

A study on phenoxy-resin esters of cinnamylideneacetic acid and its derivatives

Tsuguo Yamaoka, Koji Ueno and Takahiro Tsunoda
Faculty of Engineering, Chiba University, Chiba, Japan 280

and Kazuo Torige

Central Research Laboratory, Mitsubishi Chemical Industries Company, 1000, Kamoshida, Midori-ku, Yokohama, Japan 227

(Received 10 August 1976)

Photocrosslinkable polymers were prepared from phenoxy resin which was photoactivated by esterifying cinnamylideneacetic acid, α -cyanocinnamylideneacetic acid or cinnamylidenepyruvic acid. Relative sensitivities and spectral sensitivities of these polymers were determined by comparing with the phenoxy resin ester of cinnamic acid. It was found that the polymer which was photo-activated with cinnamylidenepyruvic acid had the highest photosensitivity and its spectral sensitivity extended up to 500 nm without the aid of any additional sensitizing dye. The mechanism of the photocrosslinking of these polymers was also considered.

INTRODUCTION

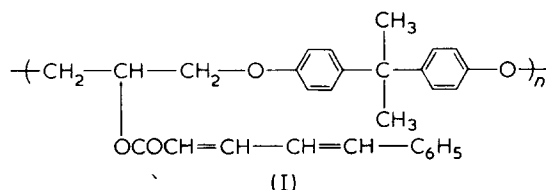
It is expected that a photopolymer prepared from the sensitization of epoxy resin has better properties such as good adhesion to metal surfaces and strong resistance to acidic etchants which are the chemical properties of epoxy resin.

A photopolymer has been prepared from epoxy resin by sensitizing with cinnamic acid¹. This polymer, however, was not sufficient in sensitivity because of the low molecular weight of epoxy resin and the low content of hydroxy group with which cinnamic acid can be reacted to form an ester. In the present study, photopolymers were prepared from phenoxy resin, which is an epoxy resin having higher molecular weight, by sensitizing with cinnamylideneacetic acid, α -cyanocinnamylideneacetic acid or cinnamylidenepyruvic acid. The photosensitivities of the above polymers were studied. When pyrilium or thiapyrilium perchlorate having alkoxy groups on their benzene rings were added to these polymers, the change in sensitizing effect was determined.

EXPERIMENTAL

Synthesis of the photopolymers

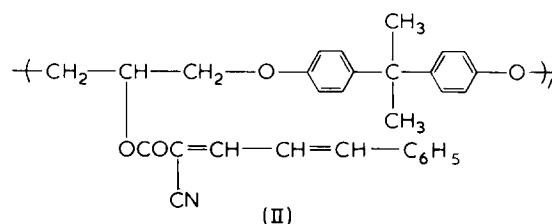
Phenoxy resin cinnamylideneacetate (I) (PhCAc).



Cinnamylideneacetyl chloride was prepared by stirring 5 g of cinnamylideneacetic acid² and 10 ml of thionyl chloride in 10 ml of toluene at 60°–70°C for 1 h, followed by the removal of excess thionyl chloride by passing nitrogen gas through the solution. A solution of cinnamylideneacetyl chloride dissolved in toluene was added gradually to a solu-

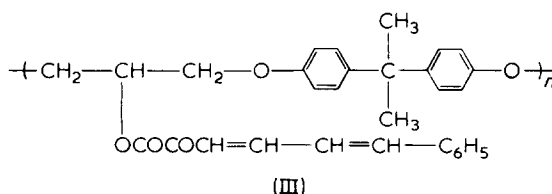
tion of 5 g of phenoxy resin (Epicat PKHH 30 000) dissolved in 50 ml of pyridine. The mixture was stirred for 4 h at ~40°C. The photopolymer (6.5 g) was precipitated by pouring the above mixture into a large volume of ethanol. The degree of esterification was 78%.

Phenoxy resin α -cyanocinnamylideneacetate (II) (PhCNAc).



