Photochemistry of Polymeric Systems.
III. Photocrosslinking of Polymers and Copolymers Including Cyanocinnamylydene–Pyridinium Groups

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Synopsis

Photocrosslinkable polymers were obtained by reacting esters of cinnamic acid or cyanocinnamylideneacetic acid onto pyridine units of a homopolymer or onto a suitable copolymer. These photosensitive polymers were characterized by conventional analysis and spectrometry. The photocrosslinking was studied on thin films measuring the threshold of insolubilization together with UV and IR spectrometry.

INTRODUCTION

In two previous reports[1,2] we studied the photoreticulation of polymeric materials containing aromatic N–oxide groups. In these materials the cleavage of N–O bonds was shown to produce active species in the photocrosslinking process. The aim of the present work was to study the photosensitive materials obtained by binding a photosensitive group to a polymeric chain containing azaaromatic units. The photosensitive group was chosen in the cinnamic series, and a quaternization reaction was used for the binding of this group on pyridine units of the polymer. Such a system allowed the fixation of dyes on free pyridine units of the polymeric materials and the visualization of photoreticulated thin films. The photoreticulation occurs through a 2 + 2 photodimerization.[3–5]

Moreover, it has been shown that the photosensitivity of a cinnamic group can be enhanced when it is bound to a pyridinium group.[6] A spectrophotometric IR and UV study was carried out along with the determination of the conditions of making the polymer insoluble.
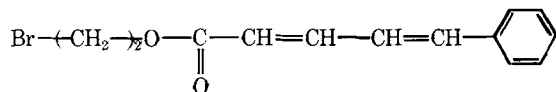
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EXPERIMENTAL

Photosensitive Groups

Ester of Cinnamylideneacetic acid (E_1)

$$Br—(CH_2—)_2O—\underset{\underset{O}{\|}}{C}—CH{=}CH—CH{=}CH—\bigcirc$$

Cinnamylideneacetic acid was synthetized from cinnamaldehyde by a Perkin reaction with potassium acetate and acetic anhydride.[7] The desired ester was obtained by esterification of the acid chloride by bromo-2-ethanol in toluene at 50°C during 1 hr (mp 70°C).

Ester of Cyanocinnamylideneacetic Acid (E_2)
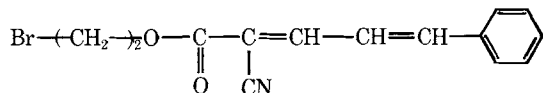
$$Br—(CH_2—)_2O—\underset{\underset{O}{\|}}{C}—\underset{\underset{CN}{|}}{C}{=}CH—CH{=}CH—\bigcirc$$

Cyanocinnamylideneacetic acid was synthetized from cinnamaldehyde by a Perkin reaction with cyanoacetic acid.[7] The ester was obtained as above (mp 120°C).

Ester of Cinnamic Acid (E_3)

$$Br—(CH_2—)_2O—\underset{\underset{O}{\|}}{C}—CH{=}CH—\bigcirc$$
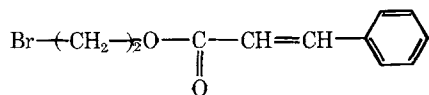
This ester was obtained directly by esterification of cinnamic acid chloride by bromo-2-ethanol in toluene at room temperature during 12 hr (mp 40–43°C).

Monomers

4-Vinylpyridine (4VP), styrene (St) and methyl methacrylate (MMA) were Merck compounds. They were used after distillation by standard procedures. 1-Vinylnaphthalene (VN) was a "Puriss" Fluka, and it was used without further purification. p-Vinylbenzophenone (VBP) was synthesized by pyrolysis of the polymer obtained by Friedel–Crafts benzoylation of polystyrene.[8,9]

Polymers and Copolymers

Homopoly(4-vinylpyridine) (P4VP) and copolymers of 4VP with St, MMA, VN, and VBP were obtained by conventional solution radical polyaddition using α,α'-azobisisobutyronitrile as initiator. All samples were polymerized at 60°C

in vacuum-degassed and sealed tubes. All polymeric materials were recovered by precipitation in a convenient precipitant.

