

THE DESIGN OF PHOTOREACTIVE POLYMER SYSTEMS FOR IMAGING PROCESSES

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Abstract - The use of polymers in photoreactive imaging systems depends upon the interrelationship between the polymer physical properties and the photosensitive response. Modifications of the structure and physical properties by synthetic means permit control over the physical properties, such as solubility, melting point, glass transition temperature, and crystallinity. Specific polymer imaging systems depend upon these properties in order to function. Modifications of light absorbing chromophores and understanding the factors controlling sensitization permit adjustment of the wavelength response over the range from 250-650 nm. Triplet energy transfer from optical sensitizers to the photoreactive moieties is the most probable mechanism of sensitization. We have found that competing side reactions such as oxidation and photoreactions of the sensitizer can reduce the efficiency of sensitization.

INTRODUCTION

Imaging with polymers can be accomplished in a number of ways using a variety of photosensitive systems which in turn can produce a variety of imaging systems. As shown in Fig. 1, there are two main groups of photosensitive systems: negative working and positive working.

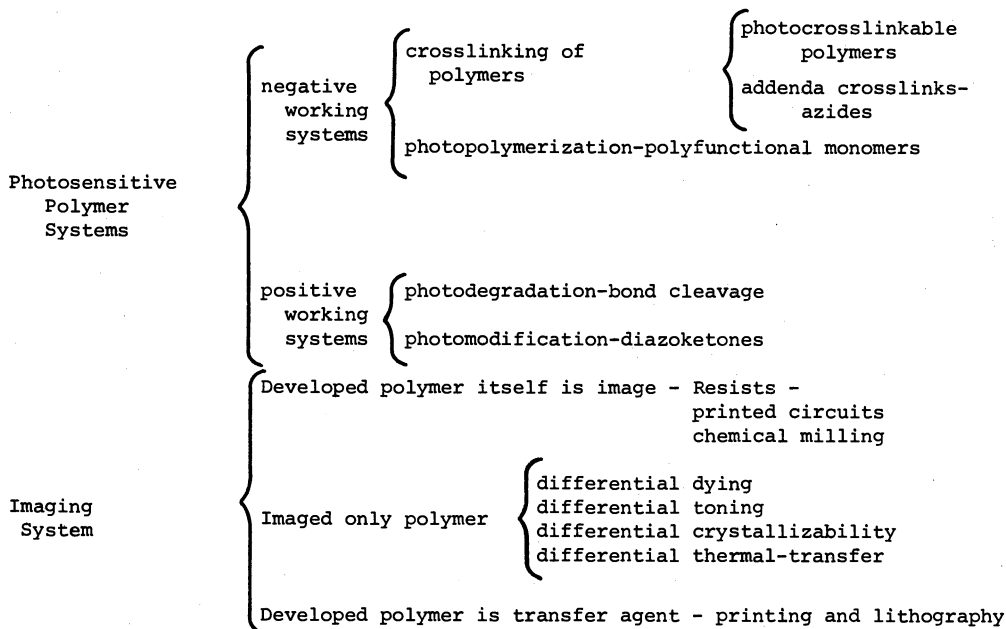


Fig. 1. Photosensitive polymer systems for imaging

The negative working systems consist of photocrosslinkable polymer systems and photopolymerizable systems. Positive-working systems are based, in practice, principally on the use of the diazoketone photolysis reaction which produces a change of functionality from oleophilic to hydrophilic. Photodegradative processes also fall into this class. Both the negative and positive working systems find practical use in printing, lithography and resist applications. The major photoimaging processes using polymers involve photoreactive functional groups which change their functionality when irradiated. Intramolecular changes of functionality can lead to increased solubility, while bimolecular or intermolecular change

usually leads to insolubilization via crosslinking. The two prime factors influencing the formation of images with polymers are the photographic speed and the physical properties (usually solubility) of the polymer system before and after exposure to light. The photographic speed depends upon the nature of the photoreactive groups attached to the polymer and their ability to respond to optical sensitization by added unattached sensitizers. Even if the bound photoreactive groups show a high quantum yield of conversion on their own, further substantial increases in overall sensitivity or speed can result using optical sensitization. Such sensitizers act as light-gathering devices and usually extend the photoresponse over a larger segment of the electromagnetic spectrum. Factors governing the overall efficiency of a polymer photoimaging process can be subdivided as follows: (a) The efficiency of the absorption of light by the sensitizer and the polymer. These are required to match the light distribution of the source; (b) The efficiency of energy transfer from sensitizer to the photoreactive groups on the polymer should be maximized by adjustment of sensitizer concentration and compatibility with a given polymer; (c) The efficiency of the photochemically induced reaction depends on structure-physical property relationships which can be adjusted by structural modifications. A change of physical properties with exposure to light forms the chemical basis on which image discrimination is made. Generally, the photoinduced chemical acts cause a change in solubility. For instance, a previously solvent-soluble polymer coating becomes solvent-insoluble in an imagewise manner as is the case for photocrosslinkable polymers. The converse is the basis for the operation of diazoketone-type polymers. Image discrimination can, however, sometimes be less than clearcut due to the characteristics of the solvent and the solubility parameters of the exposed and unexposed polymers. Marginal insolubilization of exposed image areas together with strong solvent action have a tendency to cause swelling of the developed or residual image. This can lead to poor resolution of images and loss of detail, and is a problem which appears particularly when submicron geometries are desired. It is therefore important to control or adjust the physical properties of photoreactive polymers by modification of their structures so that good image discrimination is possible. This minimizes nonselective solvent attack on images during processing as well as creates resistance to chemical destruction by etchants such as ferric chloride or strong nitric acid or to inks or fountain solutions used in printing.

Therefore, control over the physical properties of polymers used in photoreactive imaging systems coupled with adequate photographic speed-optical response are of primary importance. These two important aspects; sensitization-photographic speed and structure-properties design are the principal points to be discussed below in two sections.