α -Cyanocinnamylideneacetyl chloride was prepared by chlorination of α -cyanocinnamylideneacetic acid³ using a method similar to that described in the previous section. In this case, the excess thionyl chloride and toluene were evaporated by reducing the pressure. The precipitated chloride was filtered and washed with petroleum ether. Phenoxy resin (8 g), α -cyanocinnamylideneacetyl chloride (8 g) and pyridine (10 ml) were dissolved in 120 ml of dioxane. This solution was kept at 80°C with stirring for 4 h and poured into a large volume of ethanol. PhCNAc (10.2 g) was obtained as a pale yellow precipitate. The degree of esterification was 69%.

Phenoxy resin cinnamylidenepyruvate (III) (PhCP).



Cinnamylidenepyruvyl chloride was prepared by chlorination of cinnamylidenepyruvic acid⁴ using the same method described for α -cyanocinnamylideneacetyl chloride. Ph-

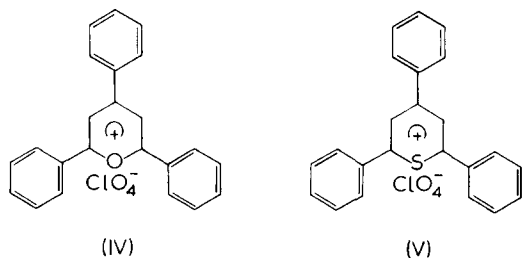
Table 1 Pyriliium salt sensitizers and their parent aldehydes and acetophenones. The absorption maxima of the sensitizers are given in the last column

Pyrilium salts	R ₁	R ₂	Aldehydes	Acetophenones	λ _{max} (nm)
2,4,6-Triphenyl-pyrilium perchlorate	H	H	Benzaldehyde	Acetophenone	355
2,4,6-Triphenylthiapyrilium perchlorate	H	H	Benzaldehyde	Acetophenone	370
4-Anisyl-2,6-bisphenyl-pyrilium perchlorate	MeO	H	Anisaldehyde	Acetophenone	415
4-Anisyl-2,6-bisphenyl-thiapyrilium perchlorate	MeO	H	Anisaldehyde	Acetophenone	420
2,4,6-Trianiylpyrilium perchlorate	MeO	MeO	Anisaldehyde	Acetylanisol	410
2,4,6-Trianiylthiapyrilium perchlorate	MeO	MeO	Anisaldehyde	Acetylanisol	435
4-(4-Amyloxyphenyl)-2,6-bisaniylpyrilium perchlorate	AmO	MeO	<i>p</i> -Amyloxybenzaldehyde	Acetylanisol	415
4-(4-Amyloxyphenyl)-2,6-bisaniylthiapyrilium perchlorate	AmO	MeO	<i>p</i> -Amyloxybenzaldehyde	Acetylanisol	445

noxy resin (3 g) and pyridine (2 ml) were dissolved in 70 ml of dioxane. To this solution, 3 g of cinnamylidene-pyruvyl chloride in 20 ml of dioxane was added dropwise. The solution was stirred for 10 h. PhCP (3.5 g) was obtained as a yellow precipitate by pouring the above solution into a large volume of ethanol. The degree of esterification was 63%. The three photopolymers thus obtained were purified by dissolving each respective polymer in dioxane solution and pouring this solution into a large volume of ethanol. This purifying process was repeated three times.

Synthesis of sensitizers

Pyrilium perchlorates (IV) and thiapyrilium perchlorates (V) were synthesised from benzaldehyde (1 mol) or its derivatives and acetophenone (2 mol) or its derivatives by the method reported by Winzinger *et al.*⁵ Pyriliium and thiapyrilium perchlorates synthesised for this study are given in Table 1 with their parent aldehydes and acetophenones, and their absorption peaks in electronic spectra.



