 for unsubstituted poly(vinyl cinnamate) and for methoxy-substituted and cyano-substituted poly(vinyl cinnamate). The distributions of site reactivities were obtained from the dependence of the overall quantum yield on reactant conversion, as indicated earlier. Figure 2 shows the histograms of the distributions together with the calculated $\phi(x)$ functions and shows the fit of the calculated curves with experiment.

It can be seen from the histograms that the electron-donating substituent OCH_3, which increases the electron density on the C=C double bond, enhances the average reactivity within the ensemble of reactive sites, while the electron-withdrawing substituent CN has the opposite effect. The change in the value of q_r on substitution is not large (see Table IV), but what change there is correlates with the Hammett constants of the substituents, as can be seen in Figure 3.

The overall fraction, F_r, of reactive sites, obtained by summation of the site numbers in the right-hand corner of the histograms (see Figure 2), varies over a wider range than q_r but clearly does *not* correlate with Hammett constants, and no coherent orientational effect on the reactants can be discerned from the data.

A clearer physical insight into the functional mechanism of the homopolymers is obtained by considering the sep-

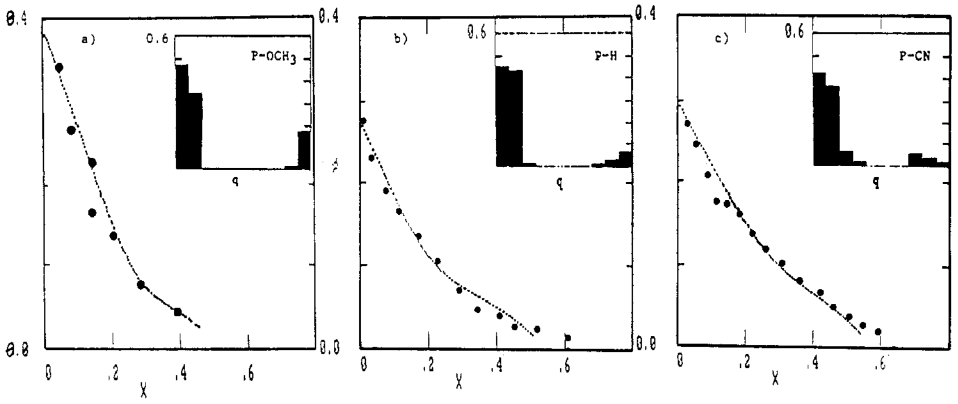


Figure 2. Reactivity distributions and quantum yield functions $\phi(x)$ for (a) methoxy-substituted, (b) unsubstituted, and (c) cyano-substituted poly(vinyl cinnamate).

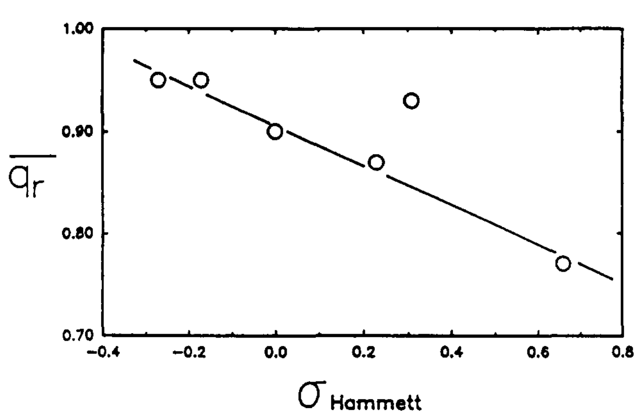


Figure 3. Average reactivity of reactive sites in para-substituted poly(vinyl cinnamates) plotted against the Hammett σ constants of the substituents.

aration of the results of cycloaddition into intermolecular and intramolecular links. The salient feature in this context is the fact that in all the systems the fraction of intramolecular links, which do not contribute to gel formation, is considerably higher than the fraction of intermolecular cross-links (see Table III). Intramolecular links are the result of cycloaddition between nearest neighbors on the polymer chain and their number is limited by the distribution of backbone conformations of the polymer. In equilibrium, three prevalent backbone conformations are available, only one of which is compatible with a reaction between nearest neighbors. If these conformations have approximately equal probability in the matrix, the reaction efficiency of *intramolecular* link formation, given by ($\phi_0 - \Phi$), should be of the order of $^1/_3$. The data in the third column of Table III support this view.