The molecular weight of homopolymer P4VP was determined from viscometric measurements using the relation given by Fuoss[10]:

$$[\eta] \text{ (in ml/g)} = 25.0 M_w{}^{0.68}, \text{ in ethanol at } 25°C$$

For copolymers, DMF was used as the solvent at 27°C. The specific viscosity η_{sp} was determined for solutions at a concentration of 1 g/100 ml. Unfortunately, these values cannot be used to give the values of the molecular weights of the copolymers.

Quaternization Reactions

All quaternization reactions were performed in tetramethylene sulfone (TMS) for compounds E_1, E_2, and E_3. A typical experience was conducted as follows: The polymer (or copolymer) was dissolved in TMS (2 g for 100 ml) at 50°C during 6 hr under nitrogen flow. Then, the ester was added (1.1 mole ester for 1 mole 4VP), and the stirred solution was allowed to react at 70°C during 70 hr. The crude quaternized material was washed many times with the precipitant. A further purification by dissolution and precipitation was necessary.

Analytic Characterization

Spectroscopic Characterization. Spectroscopic characterization of esters and polymeric materials was performed by recording IR spectra (from Beckman IR 18 spectrometer) and UV spectra (from Beckman DB.G spectrometer).

Determination of Pyridinyl Groups. The pyridinyl groups in copolymers were determined using a conductimetric method described by Decout et al.[1]

Determination of Pyridinium Groups. The determination of pyridinium groups allows knowledge of the quaternization percent of the pyridine groups by compounds E_1, E_2, or E_3. The Br^- ions were titrated by a 0.01– or 0.05N $AgNO_3$ solution using a potentiometric method (Tacussel TS 70/N pH-meter, Radiometer P 4011 silver electrode, Radiometer K 401 calomel electrode).

Irradiation Methods, Determination of Illumination Photoresist Test

The preparation of thin films, their irradiation, the determination of the energy received by a given sample, and the photoresist test used for the determination of the insolubilization of the photoirradiated films are described in details in ref. 1. However, a more simple determination of the time needed for insolubilization could be used. A thin film of polymeric material was laid out directly on the polyester support (without bismuth). The irradiation was carried out on this film; and after washing, the photoreticulated spots were visualized by soaking the film in a solution of dye (color index: Acid Red No. 57).

The photosensitivity S was defined as[11,12]

$$S = K/E = K/It$$

where E is the energy needed to insolubilize 1 cm^2 of the film, I is the illumination, t is the time needed for insolubilization, and K is a constant arbitrarily taken

as $K = 1$. This photosensitivity is defined for a given type of irradiation source. However, it is more correct to determine the photosensitivity S_λ at the wavelength λ and to characterize the sample by the variation of S_λ with λ. Such determination were made using a conventional xenon source with a GM 250 Schoeffel monochromator.

In certain cases the photosensitive material was laid out directly on a polyester texture by soaking this texture in a chloroform solution of the polymer. Irradiation and washing were carried out as before, and the determination of the insolubilization was made by dyeing. In this case the photosensitivity is designated S_T.

Spectrophotometric Study of Irradiated Films

These studies were performed exactly like in the case of N-oxidized polymeric materials[1] in order to follow the disappearance of the absorption peaks corresponding to the cinnamic conjugated double bond system.

RESULTS AND DISCUSSION

Polymeric Materials

The conditions of obtaining crude polymers and the determination of their composition are given in Tables I and II. The molecular weight of homopolymer P4VP is $M_w = 165,000$. For copolymers, the specific viscosity is given in Table I.

In Table III are given the quaternization conditions by esters E_1, E_2 or E_3 and the determination of the percent of pyridine groups reacted.

TABLE I
Polymerization Conditions

Sample No.	AIBN, mole/l.	Solvent	Time hr	Precipitant	Conversion %	η_{sp}, ml/g
1	7.4×10^{-2}	Methanol	16	diethyl ether	86	42
2	5.8×10^{-3}	Dioxane	12	petroleum ether	29	32
3	5.8×10^{-3}	Dioxane	12	petroleum ether	31	31
4	5.9×10^{-3}	Benzene	15	petroleum ether	70	67
5	6.8×10^{-3}	Dioxane	15	peroleum ether	25	34
6	6.2×10^{-3}	Dioxane	15	petroleum ether	27	20

TABLE II
Composition of Polymers[a]

Sample No.	F_{4VP}	F_{St}	F_{MMA}	F_{VPB}	F_{4VN}	f_{4VP}	f_{St}	f_{MMA}	f_{VBP}	f_{1VN}
1	1	—	—	—	—	1	—	—	—	—
2	0.060	0.940	—	—	—	0.100	0.900	—	—	—
3	0.096	0.904	—	—	—	0.142	0.858	—	—	—
4	0.100	—	0.900	—	—	0.126	—	0,874	—	—
5	0.040	0.950	—	0.010		0.069	0.902	—	0.029	—
6	0.062	0.929	—	—	0.009	0.107	0.883	—	—	0.011

[a] F refers to the molar fraction in the feeding mixture; f refers to the molar fraction in the polymer or copolymer.