Determination of the degree of esterification

The degree of esterification of photopolymer was determined from the hydroxy equivalent in the photopolymer which did not react in this esterification⁶. That is, the phenoxy resin was acetylated by reacting with acetyl chloride in dioxane in the presence of pyridine, and the excess acetyl chloride in the solution was determined by titrating with sodium hydrochloride dissolved in ethanol using cresol red as an indicator. The hydroxy equivalent of phenoxy resin [α] was determined by the amount of acetyl chloride used for the esterification. Next, the hydroxy equivalent

of the photopolymer [β] was determined by the same method as that for phenoxy resin. The degree of esterification of the photopolymer was calculated using the equation:

$$X(\%) = (\beta - \alpha) / (m + \beta) \times 100 \quad (1)$$

where, $X(\%)$ is the degree of esterification of the photopolymer and m is the molecular weight of cinnamylideneacetic acid or its derivatives used for the photosensitive group.

Measurement of spectral sensitivity of the photopolymer

Photopolymer (2 wt %) and sensitizer (0.2 wt %) (10 wt % of photopolymer) were dissolved in 1:1 mixed solvent of dimethylformamide and dioxane. This solution was then coated by whirling on the surface of an aluminium plate and dried. The thickness of the coating layer was ~10 μm. The plate was exposed to light in a Narumi spectrometer RM-23, equipped with a 500 W xenon arc lamp, and washed with dioxane.

Measurement of relative sensitivity of the photopolymer

The photopolymer coated on an aluminium plate in the method described above was exposed through a step tablet (Kodak No. 2) which was placed in contact with the polymer coating to a 250 W xenon arc lamp at a distance of 40 cm for 5 min, and then washed with dioxane. The relative sensitivity (S_r) was determined by equation (2) proposed by Minsk⁷:

$$S_r = \text{Antilog } D_s / \text{Antilog } D_0 \quad (2)$$

where, D_0 and D_s refer to the absorbances for the standard photopolymer (a phenoxy resin ester of cinnamic acid; the degree of esterification, 76%), and for the unsensitized or sensitized photopolymers synthesised for this study.

Measurements

Electronic and infra-red spectra were measured using a Hitachi 124 spectrophotometer and a Hitachi infra-red spectrophotometer, IRS-2, respectively. Spectra of the