Effect of Substitution on the Reactivity of Polymer Blends. Of the 15 possible combinations between the six homopolymers, only seven pairs are completely miscible. These are listed in Table V together with some relevant quantum yield data.

It is found that the *overall* quantum yield ϕ_0 in the blends is never higher than the ϕ_0 value of the more reactive component. In polymer blends with moderate donor–acceptor interaction between the reactants, the overall quantum yield is a linear function of blend composition as shown in the upper curves of Figure 4a,b. This unexpected result indicates that donor–acceptor interaction does not seem able to increase the overall number of reactive sites, which appears to be largely controlled by the statistics of the polymer backbone.

Table V
Quantum Yields of Cross-Linking and Related Data for Blends at the Maximum of Sensitivity[a]

blend	ϕ_0	Φ	Φ/ϕ_0	$\Delta\Phi$	$\Delta\sigma$
$POOCCH_3/PCl$	0.28	0.03	0.11	−0.07	0.08
PCH_3/PH	0.295	0.085	0.29	−0.02	0.17
PH/PCl	0.265	0.10	0.38	0.03	0.23
PCH_3O/PH	0.32	0.13	0.41	0.07	0.27
$PH/POOCCH_3$	0.27	0.11	0.41	0.125	0.31
$PCH_3/POOCCH_3$	0.28	0.125	0.45	0.145	0.48
PCH_3O/PCl	0.28	0.23	0.82	0.18	0.50

[a] The sensitivity maximum occurs at a blend composition of 50:50 by weight, except in the system $POCH_3/PH$, where it occurs at a composition of 40:60.

From a practical point of view the important characteristic of cross-linking photopolymers is the quantum yield of intermolecular cross-link formation, Φ, which determines the photographic sensitivity of the material. In polymer blends with weak interactions between the reactant groups, such as in the pairs PH/PCH_3 and $POOCCH_3/PCl$, the values of Φ in the blends show small negative deviations ($\Delta\Phi < 0$) from additivity (see Figure 4a). This effect may be seen as the result of the general desegregation tendency between noninteracting (or not sufficiently strongly interacting) polymers. When the interaction energy exceeds a certain critical value, this tendency is overcome, and positive deviations ($\Delta\Phi > 0$) from a linear mixing law are observed. Examples of this supralinear behavior are shown in Figure 4b,c, which refer to moderately and to strongly interacting polymer pairs, such as $PH/POCH_3$ and $PCl/POCH_3$. In the case of the blend $PCl/POCH_3$ which is the pair with the strongest donor–acceptor interaction in this study, these deviations are considerable, corresponding to an almost 3-fold increase in the quantum efficiency of cross-link formation.

The significant observation that emerges from a comparison of the overall quantum yield, ϕ_0, and the intermolecular cross-linking yield, Φ, in Figure 4b,c is that the increases in resist sensitivity found in blends with donor–acceptor interactions between the reactants is not the result of an increase in the overall number of reactive sites but is caused by a change from a small minority (10%) of intermolecular reactive sites to a large majority (>80%) of such sites. In other words, in polymer blends with strong interactions between the reactant groups, intermolecular cross-links are formed at the expense of the intramolecular