Structure-physical properties-sensitivity modifications of polymers

The majority of photocrosslinkable polymers which have been reported have been prepared by the reaction of a functionally reactive photosensitive moiety with a preferred polymer backbone.¹ The classical forerunner of this group, poly(vinyl cinnamate), is based on the reaction of cinnamoyl chloride or variant thereof with poly(vinyl alcohol) at moderately elevated temperatures. Typical is the synthesis of a polymer bearing p-[2-(2-ethylhexyl-oxy-carbonyl)vinyl]cinnamate photoreactive groups.²

| | |
|---|------|
| $\begin{array}{c} \text{---CH---CH}_2 \\ \\ \text{O} \\ \\ \text{C=CH}_3 \\ // \\ \text{O} \end{array}$ | 0.12 |
| $\begin{array}{c} \text{---CH---CH}_2 \\ \\ \text{O} \\ \\ \text{C}=\text{C} \begin{array}{c} \text{H} \\ // \\ \text{O} \\ \\ \text{C} \end{array} \begin{array}{c} \text{H} \\ // \\ \text{O} \\ \\ \text{C} \end{array} \\ // \quad // \\ \text{O} \quad \text{O} \\ \quad \\ \text{H} \quad \text{H} \end{array}$ | 0.38 |
| $\begin{array}{c} \text{---CH---CH}_2 \\ \\ \text{O} \\ \\ \text{C} \end{array}$ | 0.60 |

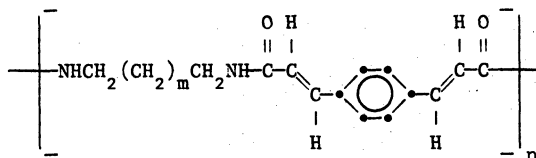
The spectral sensitivity range and photographic speed values for unsensitized and sensitized coatings of the resulting polymer are compared on Table 1. The unsensitized sensitivity range and photographic speeds are dictated by the absorption characteristics of the appended photoreactive chromophore.

TABLE 1. Sensitization of p-[2-(2-ethylhexyloxy)vinyl]cinnamate-type polymers

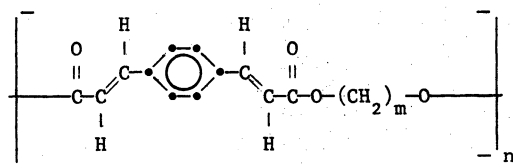
| Sensitizer | Sensitivity Value | Spectral Range (nm) |
|--|-------------------|---------------------|
| none | 2,000 | 270-380 |
| 2,6-bis(4'-ethoxyphenyl)-4-(4'-n-amyloxy-phenyl)-thiapyrylium perchlorate (TPP-type) | 8,000 | 270-520 |
| N-methyl-2-benzoyl- β -naphthothiazoline (BN) | 20,000 | 270-400 |
| 4-H-quinolizine-4-thione | 2,800 | 270-480 |

The solubility parameters of this class of polymers can readily be controlled by the nature of the alkoxyl group as well as that of the second acid residue and nonesterified hydroxyl groups.

Control of polymer thermal and solubility properties. Condensation-type photocrosslinkable polymers provide a means of varying thermal and solubility properties. A series of polyamides containing photoreactive groups was prepared by interfacial condensation of phenylene bis-diacryloyl chloride and diamines such as hexamethylene or decamethylene diamine.



Solubility limitations precluded the use of the polyamides. The corresponding N,N'-dimethyl-bis-hexamethylene diamines gave polymers of low molecular weight which were quite tacky semisolid glasses. When diethyl p-phenylene-bis-acrylate was condensed with aliphatic diols a series of crystalline polyesters of regularly-varying melting points resulted.



The reaction temperatures required for polycondensation (210-260°C) failed to cause appreciable thermal crosslinking of the polyesters. Thus, we were able to prepare a number of series of polyesters and copolyesters. Figure 2 compares the melting points of the polyesters prepared from various glycols and terephthalate with those from the p-phenylene-bis-acrylate polyesters.

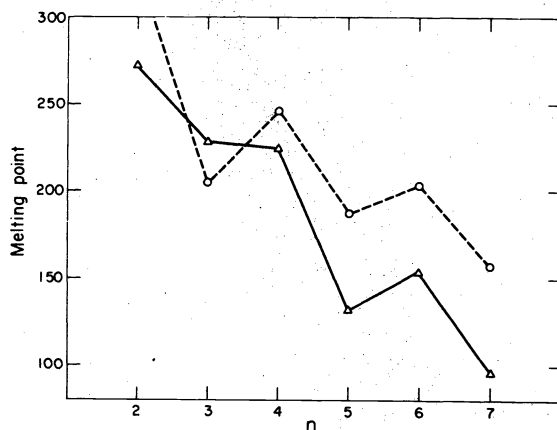


Fig. 2 Melting Point vs. Glycol for Polyesters of Terephthalate (Δ) and Phenylene-bis-acrylate (\circ)

Table 2 summarizes the corresponding glass transition temperatures for the same series of polyesters prepared from p-phenylene-bis ethylacrylate.

TABLE 2. Glass transition temperatures for polyesters of glycols and p-phenylene-bis-ethylacrylate

| Glycol | Inherent Viscosity | Tg°C |
|-----------------|--------------------|------|
| C ₃ | 0.59 | 61 |
| C ₄ | 0.63 | 54 |
| C ₅ | 0.64 | 53 |
| C ₆ | 0.68 | 49 |
| C ₇ | 0.61 | 47 |
| C ₈ | 0.71 | 47 |
| C ₉ | 0.62 | 47 |
| C ₁₀ | 0.73 | 47 |
| C ₁₁ | 0.62 | 45 |
| C ₁₂ | 0.58 | 45 |

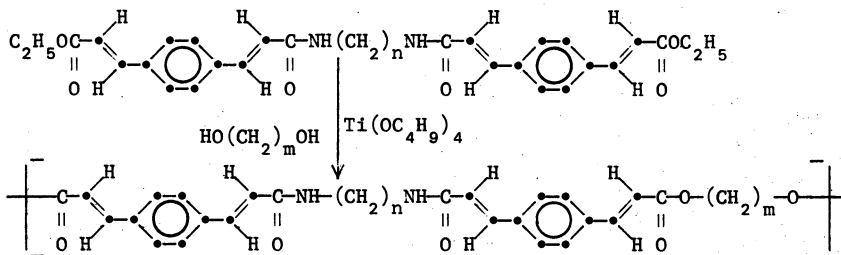
The relative speeds of photocrosslinking of all of the polyesters from C₃ to C₁₂ were nearly identical within experimental error. It is remarkable that the value of T_g was reduced by only approximately 15° in going from C₃ to C₁₂. This fact indicates that the size and shape of the p-phenylene-bis-acrylate moiety predominates over the changes in glycol length-flexibility, particularly in the flat portion of the range of C₆ to C₁₂. We should point out that the melting points of the corresponding p-phenylene-bis-acrylate polyesters are considerably higher than those of the terephthalate over the whole range of glycol chain lengths.

The solubility and crystallinity characteristics of these photoreactive polymers are undesirable since the ethylene glycol, propylene glycol, and butylene glycol polyesters are insoluble in practical solvents. However, the pentamethylene glycol shows improved solubility despite a tendency to crystallize. It was found that the C₇ and C₉ diols did provide polyesters having ideal solubility properties, though these glycols are undesirable for economic reasons. Therefore, a series of copolyesters were synthesized. Typical of these is the composition based on pentamethylene glycol, diethyl phenylene-bis-acrylate and dimethyl isophthalate (50:50) which had an inherent viscosity of 0.52 and T_g 21.5°. A corresponding C₅ (20:80) copolyester has a T_g of 12°.