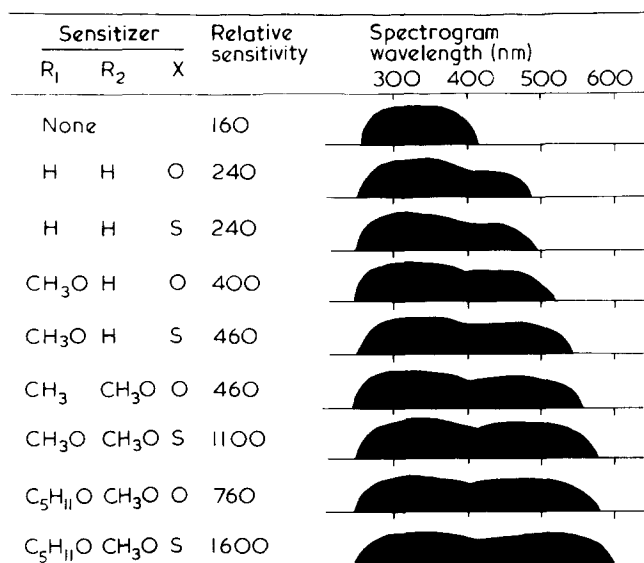


Figure 1 Sensitization of PhCAc by pyrilium and thiapyrilium salts

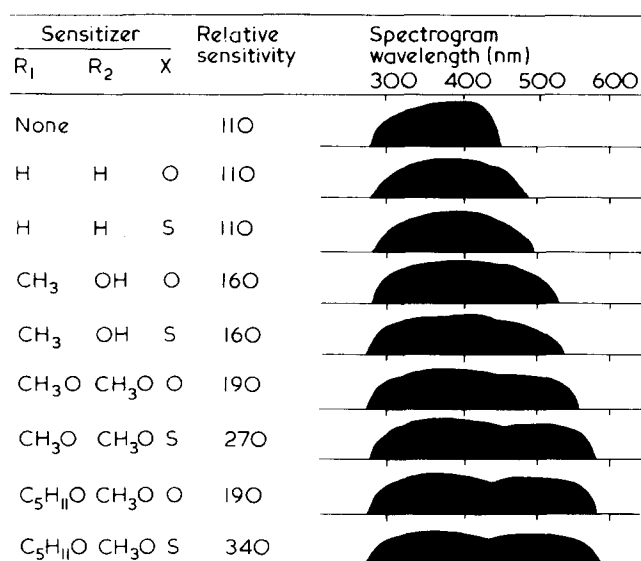


Figure 2 Sensitization of PhCNAc by pyrilium and thiapyrilium salts

photopolymers were measured with their thin film coated on a quartz plate (for electronic spectrum) or on a NaCl plate (for infra-red spectrum). A 250 W xenon arc lamp (Ushio electric Co., UXL-500) was used as a light source.

RESULTS AND DISCUSSION

Photosensitivity of PhCAc, PhCNAc and PhCP

On exposure to u.v., the synthesised photopolymer coatings become insoluble in solvents such as dioxane and methyl ethyl ketone. These photoinsolubilized polymer layers have a strong resistance against acidic etchants such as dilute nitric acid and aqueous solutions of ferric chloride. Relative sensitivities (S_r) and spectral sensitivities of the three polymers are shown in Figures 1–3.

It is seen that even in the absence of a sensitizer, PhCP has a spectral sensitivity up to 500 nm which is the longest wavelength among the three polymers. As can be seen in

Figure 4, the absorption band of PhCP in the electronic spectrum is broader than that of PhCAc or PhCNAc while its absorption peak appears at almost the same wavelength as that of PhCNAc. It seems therefore, that the broadness of the absorption band of PhCP causes its broad spectral sensitivity.

It has been reported that pyrilium and thiopyrilium perchlorates are effective sensitizers for poly(vinyl cinnamylideneacetate). In this study, it was found that pyrilium and thiapyrilium perchlorates spectrally sensitize PhCNAc and PhCP as well as PhCAc, and its effect is increased when alkoxy groups are introduced on the benzene rings as substituents. When the *para* position of each benzene ring in pyrilium salt is substituted by an alkoxy group, the spectral sensitivity of the photopolymer sensitized with these salts shifts to a longer wavelength. This is because the alkoxy group in the benzene ring effects the absorption peak of pyrilium salt to shift its wavelength toward a longer region. The sensitivity of the photopolymer extends to 590 nm when sensitized with 4-(4-amyloxyphenyl)-2,6-bisanisylthiapyrilium perchlorate. The longest wavelength of the spectral sensitivity of the sensitized photopolymer is independent of the photosensitive group in the polymer but depends upon the sensitizer.

The effect of sensitizer is greater in PhCAc than in PhCNAc or PhCP. This is because the latter two photopolymers have relatively high sensitivities which extend up to the long wavelength without the aid of any sensitizer. The infra-red spectra of PhCAc, PhCNAc and PhCP measured before and after u.v. irradiation show clear changes in absorption peaks. For example, when PhCAc is exposed, there is a decrease in intensity of the absorption peak due to $\nu(\text{C}=\text{C})$ at 1625 cm^{-1} , and a shift of the absorption peak due to $\nu(\text{C}=\text{O})$ from 1705 to 1720 cm^{-1} . Likewise on exposure, the spectrum of PhCNAc shows a decrease in the intensity of the absorption due to $f(\text{C}=\text{C})$ of the conjugated double bond, and a shift of the absorption peak due to $\nu(\text{C}=\text{O})$ of carbonyl group to the higher wavenumber. In the spectrum of PhCP, the absorption peak due to the conjugated double bond at 1580 cm^{-1} also decreases on exposure. The stretching vibrations of the two carbonyl groups in PhCP which are different in the bonding force give two absorption peaks at 1680 and 1730 cm^{-1} , res-

