

## Photocrosslinking of Stilbene-Modified Polymers

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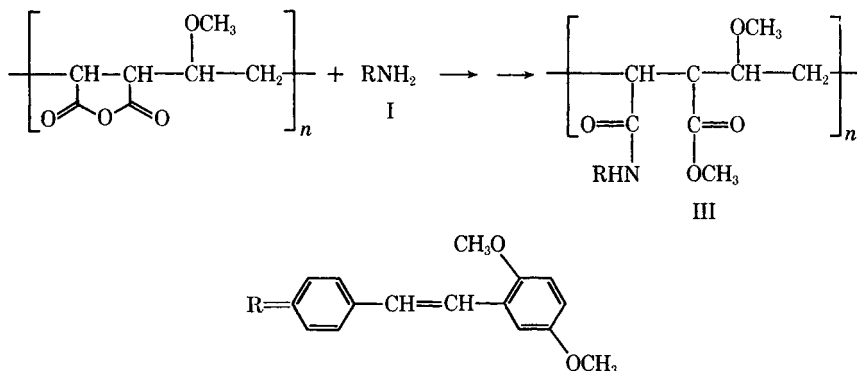
### Synopsis

The reactions of *trans*-2,5-dimethoxy-4'-aminostilbene with poly(maleic anhydride-co-methylvinyl ether) and *trans*-2,5-dimethoxy-4'-isocyanatostilbene with poly(oxy-1,4-phenyleneisopropylidene:1,4-phenyleneoxy-2-hydroxytrimethylene) yield polymeric systems which undergo rapid crosslinking upon short exposure to ultraviolet light. The extent of photocrosslinking as a function of exposure time was determined by the decrease of the *trans*-stilbene ultraviolet absorption at 350 nm.

### INTRODUCTION

Light-sensitive polymer systems are receiving increased attention owing to their broad application, in particular the printing industry. The different chemical aspects of the vast subject have been recently reviewed by Kosar.<sup>1</sup> In order to synthesize a light-sensitive polymer, several methods can be applied: (1) a light-sensitive group can be attached to a reactive polymeric substrate; (2) a vinyl monomer having a light-sensitive substituent can be homopolymerized or copolymerized; or (3) a light-sensitive difunctional additive can be added to a polymeric substrate. Different physical and chemical properties can be achieved depending on the choice of polymer, the light-sensitive group, and the manner by which this unit is linked to the polymer chain. Whether the exposed areas become insoluble or soluble, the systems are referred to as negative or positive resists. To produce a chemical reaction, ultraviolet light is necessary, since the used light-sensitive groups absorb mainly below 400 nm. Depending on the nature of these groups, the spectral sensitivity of the system can be extended into the visible region by the incorporation of appropriate sensitizers. The practical result of this technique is a decrease in exposure time by making a more efficient use of the spectral output of the light sources, and quartz optic is not indispensable. But using sensitized systems requires working under yellow light, and for certain systems the irradiation has to be conducted under nitrogen atmosphere. An example of a light-sensitive polymer system is the polyester obtained by reacting poly(vinyl alcohol) with cinnamoyl chloride (Eastman Kodak's KPR system). The linear polymer dimerizes via the C=C double bond upon irradiation to form an insoluble crosslinked network.<sup>2</sup>

In our recent investigation of the photodimerization of stilbene derivatives,<sup>3</sup> we noticed that electron-donating groups attached to the stilbene moiety enhance the rate of photodimerization considerably. While long exposure times (1–4 hr) were necessary to crosslink polyamides obtained from dimethyl 4,4'-stilbenedicarboxylate, 1,6-hexamethylene diamine, and  $\epsilon$ -caprolactam,<sup>4</sup> a more efficient system was visualized based on our findings. Since the physical properties (hydrolytic stability, abrasion resistance, etc.) of light-sensitive polymers are of importance in actual applications, we selected *trans*-2,5-dimethoxy-4'-aminostilbene (I) and *trans*-2,5-dimethoxy-4'-isocyanatostilbene (II) as light-sensitive substituents. Thus, poly(maleic anhydride-*co*-methylvinyl ether) was reacted with two equivalents of I to yield the polymer amide III, after esterification of the intermediate amide/anilinium salt with methanol.