The above polymers as coatings fail to photoisomerize despite the fact that they do so in dilute solution. Such coatings become immediately insoluble, before photoisomerization can be detected spectrophotometrically. One can prepare copolyesters possessing a wide range of melting points, T_g, tackiness and solubility by copolymerization. In practical use, these variations in physical properties lend themselves to photographic innovations involving phenomena other than solubility differences. Images can be formed by light-induced changes in tackiness, inhibition of crystallization or material transfer. The latter process has been applied to a color proofing system using color separation to produce three color printers proofs.

Action spectrograms of the above group of polyesters and copolyesters are identical since the only difference between polymers is the amount of phenylene-bis-acrylate unit introduced into the polymer. These polymers respond remarkably well to optical sensitization by typical sensitizers such as pyrylium salts.

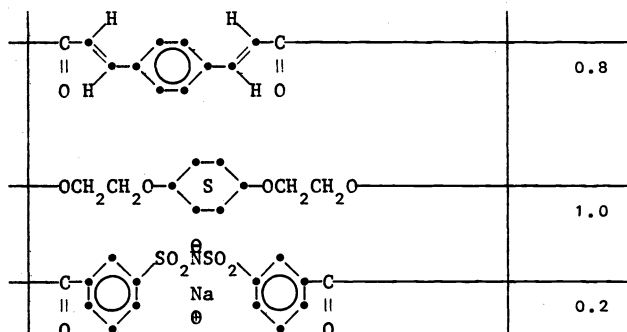
The difficulties described above found in the preparation of photocrosslinkable polyamides has to a large degree been circumvented using the technique of preparing preformed ester-amide intermediates for use in ester interchange-type polycondensation.



Where $n = 2-10$ and m is $2-12$.

As in the case of the polyester series, the lower members of the series were highly crystalline. Copolymerization with a second bis-ester has produced soluble polymers whose photographic response is essentially the same as the original polyester.

Many types of water-base-soluble photocrosslinkable polymers have been prepared using quaternary nitrogen, hydroxy, sulfonic acid and carboxylic acid as the solubilizing function.^{1,6} Recently, a novel means of preparing water-base soluble photocrosslinkable polyesters has been described by Arcesi and Rauner who utilized 3,3'-[(sodio-bis-imino)disulfonyl]dibenzoate groups as the hydrophilic function.



The photographic response of such polymers parallels that of the phenylene-bis-acrylate polyesters and polyester amides mentioned above.

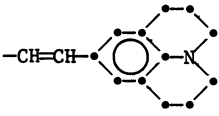
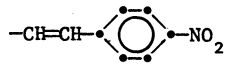
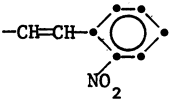
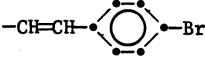
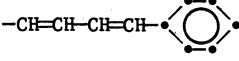
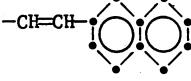
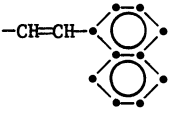
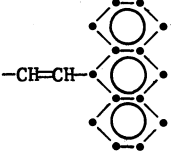
Control of spectral response. Control of the spectral response of photocrosslinkable polymers has been accomplished by chromophore modification and by use of spectral sensitizers such as those described above and in the section on sensitization.

In certain instances such as is the case for cinnamate versus styrylacrylate, both chromophore modification and optical sensitization can be used.¹

Polymers bearing chalcone or styrylpyridinium-type photosensitive groups which undergo typical singlet-type photoreactions do not respond to sensitizer such as TPP or BN. Therefore, the only recourse, which we have used in the case of the styrylpyridinium type polymers,⁷ is to modify the light absorbing chromophore. We have prepared a series of such polymers and controlled their range of spectral response and absorption maxima by modifying the nature of the aldehyde used to react with poly(2-methyl-5-vinylpyridinium methosulfate).

TABLE 3. Spectral response and photosensitivity of styryl pyridinium-type polymers

| R | λ_{\max} | Spectral Response |
|---|------------------|-------------------|
| | 344 nm | 270-430 nm |
| | 380 nm | 270-480 nm |
| | 388 nm | 270-560 nm |
| | 467 nm | 270-630 nm |

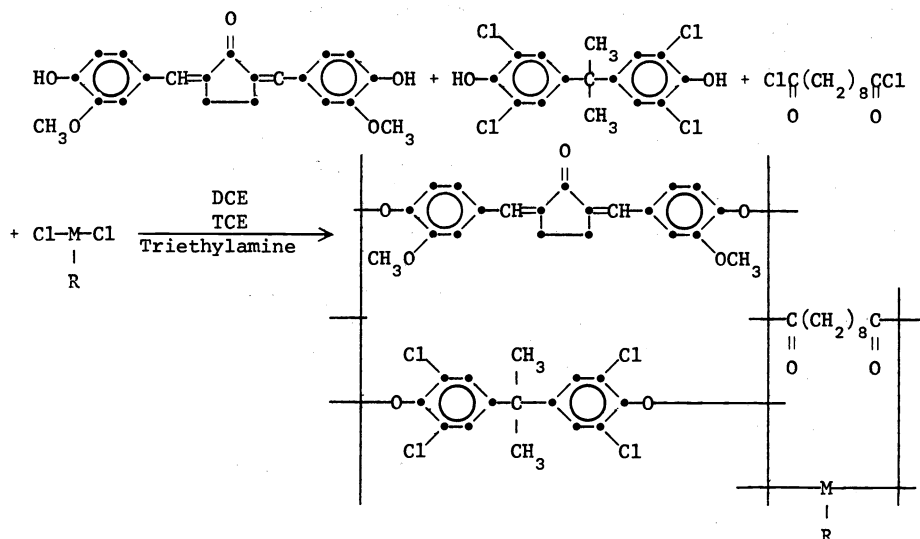
| | | |
|---|------------|------------|
|  | 486 nm | 270-630 nm |
|  | 453 nm | 270-630 nm |
|  | 345 nm | 270-430 nm |
|  | 351 nm | 270-460 nm |
|  | 375 nm | 270-500 nm |
|  | 365 nm | 270-450 nm |
|  | 383 nm | 270-460 nm |
|  | 309-408 nm | 270-580 nm |

The examples in Table 3 illustrate that λ_{\max} values of the polymers can be controlled to range from 344nm to 486 nm with corresponding spectral response ranges of 270-630 nm.⁸

The practical photographic speeds of these polymers depend on the degree of reaction, the structure of the aldehyde used and the solvent for processing. The water and alcohol soluble polymers prepared using anisaldehyde have been found to have relative photographic speeds of from 20,000-30,000 times that of unsensitized poly(vinyl cinnamate). These polymers become insoluble on exposure to light and are therefore negative working. By exchange of the methosulfate counterions with the tetraphenylborate anion, the polymers become organic solvent soluble. On exposure to light they then again become hydrophilic in the exposed areas and as such are positive working with respect to ink-water discrimination. The conversion to hydrophilicity by light is due to the formation of water soluble photochemical products from rearrangement of the tetraphenylborate anion.