TABLE III
Quaternization Conditions and Composition of Photosensitive Polymers[a]

Sample No.	Reaction temp., °C	Reaction time, hr	Precipitant[b]	Quaternization, %	f_E[c]	λ_{max}, nm
1/E$_2$/20	70	3	3	20	0.20	355
1/E$_2$/30	70	6½	3	27	0.27	355
1/E$_2$/50	70	23	3	50	0.50	355
1/E$_2$/60	70	5	3	62	0.62	355
1/E$_2$/85	70	28	3	85	0.85	355
3/E$_3$	55	20	1 + 2	75	0.11	280
2 E$_2$	70	70	1 + 2	66	0.065	355
4 E$_2$	70	70	1	53	0.067	355
5 E$_2$	70	70	1 + 2	70	0.048	355
6 E$_2$	70	70	1 + 2	67	0.073	355
6 E$_1$	70	70	1 + 2	68	0.074	310

[a] 1/E$_2$/20 refers to polymer no. 1 quaternized by E$_2$ (quaternization 20%), etc.

[b] 1 = Diethyl ether, 2 = petroleum ether, 3 = toluene.

[c] f_E refers to the molar fraction of ester in the polymer.

In order to characterize the UV absorption range of the photosensitive polymeric materials, some films were evaporated from chloroform solutions on quartz plates. Figure 1 shows typical spectra for polymers quaternized with E$_1$, E$_2$ and E$_3$ respectively. The IR characterization of the quaternized materials was carried out from films evaporated on KBr pellets. The band centered at 1420 cm^{-1} corresponding to the pyridine ring disappears when quaternization occurs.

The bands corresponding to esters E$_1$, E$_2$ and E$_3$ appear and are superimposed on those of the polymers. As an example, Figure 2 shows both spectra for pure P4VP (sample 1) and P4VP quaternized by E$_2$ (sample 1/E$_2$/85).
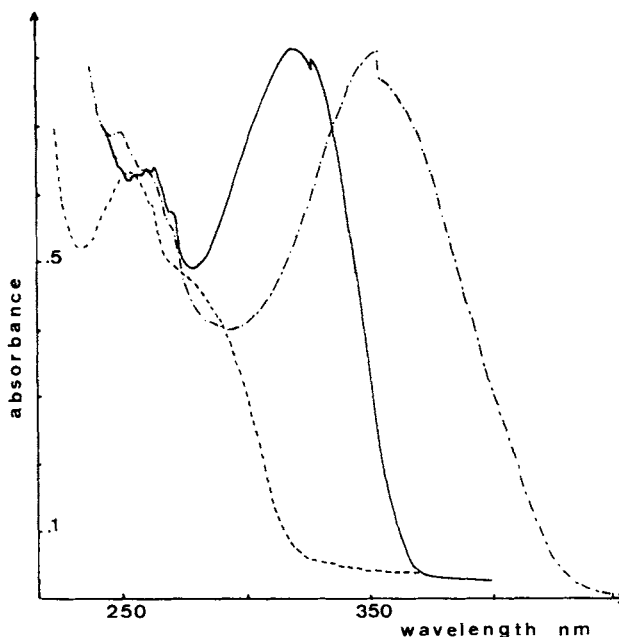

Fig. 1. Ultraviolet spectra of photosensitive polymers: (— · —) 6/E$_2$; (—) 6/E$_1$; (- - -) 3/E$_3$.

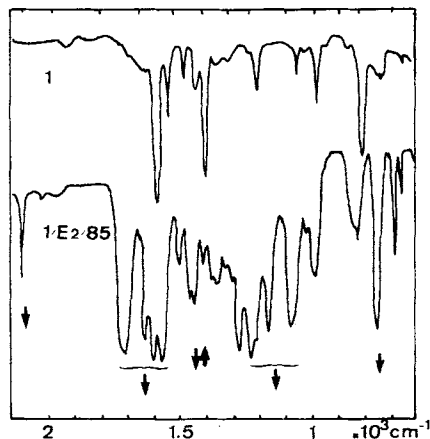Fig. 2. Infrared spectra of pure P4VP (1) and P4VP quaternized by E_2 (1/E_2/85).