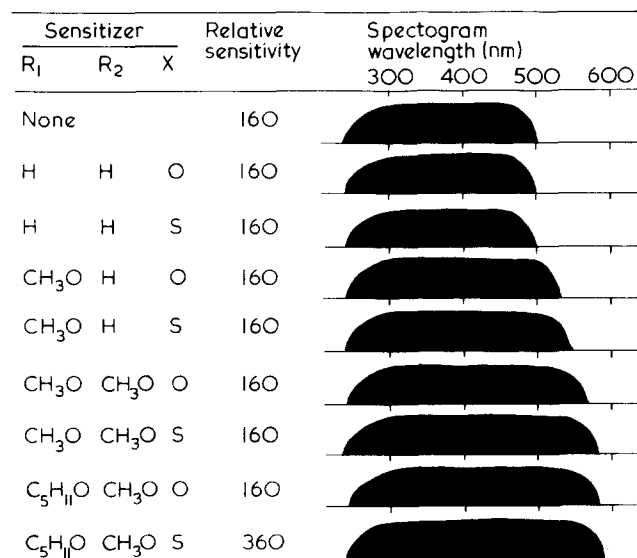


Figure 3 Sensitization of PhCP by pyrilium and thiapyrilium salts

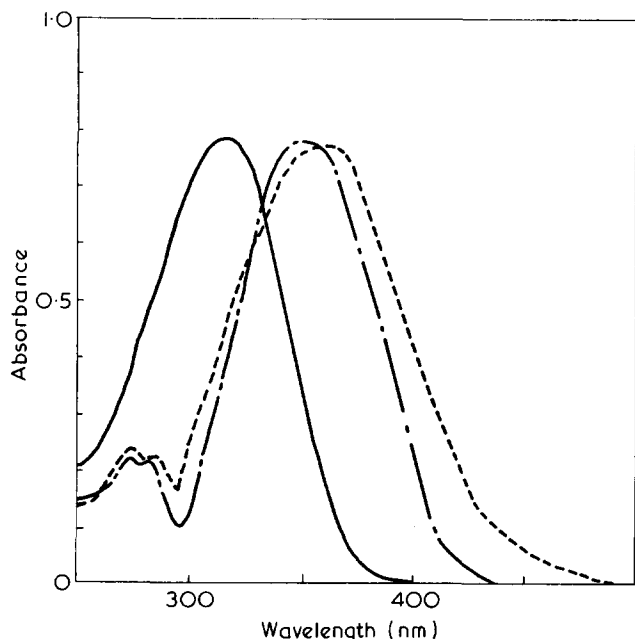
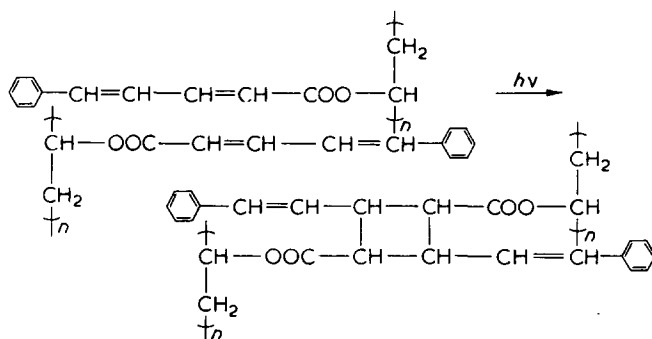


Figure 4 Electronic spectra of PhCAc(—), PhCNAc(---) and PhCP(-·-·-)

pectively. On exposure, the absorption peak of the lower wavenumber decreases and the other increases. As a result of this it is assumed that the two carbonyl groups are isolated from the conjugation system and may become identical in their force constants of the stretching vibration. Figure 5 shows the change in electronic spectra of PhCAc film when exposed to u.v. The absorption peak at 315 nm decreases with irradiation and the final spectrum is almost identical with that of methylstyrene. A similar behaviour in electronic spectrum is observed in PhCNAc and PhCP. With this fact, it can be understood that the double bond which is adjacent to the carbonyl group reacted causing the two carbonyl groups in PhCP to be unconjugated with the styryl group.

It is known that cinnamylideneacetyl and cyanocinnamylideneacetyl group undergo the photodimerization reaction as shown below⁸.