Photoreactive organometallic polymers. Modification of the photoactive group and the means of incorporation into or onto a polymer backbone has generally involved the use of ester type functional groups to provide polyester, polycarbonate or polysulfonate structures. Recently Borden has made use of interfacial polycondensation to incorporate metal groups into the polymer chain. This was accomplished by replacing a portion of the usual bis-acid chloride by a metal dihalide for reaction with light sensitive bisphenols. As, Sb, B,

Ge, Hf, Fe, Pb, Mn, Pd, Pt, Ru, Se, Si, Sn, Ti, Va, and Zr bonds were incorporated into the following polymer structure.

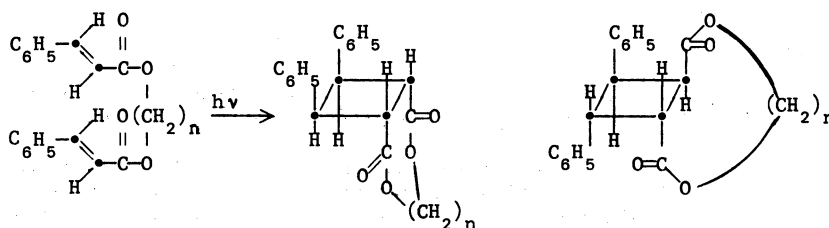


These polyesters are organic solvent soluble and are readily crosslinked on exposure to ultraviolet-rich light. They contain up to 30 percent by weight of the metal.

We have illustrated above by chemical modifications, the means of tailoring photocrosslinkable polymers to meet specific needs. The use of polyester-type structures facilitates control over properties such as solubility, melting point, crystallization rate, glass transition temperature and permits wide variation of the specific interconnecting units. Chromophore modification in quaternary-type polymers permits a wide choice of the sensitivity response in the range between 250 and 650 nm.

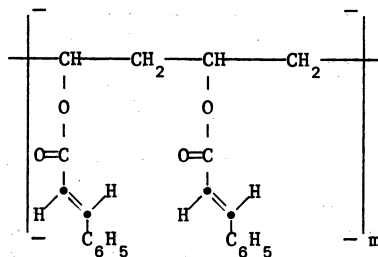
SENSITIZER STUDIES

Although poly(vinylcinnamate) has been discussed and studied by a number of groups over the past two decades it still remains the ideal system in which to study the various parameters effecting the photocrosslinking of polymers. The exact mechanism of photocrosslinking has not to this date been unravelled. An interesting means of studying the possibility of intramolecular versus intermolecular bimolecular reaction of poly(vinyl cinnamate) was generated by the work of Freedman, Magadgen, Rennert, Soloway and Waltchen¹⁰ who studied the intramolecular photodimerization of ethylene-bis-cinnamate. Our study¹¹ verified that



Freedman, et al. (1969) β -truxinate

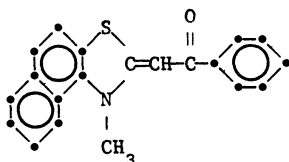
δ -truxinate



Poly(vinyl cinnamate)

bis-cinnamates underwent 2 + 2 photocyclization. We found that when n was 3 the ratio of β to δ truxinate was 4:1, whereas with n equal to 4 or 5 the ratio was 1:4. Certain structures gave cyclic dimers while those having the appropriate chain lengths led to polymers of the type described by Hasegawa and Suzuki,¹² as well as Miura, Kitami and Nagakubo.¹³ Such polymerization systems were further elucidated and described more correctly as true photopolymerizations by De Schryver,¹⁴ who pointed out that earlier systems termed photopolymerization by Oster, Oster and Prati¹⁵ were really photoinitiated vinyl-type polymerizations.

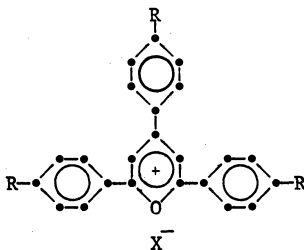
Much discussion was given in the 1960's and early 1970's to triplet energy transfer from a sensitizer to a photoreactive chromophore attached to a polymer chain. In specific cases such as cinnamate and related moieties it was proposed that energy transfer to cinnamate was followed by a photodimerization-type of photoinduced crosslinking which occurred between two cinnamate units attached to different individual polymer backbone chains. Clearly, triplet energy transfer to cinnamate was a very probable process involving such specific sensitizers as aromatic ketones like Michler's ketone and N-methyl-2-benzoyl-naphthothiazoline (BN). Curme, Natalie, and Kelley¹⁶ had shown earlier that ethyl cinnamate quenched the phosphorescence but not the fluorescence of Michler's ketone and picric acid. They had concluded that triplet energy transfer from the sensitizer was involved in both



N-methyl-2-benzoyl- β -naphthothiazoline (BN)

the sensitized photochemistry of ethyl cinnamate and that of poly(vinyl cinnamate).

In our work we began to find differences in the response of certain chromophore sensitizer combinations which would have been expected to operate via a triplet-triplet energy transfer mechanism. The first of these were combinations of pyrylium salts with stilbene for which unusual photostationary state equilibria were observed. The photostationary cis-



Substituted Triphenylpyrylium Salt Structure

trans product ratios disagreed with those ratios predicted from triplet energies of pyrylium salts using the Hammond-Saltiel⁷ scheme since they were too rich in trans isomer.¹⁸

The triplet energies of the pyrylium salts were determined by emission spectroscopy which revealed an unusual additional luminescence. At liquid nitrogen temperatures pyrylium