Study of Photoreticulation

All samples were irradiated with a high-pressure mercury source (Philips SP 500).

Table IV summarizes the results of the determination of the threshold of insolubilization by the photoresist test in the same conditions of irradiation. The photosensitivity S is directly calculated from the time needed for insolubilization.

If f_E is the molar fraction of ester in a given copolymer, S/f_E represents the photosensitivity rapported to a photosensitive unit of the polymeric material. This value makes available a comparison of different photosensitive groups in different environments.

It can be seen that for Kodak PE 4125 photopolymer,[3] which is one of the best commercial products, $S/f_E = 50$, whereas our 4/E_2 sample exhibits $S/f_E = 164$.

Influence of Photosensitive Ester

The ester E_1 shows the best photosensitivity but its absorption maximum at 310 nm makes its use impossible in the absence of any sensitizer when irradiating through a glass plate. The ester E_3 gives rather poor performances. The ester E_2 was chosen for number of our tests since its absorption maximum appears at 355 nm. Moreover its good thermal stability is another advantage.[7] P4VP was quaternized at different extents by E_2.

Influence of Percent Photosensitive Groups

A systematic study of the influence of the amount of photosensitive ester in a polymer was carried out on P4VP quaternized by E_2. However, for 1/E_2/20, $S/f_E = 100$, whereas for 1/E_2/85, $S/f_E = 29$. This surprising behavior is easily interpreted in terms of screening effect.[13,14] The absorption of the film is so high that only the surface exposed to the light can be crosslinked. The deeper material is not reached by the radiation and remains soluble. A test on a polyester texture avoids this behavior, but the photosensitivities measured are higher due

TABLE IV
Photosensitivity of the Different Polymers[a]

Sample No.	Composition	Development solvent	S, J^{-1} cm^2	S/f_E, J^{-1} cm^2	S_T J^{-1} cm^2	S_T/F_E J^{-1} cm^2	Spectral response λ_{nm}
1/E$_2$/20	4VP 20% QE$_2$	CHCl$_3$–CH$_3$OH (1:1)	20	100	28	142.5	210–430
1/E$_2$/30	4VP 23% QE$_2$	CHCl$_3$–CH$_3$OH (1:1)			77	285	210–430
1/E$_2$/50	4VP 50% QE$_2$	CHCl$_3$–CH$_3$OH (1:1)			166	332	210–430
1/E$_2$/60	4VP 62% QE$_2$	CHCl$_3$–CH$_3$OH (1:1)			166	268	210–430
1/E$_2$/85	4VP 85% QE$_2$	CHCl$_3$–CH$_3$OH (1:1)	25	29	250	294	210–430
2/E$_2$	ST/4VP 6.5% QE$_2$	CHCl$_3$	1.3	20			210–430
4/E$_2$	MMA/4VP 6.7% QE$_2$	CHCl$_3$–CH$_3$OH (1:1)	11	164	15	224	210–430
5/E$_2$	ST/VBP/4VP 4.8% QE$_2$	CHCl$_3$	2.2	45	3.1	65	210–430
6/E$_2$	ST/1VN/4VP 7.3% QE$_2$	CHCl$_3$	1.1	15			210–430
6/E$_1$	ST/1VN/4VP 7.4% QE$_1$	CHCl$_3$	2.6	35			210–360
3/E$_3$	ST/4VP 11% QE$_3$	CHCl$_3$	0.75	7			210–310
KODAK KPR	E$_3$ polyester	ethylene glycol acetate	10	20			
KODAK PE 4125	E$_1$ malonate	butyl phthalate	25	50			

[a] S is the photosensitivity to 250–800 nm light (SP 500 Philips lamp) photoresist test; f_E the molar fraction of ester in the polymer; and S_T the photosensitivity to 250–800 nm light (SP 500 Philips lamp) photoresist test on texture.

to better adhesive properties and to a smaller thickness of the coating. In Table IV it can be seen that the photosensitivity S_T increases with ester E$_2$ content, however, S_T/f_E exhibits a limiting value.