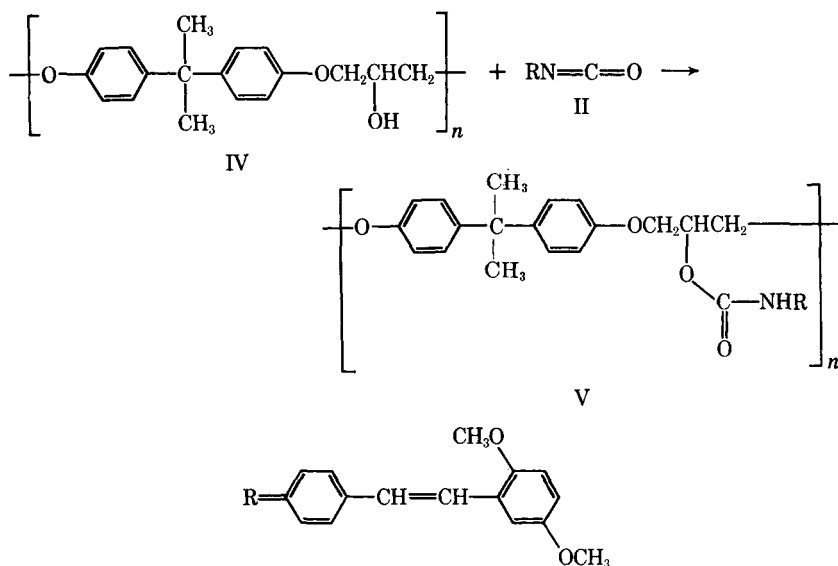


Depending on the used amount of substituted stilbene, the ratio of ester groups in the polymer chain per light-sensitive group can be varied indefinitely.

The isocyanate II can be readily reacted with poly(vinyl alcohol) or phenoxy resins, such as IV, to yield the corresponding polyurethanes. The coatings obtained from polyurethanes have good abrasion resistance. The good solubility in organic solvents prompted the use of IV as the base polymer. Thus, reaction of IV with an equivalent amount of II yielded the polyurethane V.

Polymers III and V form yellow solutions in acetone, tetrahydrofuran, and Cellosolve, and transparent films cast from these solutions are dimerized upon exposure to ultraviolet light via the stilbene double bond. If the stilbene moieties belong to different polymer chains, crosslinking occurs and the linear polymer becomes insoluble in the originally used solvent.

To assess the photosensitivity of a light-sensitive polymer system, different methods have been used. Sonntag and Srinivasan<sup>2</sup> have studied the photochemical behavior of sensitized and unsensitized poly(vinyl cinnamate)-based resists by measuring the loss of unsaturation in the exposed films. Htoo<sup>5</sup> determined the exposure energy requirements for various commercial photoresists; the values corresponded to the point where 100%



of the exposed area became covered with insoluble resist. However, the exposure energy values are a function of the film thickness, the processing conditions, the wavelength region of the light source, and the required resolution. The object of the present study is to determine the effectiveness of crosslinking in the exposed film, i.e., the amount of insoluble polymer formed in the developed image, as a function of exposure time, concentration of light-sensitive groups, film thickness, and type of polymer.

## EXPERIMENTAL

### Polymer III: General Procedure

To a 3% solution of poly(maleic anhydride-*co*-methylvinyl ether) in refluxing dry tetrahydrofuran the required amount of 2,5-dimethoxy-4'-amino-*trans*-stilbene (I)<sup>3</sup> was added. The reaction was followed by infrared spectroscopy (until maximum absorption of the amide band at 5.9  $\mu$  was observed). An excess of methanol was added and refluxing was continued for approximately 16 hr. Addition of carbon tetrachloride precipitated the polymer. Repeated dissolution in acetone followed by precipitation with carbon tetrachloride removed half of the initially used I which was generated in the esterification reaction. The purified polymer was dissolved in acetone and characterized by ultraviolet spectroscopy.

Poly(maleic anhydride-*co*-methylvinyl ether) was obtained from GAF Corp. under the trade name Gantrez AN119; average mol wt is 250,000. The drying of tetrahydrofuran was conveniently conducted by adding the required amount of *p*-toluenesulfonyl isocyanate to the reagent-grade solvent and subsequent distillation. For the calibration of the stilbene-

modified polymer, the ultraviolet absorbance of the N-acetyl derivative<sup>3</sup> of I has been used.