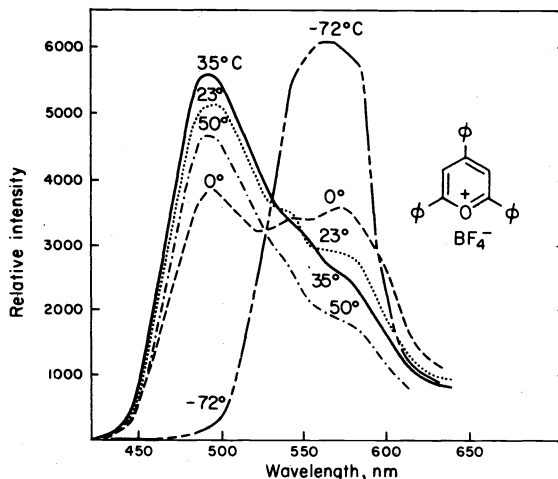


Fig. 3 Temperature dependence of fluorescence versus phosphorescence of Triphenylpyrylium Borofluoride

salts showed only phosphorescence while at room temperature an unexpected combination of delayed fluorescence and phosphorescence was observed. As the temperature was lowered the ratio of fluorescence to phosphorescence decreased to nearly zero at liquid nitrogen temperatures. Typical of these sensitizers was 2,4,6-triphenylpyrylium perchlorate, (triplet energy 53 kcal/mole), which produced a photostationary state containing 96 percent trans stilbene. The photostationary state ratio predicted from the Hammond-Saltiel plot was 14 percent trans stilbene.

In Table 4 are four pyrylium salts having triplet energies between 51 and 56 kcal/mole which produced photostationary states ranging from 56-98 percent trans stilbene while the predicted corresponding range was 7-23 percent. Clearly triplet energy transfer was not controlling the processes involved. A survey of several other typical triplet sensitizers such as 5-nitrofluorene revealed that normal triplet behavior occurred. This again was determined by comparison of the predicted and experimental percentages of trans stilbene at the photostationary state. The same was found for N-methyl-2-benzoyl- β -naphthothiazole (BN).

These findings, combined with the knowledge that pyrylium salts themselves show the unusual properties of interrelated delayed fluorescence and phosphorescence, led us to believe that



TABLE 4. Product ratios for the cis-trans-photoisomerization of stilbene sensitized by pyrylium perchlorates

| | E_t (kcal/mole) | Percent trans-stilbene at photostationary state | |
|-------------------------------------|-------------------|---|-----------|
| | | Found | Predicted |
| 2-Methyl-4,6-diphenylpyrylium | 56 | 87 \pm 9 | 23 |
| 2,4,6-Triphenylpyrylium | 53 | 96 \pm 1 | 14 |
| 2,4,6-Triphenylthiapyrylium | 52 | 98 \pm 1 | 10 |
| 2,4,6-Tris(4-methoxyphenyl)pyrylium | 51 | 56 \pm 0.2 | 7 |

more than one mechanistic pathway for sensitization was present. It had been shown by Crellen, Lambert and Ledwith¹⁹ that pyrylium salts could act as charge transfer initiators for monomer polymerization. Experiments using dienes, such as piperylene, showed that excited pyrylium salts photoinitiated polymerization of the diene to yield species as large as pentamers. These results indicated strongly that pyrylium cation radicals initiated polymerization and involved excited state electron transfer reactions. We found that ethyl cinnamate could be polymerized to yield low molecular weight polymers using light and pyrylium salts. However, in this case the pyrylium salt was destroyed.

Photoexcited pyrylium salts underwent a very fast reaction with bis-cinnamates leading to polymerization. The rate of decomposition of 2,4,6-triphenylpyrylium perchlorate depended on the structure of the bis cinnamate.

TABLE 5. Rate of photodecomposition of 2,4,6-triphenylpyrylium fluoroborate with cinnamates in acetonitrile

| | 0 | 0 |
|-----------------|---|---|
| | | |
| |  |  |
| Cinnamate | Relative Rate | Cinnamate Lost % |
| Ethyl cinnamate | .22 | 60 |
| n=2 | .58 | 62 |
| n=3 | .45 | 58 |
| n=3 | .45 | 46 |
| n=4 | 1.00 | 45 |
| n=5 | .85 | 48 |
| n=6 | .76 | 43 |
| n=9 | .87 | 40 |
| n=10 | .74 | 52 |

The results from the investigation of the relationship between sensitizer and the corresponding photostationary state made with a series of sensitizers using 1,3-dicinnamoyl-oxo-2,2-dimethylpropane are shown in Table 6.

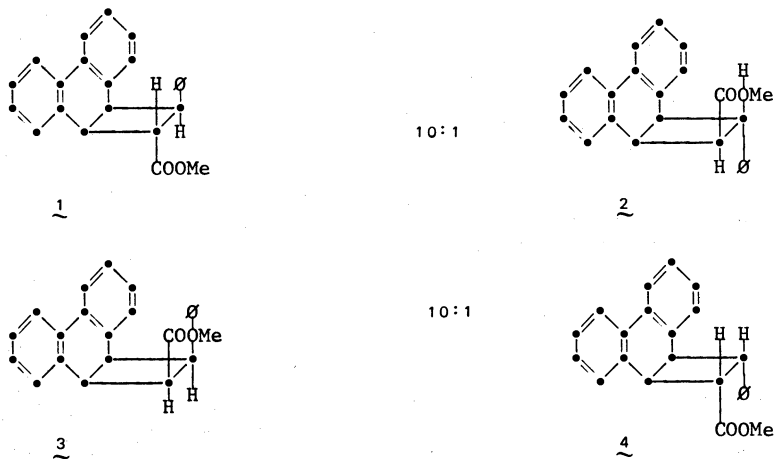
TABLE 6. "Pseudophotostationary States" of 1,3-dicinnamoyl-oxy-2,2-dimethylpropane with triplet sensitizers

| Sensitizer | Triplet Energy (kcal) | Total Cis/Total Trans |
|--------------------------------------|-----------------------|-----------------------|
| Acetophenone | 73.6 | 1.04 ± .05 |
| Benzaldehyde | 71.9 | 1.05 ± .02 |
| Benzophenone | 68.5 | 1.29 ± .01 |
| Triphenylene | 66.6 | * |
| 2-Aminofluorene | 65 | 1.21*± .02 |
| Anthraquinone | 62.4 | 1.31 ± .02 |
| Phenanthrene | 62.2 | * |
| 4,4'-Bis(dimethylamino)-benzophenone | 61.0 | 1.19 ± .02 |
| 2-Naphthylphenone | 59.6 | 2.30 ± .02 |
| 2-Acetonaphthone | 59.3 | 2.17 ± .01 |
| 2-Nitrofluorene | 59 | 1.65 ± .01 |
| 1(1-naphthyl)-4-ethylphenone | 57.5 | 3.17 ± .05 |
| 1',2-benzofluorene | 57 | * |
| 1-Acetonaphthone | 56.4 | 2.87 ± .05 |
| 1-Naphthaldehyde | 56.3 | 2.65 ± .08 |
| Coronene | 55 | 1.43 ± .02 |
| p-Nitroaniline | 55 | * |
| Fluorenone | 53.3 | 0.80 ± .03 |
| 1,2 Benzpyrene | 53 | * |
| Pyrene | 48.7 | * |