Influence of Composition of Backbone

A study of the influence of the composition of the backbone of the polymers was carried out with a low percent of photosensitive groups E$_2$ (molar fraction of photosensitive units less than 10%). Under these conditions no screening effect was observed. The MMA-4VP copolymer exhibits much better results

TABLE V
Influence of the Addition of 10% in Bulk of Some Photosensitizers

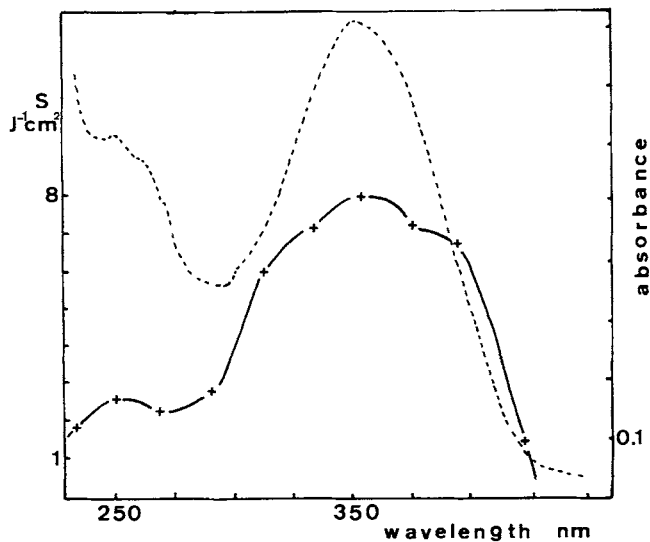| Polymer	Photosensitizer	S, J^{-1} cm^2
2/E$_2$		1.3
2/E$_2$	p-Benzophenone	1.6
2/E$_2$	N-Methyl-2-benzoyl-p-naphthathiazoline (Kodak)	0.6
2/E$_2$	N-Methyl-2-benzoylbenzothiazoline(Agfa)	0.8
2/E$_2$	Michler's ketone	0.4

Fig. 3. (—) Spectral sensitivity of polymer 2/E_2, and (- - -) ultraviolet spectrum of polymer 2/E_2.

than St/4VP copolymers.   For example, the photosensitivity of 4/E_2 sample is $S/f_E = 164$.

However, considering the specific viscosity of 4/E_2 copolymer, it seems that its higher photosensitivity could be the consequence of a higher molecular weight. In the same way, the poor photosensitivity of 6/E_2 could be attributed to a rather low molecular weight ($\eta_{sp} = 20$ ml/g).
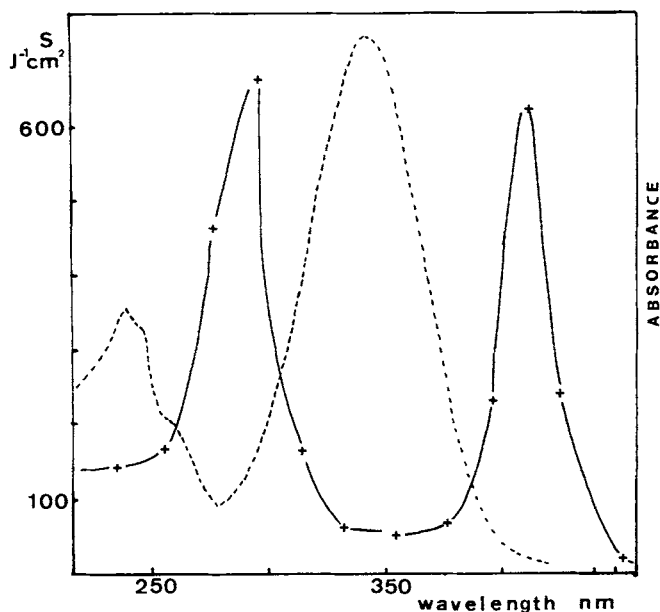