### **Polymers V–VII: General Procedure**

To a 5% solution of poly(oxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxy-2-hydroxytrimethylene) (Bakelite Phenoxy Resin PKHH, Union Carbide Corp., mol wt approx. 28,000) in refluxing dry tetrahydrofuran, the required amount of 2,5-dimethoxy-4'-isocyanato-*trans*-stilbene (II)<sup>3</sup> and a catalytic amount of DABCO were added. The progress of the reaction was monitored by infrared spectroscopy (disappearance of the isocyanate band at 4.43  $\mu$ ). The polymer was precipitated by the addition of methanol and repeatedly dissolved and precipitated. The purified polymer was characterized by UV spectroscopy. For calibration of the polymer, the ultraviolet absorbance of the methyl carbamate<sup>3</sup> of II was used.

### **Light Source**

Irradiations were conducted using a high-pressure mercury arc lamp, type GE H100 A4/T. Sample holder and lamp were mounted on an optical bench to secure reproducible geometry. The lamp consists of a cylindrical glass jacket within which a quartz bulb is supported; the spectral distribution of the radiated light is characterized by five main bands at 365, 404, 435, 546, and 579 nm. The radiant power ratio of ultraviolet light to visible light amounts to about 1:4.

### **Film Preparation**

Films were cast using a Gardner film casting knife for film thicknesses above one micron. For thin films, high-speed whirler coating is the most adequate method. Because coating thickness is a function of whirler speed and solid content of the solution, both parameters had to be adjusted empirically for a specific thickness.

The films were coated on quartz plates  $2 \times 2 \times \frac{1}{16}$  in. To determine the thickness, the absorbance at 350 nm was measured using a Cary 14 spectrophotometer; with the help of a calibration curve the corresponding thickness (mg/cm<sup>2</sup>) to a particular absorbance can be found (Fig. 1).

The films were cast from acetone–Cellosolve solutions for polymer III and from tetrahydrofuran–Cellosolve solutions for polymers V–VII. The addition of Cellosolve was found necessary to prevent a powdery appearance of the film. Prior to exposure to ultraviolet light, the films were dried at 80°C for 5 min.

### **Photocrosslinking**

The resist-coated plates were mounted on a holder allowing the light beam to pass through a circular opening of 1.9 cm in diameter. The same holder was used to measure the absorbance at 350 nm in the Cary 14 spectrophotometer. The distance from the exposure plane to the front of the mercury arc was set at 30 cm. At this distance the intensity of radi-

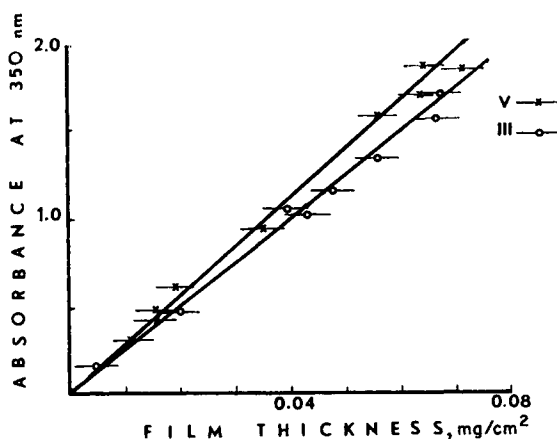


Fig. 1. Absorbance as function of film thickness for polymers III and V.

ation measured with a Blak-Ray ultraviolet intensity meter (Ultraviolet Products, Inc.) was averaging  $170 \mu\text{W}/\text{cm}^2$ , which corresponds at 365 nm to a bombardment of about  $3 \times 10^{14}$  photons per  $\text{cm}^2\text{-sec}$ .

### Processing of the Image

To develop the image, the exposed plates were immersed with agitation and at room temperature in a solvent. The composition of the solvents, shown in Table I, was adjusted so that the unexposed areas were removed within 2 min.

TABLE I  
Solvent Systems Used for the Development of Negative Images

Polymer	No. of polymer units per light-sensitive group	Developer
III	1	methanol, acetone, Cellosolve (30:10:10)
V	1	xylene, Cellosolve, tetrahydrofuran (20:10:1)
VI <sup>a</sup>	2	xylene, Cellosolve, tetrahydrofuran (20:10:5)
VII <sup>a</sup>	10	xylene, Cellosolve, tetrahydrofuran (20:10:10)

<sup>a</sup> Obtained by the reaction of poly(oxy-1,4-phenyleneisopropylidene-1,4-phenylene-oxy-2-hydroxytrimethylene) with the required amount of II.