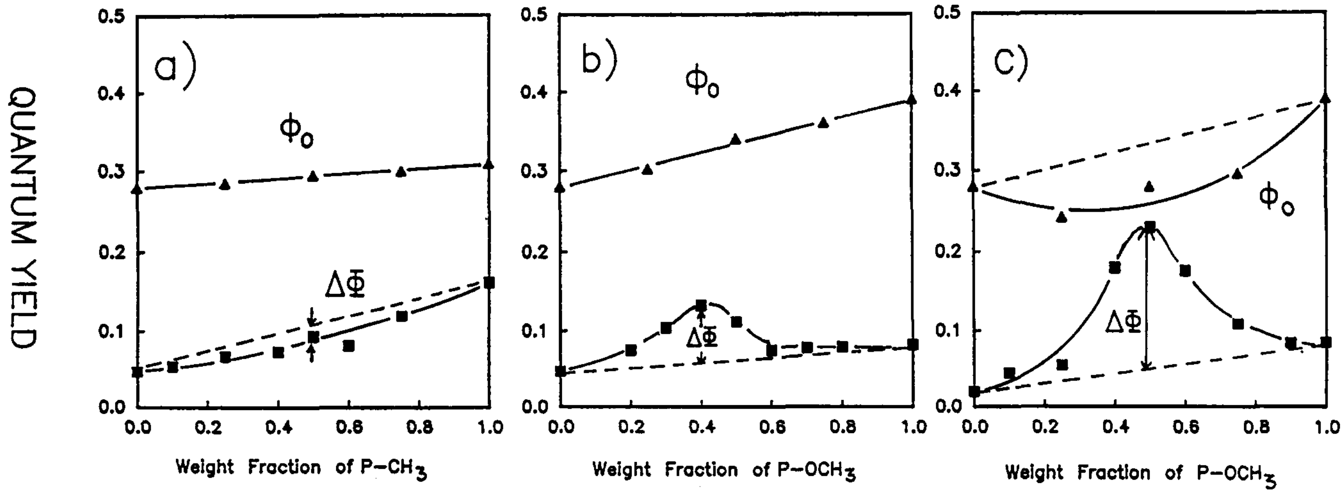


Figure 4. Overall quantum yield ϕ_0 and intermolecular cross-linking yield Φ plotted as a function of blend composition for the systems (a) PH/PCH_3, (b) $PH/POCH_3$, and (c) $PCl/POCH_3$.

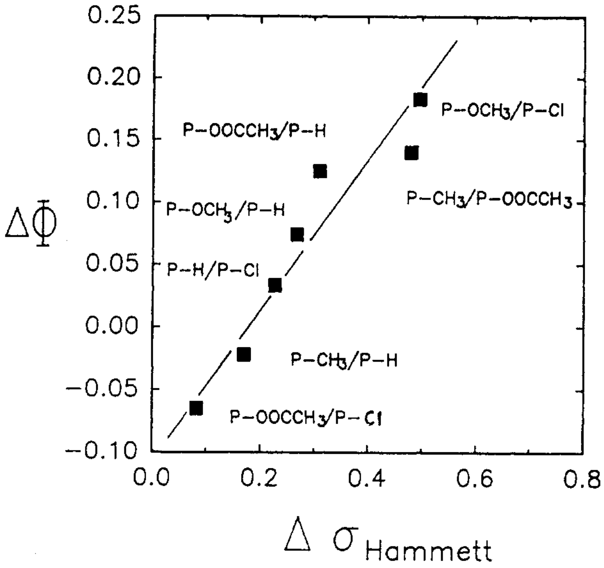


Figure 5. Plot of the excess quantum yield of cross-linking, $\Delta\Phi$, as a function of the difference, $\Delta\sigma$, in the Hammett σ constants of the substituents.

links, which are normally prevalent in the homopolymers.

This result seems to indicate that the overall number of links in the polymer matrix is controlled mainly by the number of available conformations of the backbone. Conformations that favor intermolecular links have a higher energy content, while the low-energy equilibrium conformations of the isolated chain favor intramolecular links. The change in photosensitivity is therefore the result of a fundamental change in the molecular morphology of the solid matrix, brought about by electron-donor–acceptor interactions. The change, $\Delta\Phi$, in the intermolecular cross-linking yield at the sensitivity maximum of the blends is found to be correlated with the donor–acceptor interaction energy, as measured by the difference in the Hammett substituent constants, $\Delta\sigma$, of the components of the blend (see Figure 5). It can be seen that the correlation line passes through $\Delta\Phi = 0$ at $\Delta\sigma = 0.17$. Below that value, $\Delta\Phi$ is negative, corresponding to a slight desegregation of the two polymers with differently substituted cinnamoyl groups. Above the critical value of interchromophore interaction, the fraction of intermolecular cross-links in the blends is higher than predicted by a linear mixing law.

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Registry No. Poly(vinyl alcohol) *p*-methoxycinnamate, 121288-47-9; poly(vinyl alcohol) *p*-methylcinnamate, 121288-48-0; poly(vinyl alcohol) cinnamate, 9050-06-0; poly(vinyl alcohol) *p*-chlorocinnamate, 121288-46-8; poly(vinyl alcohol) *p*-acetoxycinnamate, 121288-45-7; poly(vinyl alcohol) *p*-cyanocinnamate, 76544-23-5; ethyl *p*-methoxycinnamate, 1929-30-2; ethyl *p*-methylcinnamate, 20511-20-0; ethyl cinnamate, 103-36-6; ethyl *p*-chlorocinnamate, 6048-06-2; ethyl *p*-acetoxycinnamate, 25743-64-0; ethyl *p*-cyanocinnamate, 20655-58-7.

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