Fig. 4. (—) Spectral sensitivity of polymer 1/E_2/60, and (- - -) ultraviolet spectrum of polymer 1/E_2/60.
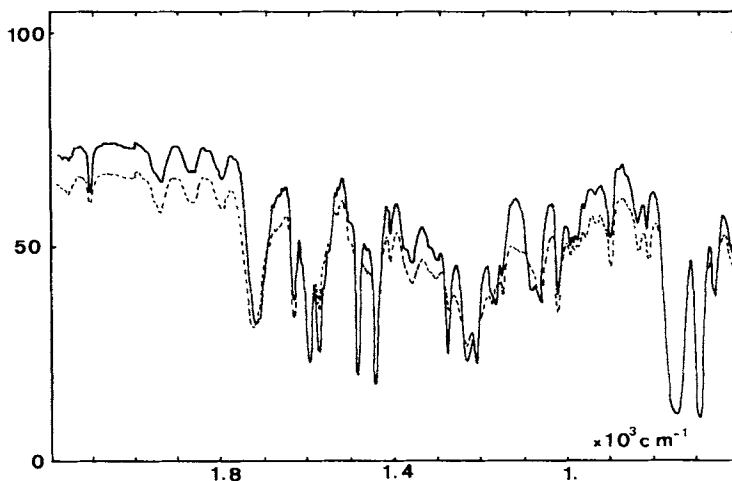
Fig. 5. Infrared spectra of copolymer 2/E$_2$ taken before (——) and after light irradiation (- - -) with a polychromatic source (I = 0.2 W/cm^2).

Influence of Sensitizers

Some conventional triplet-state sensitizers were added to the photopolymers in the bulk. Table V gives the values of the photosensitivity S for 2/E$_2$ after addition of 10% (in weight) of different sensitizers. The addition of benzophenone seems to increase slightly the photosensitivity, whereas the addition of the other compounds decreases the photosensitivity. This type of behavior was described by Williams in the case of styrylpyridinium-substituted vinyl polymers.[5]

Some terpolymers were prepared in order to study the influence of photosensitive species as benzophenone or naphthalene. Significative results were observed in the case of benzophenone.

For the terpolymer 5/E$_2$ including 2.9% vinylbenzophenone, the value of S/f_E is 45, instead of 20 in the absence of vinylbenzophenone.
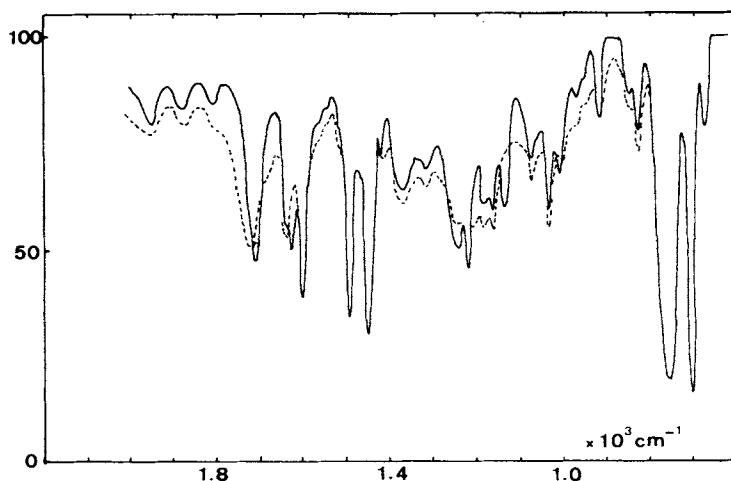

Fig. 6. Infrared spectra of copolymer 6/E$_1$ taken before (——) and after light irradiation (- - -) with a polychromatic source (I = 0.2 W/cm^2).
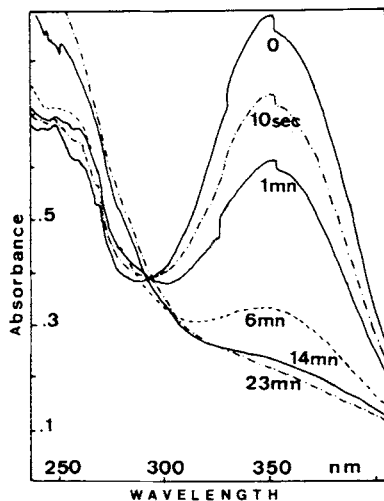
Fig. 7. Changes in ultraviolet spectra of copolymer 2/E_2 with irradiation time.

Spectral Sensitivity

The spectral sensitivity S_λ was determined between 205 and 445 nm with a wavelength width of 20 nm. If no screening effect takes place, the variations of S_λ parallel the absorption spectrum (Fig. 3). If the screening effect described above is present, a minimum of S_λ corresponds to a maximum of optical density of the absorption spectrum (Fig. 4).