These equations also explain the change of electronic spectra in Figure 5. The photochemical reaction of cinnamylideneacetyl group is not known. However, since the structure and the spectral behaviours of PhCP upon exposure to u.v. resemble those of PhCAc, it is considered that the cinnamylideneacetyl group performs a similar photodimerization reaction.

Reaction rate of the photosensitive groups on irradiation to light

Since the insolubilization of the photopolymers is per-

formed by crosslinking due to the photodimerization of the photosensitive group, the reaction rate of the photosensitive group will govern the sensitivity of the polymers. The photochemical reaction of the sensitive group was followed by the decrease in the absorbance at 300–350 nm in the electronic spectrum of the photopolymer film. The photodimerization reaction is represented by equations (3)–(7):

$$C \xrightarrow{I_0(1-\exp(-2.303\epsilon[c]l))} C^* \quad (3)$$

$$C^* \xrightarrow{k_d} C \quad (4)$$

$$C^* \xrightarrow{k_{ISC}} {}^3C \quad (5)$$

$${}^3C \xrightarrow{k'_d} C \quad (6)$$

$${}^3C + C \xrightarrow{k} C_2 \quad (7)$$

where, C is the photosensitive group in the ground state, C* is the photosensitive group in the singlet excited state, ³C is the photosensitive group in the triplet excited state, C₂ the photodimerized species, I₀ is the intensity of the exposure light, ε is the molar extinction coefficient of the photosensitive group, and l is the thickness of the photopolymer films.

If the stationary state is approximated for [C*] and [³C],

$$-\frac{d[C]}{dt} = \frac{2I_0kk_{ISC}}{k_d + k_{ISC}} \times \frac{[1 - \exp(-2.303\epsilon[c]l)] [C]}{k'_d + k[C]} \quad (8)$$

is obtained. It can be seen from Figure 6 that the exponential term in equation (8) can be approximated to equa-

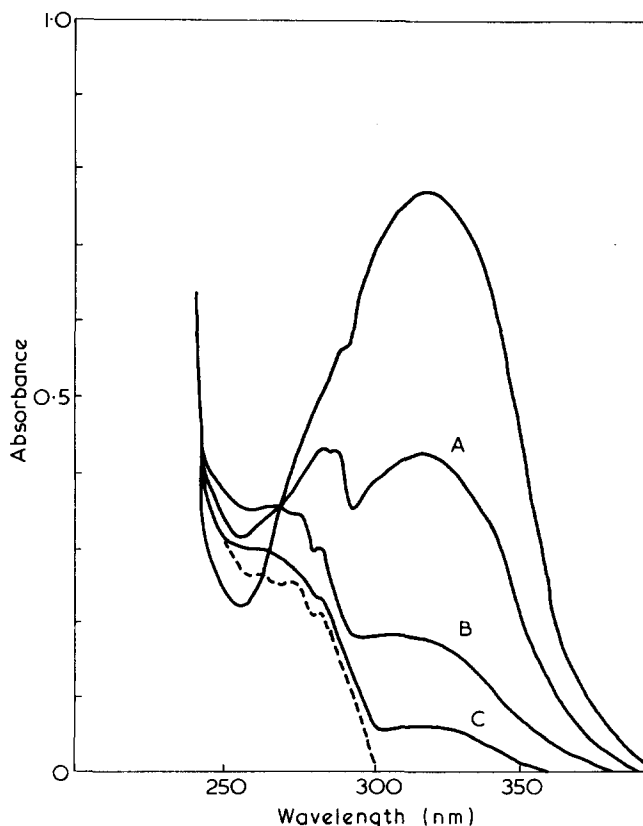


Figure 5 Change in electronic spectrum of PhCAc by u.v. irradiation: A, 1 min; B, 5 min; C, 30 min; ---, methylstyrene