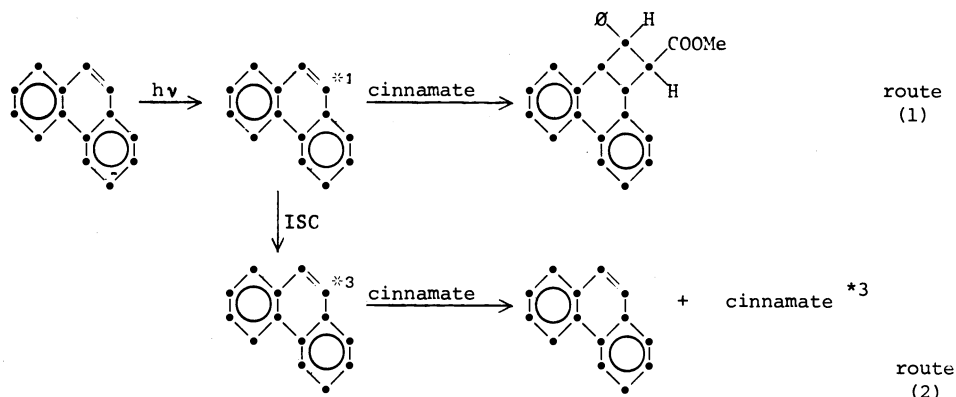
*reacted with the dicinnamate chemically as shown by loss of sensitizer and decrease in amount of dicinnamate.

It is noted that while the aromatic hydrocarbons triphenylene, phenanthrene, 1,2-benzfluorene, 1,2-benzpyrene and pyrene have been considered as triplet sensitizers, they react and disappear during irradiation with bis cinnamates. We decided to investigate hydrocarbons and ketone sensitizers in more detail and as separate classes. Phenanthrene, selected as the model for the group of compounds, was found to definitely react with cinnamate.

The products obtained from the irradiation of phenanthrene in the presence of trans-methyl cinnamate in cyclohexane solution are a mixture of two adducts 1 and 2 in a ten-to-one ratio respectively. The photoaddition of phenanthrene to cis-methylcinnamate yields two isomeric cyclobutanes, 3 and 4, also in a ten-to-one ratio. The structures shown below have been assigned on the basis of the reaction kinetics and nmr spectroscopy.



Though phenanthrene reacts photochemically as the singlet with cinnamate esters, to form cyclobutanes (via route 1, below) it can also function as a triplet sensitizer and simply transfer the excitation polymer energy (route 2). The attachment of phenanthroate and cinnamate moieties to the same polymer backbone should take advantage of both reactions and provide



faster photocrosslinking. Also the mixed crosslinking reaction may have an ionic character in the transition state which might be formed from a pyrylium salt sensitizer. The transition state of the cinnamate dimerization cannot have a charged character and is very poorly sensitized by pyrylium salts.

The desired polymers were synthesized using the appropriate phenanthroic acid chloride, cinnamoyl chloride and poly(vinyl alcohol-co-acetate) and had the following structure and compositions.

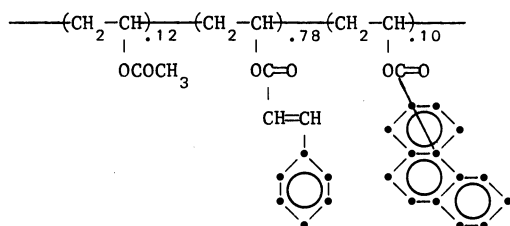


TABLE 7. Percent composition of cinnamate-phenanthrene polymers

| Moiety | A | B | C | D |
|-----------------|----|----|----|----|
| Acetate | 12 | 12 | 12 | 12 |
| Cinnamate | 78 | 78 | 78 | 88 |
| 2-Phenanthroate | 10 | -- | -- | -- |
| 3-Phenanthroate | -- | 10 | -- | -- |
| 9-Phenanthroate | -- | -- | 10 | -- |

The results obtained when the photographic speeds of polymers A, B, C, and D were compared using a typical triplet type sensitizer (BN) and a pyrylium salt sensitizer, 2,4,6-tris(4-methoxyphenyl)pyrylium perchlorate (TPP) are summarized in Table 8.

TABLE 8. Comparison of relative speed of phenanthrene-cinnamate polymers

| Sensitizer | Polymer A | Polymer B | Polymer C | Polymer D |
|--------------------|-----------|-----------|-----------|-----------|
| Unsensitized | 88 | 78 | 20 | 3 |
| BN | 2700 | 2900 | 2900 | 2900 |
| TPP | 100 | 110 | - | 85 |
| Added Phenanthrene | - | - | - | 17 |

The relative speeds of the polymers show that Polymers A and B with phenanthrene attached at the 2- or 3-position were more than 30 times as fast as polymer D, containing no phenanthrene. Polymer C, containing the 9-phenanthroate, crosslinked about 5 times as fast as polymer D. The addition of free phenanthrene to polymer D gave it a rate comparable to polymer C.

These observations are in line with the idea that 2- and 3-substituted phenanthrenes can interact with the cinnamate by both routes 1 and 2 above. The mixed crosslinking reaction is unlikely with the 9-substituted system because of steric hindrance. Furthermore, the photoreaction of the free phenanthrene with the cinnamate cannot yield a crosslink. In the latter two cases, only the triplet sensitization can occur and this is not an efficient process.

The same polymers were then sensitized with BN. All of the speeds were greatly increased, but the phenanthrene polymers are no longer faster. The rates of all of the sensitized reactions are essentially the same. This is quite reasonable since BN absorbs the vast majority of the light and converts it into triplet energy which is transferred to the cinnamate. The phenanthrene singlet is not formed and, therefore, no mixed crosslink is formed.

The addition of pyrylium salt sensitizer resulted in an increase of speed for the polymers tested. The speed was increased slightly more for the phenanthrene containing polymers A and B than for D which had no phenanthrene. However, the rate of crosslinking is still 30 times less than the BN sensitized reaction. As mentioned before, the cosensitization of phenanthrene and TPP would be expected if a somewhat polar transition state can exist for the mixed crosslinking.

In summary, phenanthrene can form an effective photocrosslink when attached on a polymer which also contains cinnamate groups. The phenanthroate, cinnamate copolymers cannot be sensitized to a speed greater than that obtained for poly(vinyl cinnamate).

Another interesting aspect of the photochemistry of cinnamate-aromatic hydrocarbons which grew out of our study involves the consideration of exciplex formation.