Spectroscopic Studies

Typical examples of the IR study of photoreticulation are given in Figures 5 and 6 for 2/E_2 and 6/E_1 copolymers after 10 min of irradiation using the Philips SP 500 polychromatic source (I = 0.2 W/cm^2). The bands assigned to the
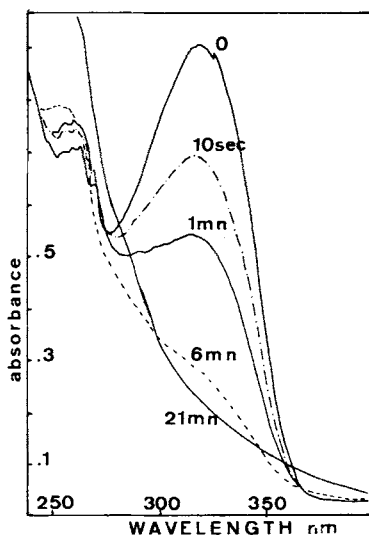

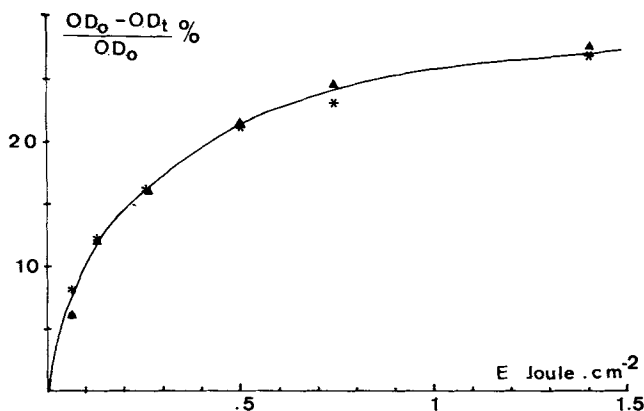Fig. 8. Changes in ultraviolet spectra of copolymer 6/E_1 with irradiation time.

Fig. 9. Reaction rate vs. energy E for copolymers 2/E$_2$ and 4/E$_2$: ($*$) 2/E$_2$; ($\blacktriangle$) 4/E$_2$.

polymeric skeleton are not modified. The carbonyl peak at 1720 cm^{-1} for 2/E$_2$ and 1710 cm^{-1} for 6/E$_1$ are shifted respectively at 1740 cm^{-1} and 1720 cm^{-1}. The intensity of the ester bands at 1290 cm^{-1} for 2/E$_2$ and 1240 cm^{-1} for 6/E$_1$ decreases along with the intensity of the bands assigned to the conjugated double bonds at 1580 cm^{-1} for 2/E$_2$ and 1620 cm^{-1} for 6/E$_1$.

Both phenomena can be interpreted in terms of a decrease of the conjugation of the ester group due to the disappearance of a double bond in the photocycloaddition.[7,15,16]

A UV study of the photoreticulation was carried out on the same samples, namely, 2/E$_2$ and 6/E$_1$. The spectra are shown in Figures 7 and 8 after irradiation times from 1 to 21 or 23 min with the Philips SP 500 polychromatic source ($I = 0.2$ Watt/cm^2). The disappearance of the peaks at 310 nm for 6/E$_1$ and at 355 nm for 2/E$_2$ is due to the disappearance of the conjugated double bond system. These results can be used in simple kinetic calculations. A reaction rate τ_r can be defined as

$$\tau_r = \frac{(OD)_{\lambda,0} - (OD)_{\lambda,t}}{(OD)_{\lambda,0}} \times 100$$

where $(OD)_{\lambda,t}$ is the optical density at the wavelength λ and at time t and $(OD)_{\lambda,0}$ is the optical density at the wavelength λ and at time zero.

It is interesting to see that the results obtained for different copolymers quaternized with the same E$_2$ ester can be represented on a unique curve (Fig. 9). The difference between the sensitivities determined by the use of the photoresist test originate from differences in the composition of the copolymer, the kinetics of photoaddition not being changed.

CONCLUSIONS

High-sensitivity photopolymers were synthetized and studied. The cyanocinnamylidene/pyridinium systems have better performances than conventional cinnamylideneacetic ester systems. A large variety of copolymers can be used to bind the cyanocinnamylidene groups, increasing the field of application of these photopolymers.

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