## RESULTS AND DISCUSSION

To evaluate quantitatively the amount of insoluble polymer formed upon irradiation, the absorbance in the ultraviolet region has been used as criterion. The ultraviolet spectra of typical unexposed films of polymers

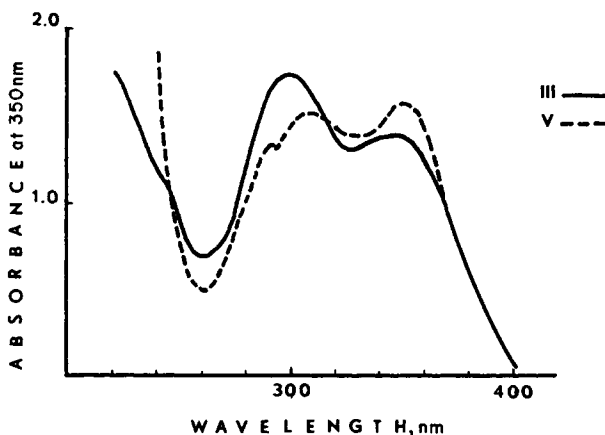


Fig. 2. Ultraviolet absorption spectra of polymers III and V (film thickness 0.056 mg/cm<sup>2</sup>).

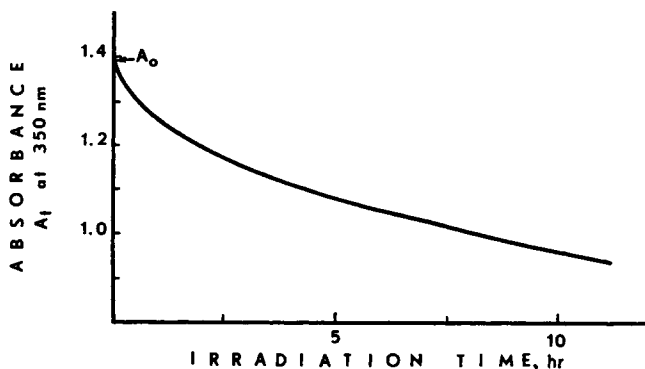


Fig. 3. Absorbance at 350 nm of a polymer III film as function of irradiation time (film thickness 0.056 mg/cm<sup>2</sup>).

III and V are shown in Figure 2. From the calibration curves (Fig. 1) it appears that a linear relationship exists between absorbance and film thickness.

For each experiment the absorbances at the maximum at 350 nm were determined for the unexposed ( $A_0$ ), the exposed ( $A_t$ ), and the processed ( $A_{td}$ ) film. The loss of unsaturation is reflected in the difference  $\Delta A = A_0 - A_t$ , but this decrease in absorbance also includes the amount of isomerization of the *trans*- to the *cis*-stilbene derivative, which absorbs at shorter wavelength and with lower intensity. From a long-term irradiation study it appears that the absorbance decreases first sharply, then progressively to a lesser extent (Fig. 3). This result can be interpreted by the fact that dimerization is more probable at higher double-bond concentration, whereas isomerization is concentration independent. From

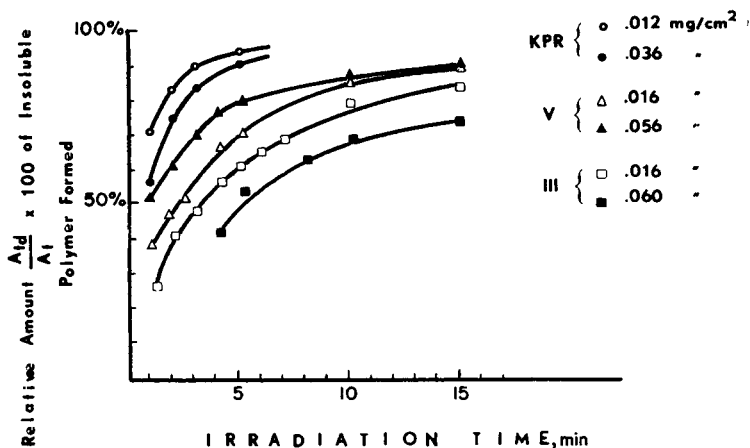


Fig. 4. Relative amount of insoluble polymer formed for three types of resists (KPR, polymers III and V) as function of irradiation time. Irradiations were conducted using a high-pressure mercury arc lamp type GE H100 A4/T.

the decrease in absorbance due to dimerization, one calculates that approximately 1% of the ultraviolet radiation leads to the crosslinking reaction, the rest of the absorbed light being dissipated as fluorescence and radiationless processes.