The photoaddition of phenanthrene to cinnamate esters is a reaction from the singlet excited state of the aromatic hydrocarbon and is most probably a concerted reaction preceded by exciplex formation. This is supported by the fact that adduct formation parallels the fluorescence quenching by the cinnamate, that the reaction is not triplet sensitizable, and that it is a highly stereospecific reaction. The intermediacy of an exciplex is supported by the fact that the major adducts have the aromatic rings of both moieties in syn position, even if this leads to the most sterically hindered product. Although exciplex emission was not observed from the phenanthrene/cinnamate system, such an emission

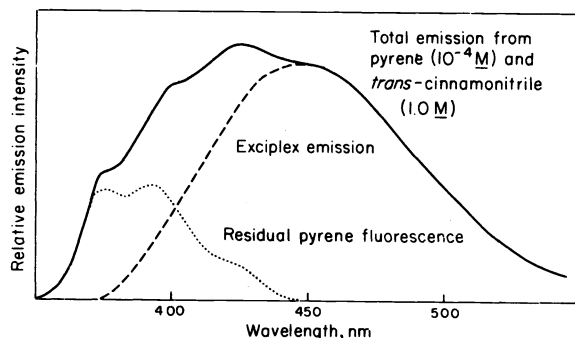
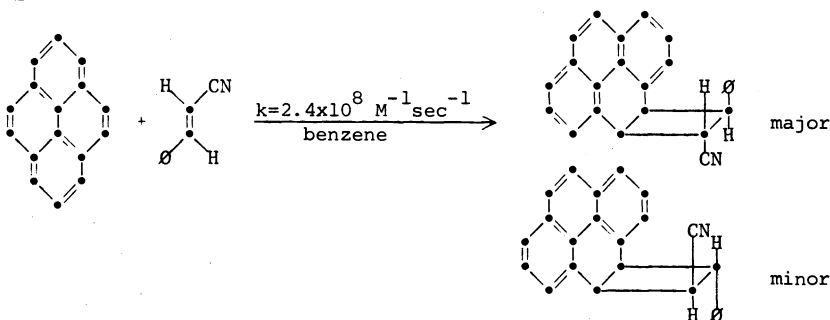
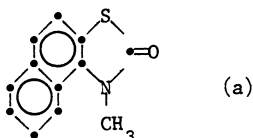


Fig 4 Exciplex emission of pyrene-cinnamitrile

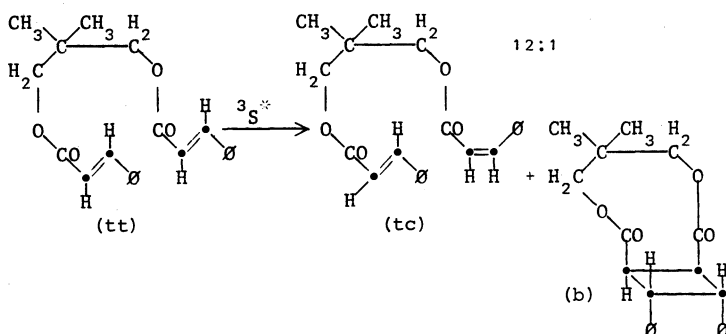
was observed in a very closely related system of pyrene/trans-cinnamitrile. This reaction, like that of phenanthrene, proceeds via the singlet-excited state, is highly stereospecific and the major product has both aromatic rings in syn positions. It is interesting to note that this is the first example of a photocycloaddition reaction of pyrene.



N-methyl-2-benzoyl- β -Naphthothiazoline (BN) was selected to be studied as a typical ketone sensitizer in view of our earlier results using stilbene. To establish the sensitization mechanism of crosslinking of polymers by this complex molecule we investigated some of its own photochemical reactions. In degassed benzene or acetonitrile BN proved to be photochemically stable. In the presence of O_2 , however, degradation to compound (a) takes place. The same product is also obtained via selectively



excited Rose Bengal. Energy transfer from $^3BN^*$ to O_2 followed by attack of singlet oxygen on a ground-state BN forming a dioxetane followed by 2 cleavage to (a) is the most likely mechanism. The involvement of singlet oxygen in the crosslinking reactions is, however, to be ruled out. Extensive flushing of the exposure system with N_2 did not effect the photographic speed. Secondly, typical singlet oxygen sensitizers do not themselves sensitize PVC crosslinking. Any reactions of the singlet-excited BN with cinnamates is also ruled out since the fluorescence of BN is not quenched with methyl cinnamate even at concentrations $>1 M$. Support for triplet-triplet energy transfer to the cinnamates as the only possible reaction was obtained from the following experiment. The primary photochemical products of the triplet-sensitized reaction of the bis cinnamates (trans-trans) are the trans-cis isomer and the cyclization product (b).

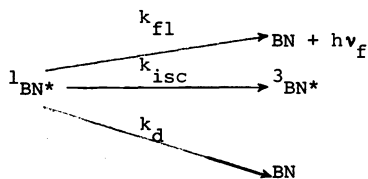


Several triplet sensitizers, regardless of their triplet energies, gave the same product ratio of (tc):(b), 12:1. The sensitizers used were acetophenone, benzophenone, 1- and 2-acetonaphthone and p-nitroaniline. BN gave the same product ratio as the sensitizers. Addition of $^3BN^*$ to the cinnamate moiety and formation of biradicals are, therefore, unlikely to be involved. Surprisingly, however, the triplet yield of this sensitizer for crosslinkable polymers was found to be quite low, especially in polar solvents. The sum of ϕ_{isc} and ϕ_{fl} indicates that the radiationless decay from the singlet excited state must be a major process, at least in solutions.

TABLE 9. Quantum yields of intersystem crossing and fluorescence for BN

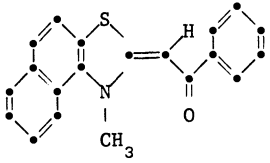
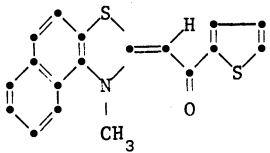
| Solvent | ϕ_{isc} | ϕ_{fl} |
|--------------|--------------|-------------|
| Benzene | 0.24 | 0.012 |
| Acetonitrile | 0.033 | 0.0015 |

Within the limits of experimental error, the ratio of isc/fluorescence is the same in benzene as in acetonitrile although the absolute values drop by almost an order of magnitude on going from benzene to acetonitrile. This probably indicates that the rate of radiationless decay (k_d) is one mainly influenced by solvent polarity.