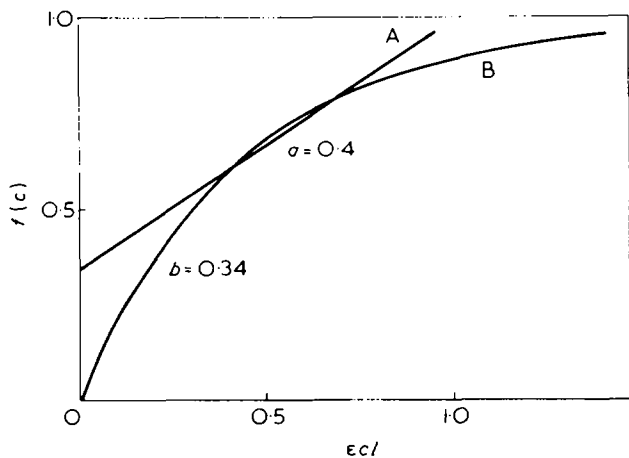


Figure 6 An approximation of the exponential curve by the straight line between the absorbances, 0.4–0.7. A, $f(c) = 0.4\epsilon cl + 0.34$; B, $f(c) = 1 - \exp(-2.303\epsilon cl)$

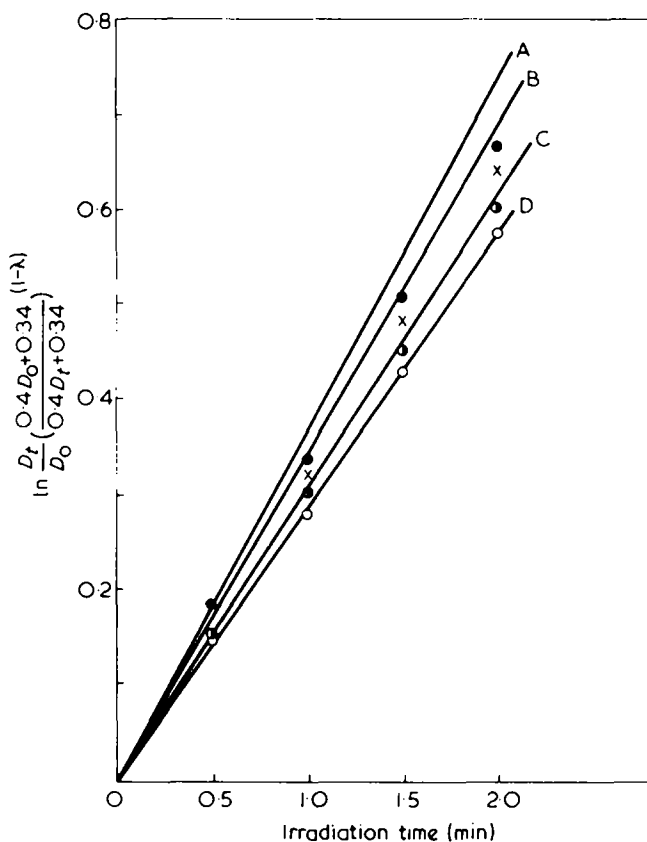


Figure 7 Plots of the absorbance change of PhCP against irradiation time for various λ values based on equation (11) A, $\lambda = 0.3$; B, $\lambda = 0.2$; C, $\lambda = 0.1$; D, $\lambda = 0$

tion (9) as long as the change in the absorbance due to the irradiation with light is not so large.

$$1 - \exp(-2.303\epsilon[c]l) \approx a\epsilon cl + b \quad (9)$$

By substituting equation (9) into equation (8) and then integrating it, equation (10) is obtained.

$$-\frac{2I_0kk_{ISC}b}{(k_d + k_{ISC})k'_d} t = \ln \frac{D_t}{D_0} \left[\frac{(aD_0 + b)}{(aD_t + b)} \right]^{(1-\lambda)} \quad (10)$$