A large change in solubility of the light-sensitive systems is obtained with a relatively small loss in unsaturation, so that the  $\Delta A$  values will be small and difficult to determine accurately.

To determine the effectiveness of crosslinking following irradiation, the absorbances of the exposed and processed films were determined. The ratio  $A_{id}/A_t$  gives the relative amount of insoluble material formed.

An attempt was made to compare our polymers III and V with Kodak's KPR system. The latter contains a sensitizer so that its spectral response is wider and extends into the visible, whereas our stilbene polymers are excited by the light at 365 nm emitted by the GE H100 A4/T mercury lamp. The comparison has been made without filtering the visible light in order to simulate practical application conditions. Hence, the relative amounts of insoluble polymer formed are given as function of exposure time instead of required exposure energy. For polymers III and V, the required energies can be calculated since for all the exposures the intensity of radiation at 365 nm was kept at  $170 \mu\text{W}/\text{cm}^2$ .

For all the systems investigated, the processed films showed sharp edges already after 1 min of irradiation. KPR shows the fastest increase in insoluble material formed ( $A_t$  and  $A_{id}$  were determined using the absorbance at 274 nm), which can be attributed to the added sensitizer. Nevertheless, polymers III and V, which are not sensitized, are comparable in speed. Direct comparison of the three systems is difficult because of the use of different solvent mixtures in the processing of the exposed films.

The thickness of the films (reported here in mg/cm<sup>2</sup>, which corresponds to 10  $\mu$  for a polymer having unit density) affects the amount of insoluble polymer formed and is dependent on the type of polymer used. Generally, thicker films require longer irradiation times than thinner ones. In the case of polymer V, it appears that because of the increased absorption, the formation of crosslinks is more efficient, but this is only true as long as the upper layer does not absorb all the ultraviolet light. As mentioned before, the efficiency of a light-sensitive system is also dependent on the developer, i.e., the change of solubility with increased crosslinking and the permeability of the solvent through the crosslinked layer.

The effect of the concentration of the light-sensitive groups is depicted in Table II. The drastic drop in the amount of insoluble polymer formed can be explained by the less favorable spacing of the stilbene groups along the polymer chains which would favor isomerization over dimerization. A lower concentration of crosslinker (stilbene moiety) would allow processing of thicker films because the loss of efficiency due to absorbance of this group is reduced. Thus crosslinking throughout the whole layer can be expected. However, longer exposure times would establish a photostationary mixture of *trans*- and *cis*-stilbene, enriched in the *cis*-isomer, the latter contributing to a better transparency.

TABLE II  
Effect of the Light-Sensitive Groups Concentration  
on the Crosslinking Efficiency of the Phenoxy Polymer

Polymer	Rel. amt. of insol. polymer formed, %	Irradiation time, min	Film thickness, mg/cm <sup>2</sup>
V	70	3	0.016
VI	70	45	0.026
VII	14	90	0.020

In the application of polymers III and V to etch a pattern on a copper-clad laminate, resist films with 0.06 mg/cm<sup>2</sup> withstood contact with a 38% ferric chloride solution used to etch the 1-mil-thick copper.

## CONCLUSIONS

It has been shown that stilbene-modified polymers are rapidly crosslinked upon exposure to ultraviolet light. This property renders these polymers useful for photofabrication and printing applications. The ability of light-induced *trans*- to *cis*-isomerization allows for enhanced ultraviolet transparency, because the absorbance of the *cis*-isomer is considerably reduced. While crosslinking occurs, the unreacted stilbene moieties have no light-reactive group in their immediate vicinity and therefore undergo photoisomerization. The photochemical reaction can be conducted in the presence of oxygen because excited singlet-state intermediates are responsible for the



dimerization.<sup>3</sup> The geometry of the polymer backbone has some influence on the efficiency of the dimerization process and the extent of crosslinking is a function of the concentration of light-sensitive groups and the exposure time.

### References

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