We prepared several other related derivatives to BN, some of them, notably TN shows higher efficiency for isc. In benzene for example, $(\phi_{isc})_{TN}/(\phi_{isc})_{BN} = 2.5$. The relative

TABLE 10. Quantum yields of intersystem crossing of BN-type ketones versus solvent (polarity)

| | ϕ_{isc} | | |
|---|--------------|-----------------|----------|
| | C_6H_6 | $CH_3COOC_2H_5$ | CH_3CN |
|  (BN) | 0.24 | 0.15 | 0.033 |
|  (TN) | 0.60 | 0.33 | 0.046 |

photographic speed of crosslinking of poly(vinyl cinnamate) (PVC) using BN and TN (excitation at 405 nm, equimolar concentration and equal optical densities) as sensitizers were, however, identical. Michler's ketone (MK), which intersystem crosses to the triplet with practically 100 percent efficiency is also known to be an efficient sensitizer for crosslinking PVC. At equimolar concentrations (0.3 molal) BN and MK have the same optical

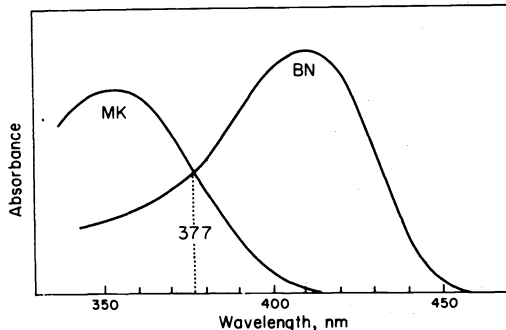


Fig.5 Absorption spectra of MK and BN in PVC Film

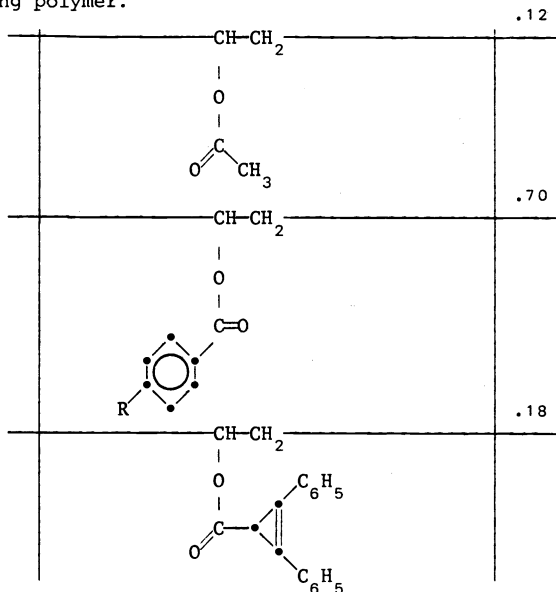
densities at 377 nm. Excitation at this wavelength showed a relative response speed of MK:BN of 1:0.7. We believe that the isc efficiency of BN and TN in PVC matrix is about 0.7, which is much higher than the values measured in ethylacetate. The radiationless decay of BN^* is probably slower in the polymeric matrix. We therefore proposed that in a polymer coating or matrix, that certain energy dissipating pathways which were present in solution do not exist. The role of T_g in controlling solute-polymer interactions is well established. A copolymer was prepared from 1,4-cyclohexanedimethanol condensed with adipic acid, azelaic acid and cinnamylidenemalonic acid (25:25:50), and had a T_g of 16°.

| | |
|--|------|
| $\begin{array}{c} O & O \\ & \\ -C-(CH_2)_4-C- \end{array}$ | 0.25 |
| $\begin{array}{c} O & O \\ & \\ -C-(CH_2)_7-C- \end{array}$ | 0.25 |
| $\begin{array}{c} C & C \\ & \\ O & O \\ & \\ CH & \\ & \\ CH & \\ & \\ C_6H_5 & \end{array}$ | 0.50 |
| $\begin{array}{c} O-CH_2-S-CH_2-O \\ & \\ \cdot & \cdot \\ & \\ \cdot & \cdot \end{array}$ | 1.0 |

The rates of photocrosslinking were determined at 10°, 30°, and 60° using BN as the sensitizer. It was found that there was no apparent decrease in relative photographic response speed at 30 and 60°, temperatures at which one might have expected that triplet yields would be inhibited by conformation relaxation of the polymer. We suggest that the change in molecular dimension of the triplet sensitizer might be too small for the polymer to detect.

The above finding that BN-type sensitizers showed reduced intersystem crossing efficiencies in more polar solvents together with the idea that the same solvents would be expected to promote electron transfer processes of pyrylium type sensitizers led us to compare these two classes of sensitizers in polymer coatings. This was carried out using the diphenylcyclopropene-type polymers prepared and studied earlier by DeBoer²¹ and DeBoer, Wadsworth and Perkins.²²

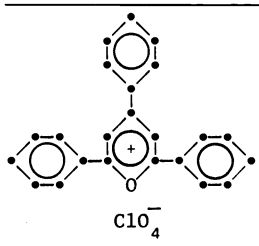
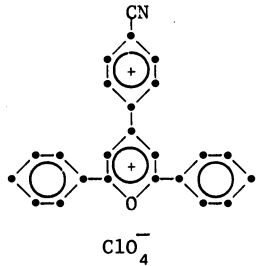
Nitrobenzoate groups were included in one polymer group in order to increase the polarity of the resulting polymer for sensitization comparison with the corresponding unsubstituted benzoate bearing polymer.



where R = H or NO₂.

The data in Table 11 indicates that the presence of nitro groups on the benzoate units attached to the diphenylcyclopropene carboxylate polymers increases the efficiency of

TABLE 11. Relative photographic speed of diphenylcyclopropene carboxylate polymers

| Sensitizer | Relative Speed | |
|---|----------------|-----------------|
| | H | NO ₂ |
|  | 1 | 1.4 |
|  | 1 | 2.5 |
| BN | 1 | 0.01 |

sensitizations by pyrylium salts and at the same time decreases the effect of triplet sensitizers such as BN.

We have shown above that competing chemical reactions can reduce the efficiency of certain sensitizers which previously were believed to operate only by photophysical processes. Aromatic hydrocarbon and pyrylium salt sensitizers react with olefins such as cinnamate. BN is destroyed by self generation of singlet oxygen. There is no doubt that ketones, particularly BN, act as triplet sensitizers. We are unable at the present time to rule out triplet energy transfer processes in favor of an electron transfer process in the case of pyrylium salts since they readily intersystem cross. It can be concluded that an efficient sensitizer for photocrosslinkable polymers must have the following characteristics:

- (a) A high extinction coefficient;
- (b) Undergo efficient intersystem crossing;
- (c) Have sufficiently high triplet energy in order that efficient energy transfer takes place to the photoreactive sites;
- (d) A small singlet-triplet gap is desired in order to extend the polymer response to longer wavelengths;
- (e) Good solubility as well as compatibility with a given polymer system.

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