$$\left(\lambda = \frac{bk}{a\epsilon l k'_d}, D = \epsilon[c]l \right)$$

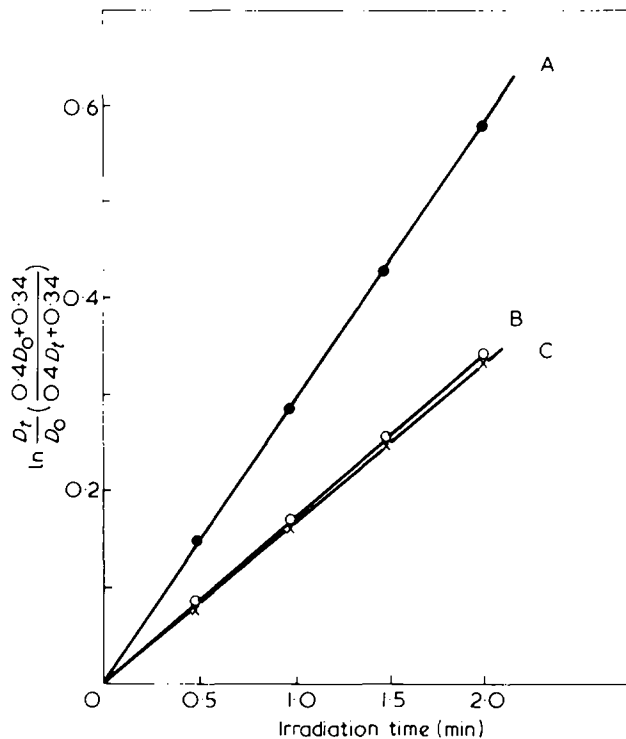


Figure 8 Plots of the absorbance change of PhCP(A), PhCAc(B) and PhCNAc(C) against irradiation time based on equation (12)

Since the initial absorbances (D_0) of the photopolymers are adjusted to 0.7 as shown in Figure 5, equation (11) can be used between the region of the absorbances 0.4 to 0.7, taking 0.4 and 0.34 for the values of a and b , respectively.

$$-\frac{2 \times 0.34 I_0 k k_{ISC}}{(k_d + k_{ISC})k'_d} t = \ln \frac{D_t}{D_0} \left(\frac{0.4D_0 + 0.34}{0.4D_t + 0.34} \right)^{(1-\lambda)} \quad (11)$$

$$\left(\lambda = \frac{0.34k}{0.4\epsilon l k'_d} \right)$$

Figure 7 shows the plots of the experimental values for absorbance changes in the electronic spectra of PhCP against the irradiation times based on equation (11) for various values of λ .

As is seen in Figure 7, equation (11) gives a straight line when λ is zero. This result means that the condition, $0.34k/0.4\epsilon l k'_d \ll 1$ is satisfied for the photodimerization of cinnamylidenepyruvyl group in PhCP film. Equation (12), therefore, can be used instead of equation (11).

$$-\frac{0.68 I_0 k k_{ISC}}{(k_d + k_{ISC})k'_d} t = \ln \frac{D_t}{D_0} \left(\frac{0.4D_0 + 0.34}{0.4D_t + 0.34} \right) \quad (12)$$

The experimental values for PhCNAc and PhCAc also give straight lines when plotted using equation (12) (Figure 8).

From these results, the relative rate of the reaction of the photosensitive groups upon irradiation can be represented by the slope of the straight lines. Figure 8 shows that the slope of the straight line for PhCP is the steepest and therefore, the sensitivity of PhCP is the highest among those of the three photopolymers synthesised in this study.

REFERENCES

- 1 Br. Pat. 921 530
- 2 US Pat. 3 257 664
- 3 Wittig, G. and Kethus, R. *Ber.* 1936, **69**, 2078
- 4 Erlenmeyer, E. *Ber.* 1904, **37**, 1318
- 5 Wizinger, R. and Ulrich, P. *Helv. Chim. Acta.* 1956, **39**, 5
- 6 Lee, H. 'Handbook of Epoxy Resins', McGraw-Hill, New York, 1967, p 4
- 7 Minsk, L. M., VanDeusen, W. P. and Robertson, E. M. *J. Appl. Polym. Sci.* 1959, **2**, 302
- 8 Tanaka, H., Watanabe, I., Nakanishi, H., Honda, K. and Tsuda, M. *26th Annu. Meet. Chem. Soc. Japan* 1972
- 9 Hammond, G. S., Atout, C. A. and Lamola, A. A. *J. Am. Chem. Soc.* 1964, **86**, 3103