

Photo-Crosslinkable Polymers with Benzylideneacetophenone (Chalkone) Structure in the Side Chains

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Synopsis

Four soluble types of polymers have been synthesized by grafting 4- and 4'-chalkonyl glycidyl ethers onto an aromatic polyamine (aniline-formaldehyde linear resin) and a polyamide (condensation product of dimerized linseed oil and an aliphatic polyamine) to obtain photo-crosslinkable chalkone structure in the side chains which are also expected to contain one —OH group each. The completion of grafting reactions has been followed by the disappearance of the epoxide absorption around 918 cm^{-1} . The characterization of the resins was done by melting point, solubility, and IR measurements. Irradiation was carried out with a 100-watt Hanovia high-pressure mercury arc lamp. Irradiated samples were studied by UV spectral measurements and their insolubility in CHCl_3 . It was observed that polymers grafted with 4'-chalkonyl glycidyl ether possibly undergo both isomerization and crosslinking reactions under UV irradiation while those grafted with 4-chalkonyl glycidyl ether undergo crosslinking reaction predominantly.

INTRODUCTION

Unruh¹ and Kato et al.² have reported syntheses, characterization, and photo-crosslinkability of polymers having chalkonyl side chains. Their syntheses are novel and interesting. As polymers having chalkone structure can be of considerable interest in the preparation of photo-resistant resins for use in printing of electronic circuits³ and reproduction by offset printing,⁴ it was thought worthwhile to synthesize photo-crosslinkable polymers having chalkone structure in the side chains through a simpler route with the additional advantage of one —OH group per side chain to provide adhesion on substrate surfaces. In this paper, synthesis, characterization, and photo-crosslinkability of four such resins obtained by curing 4- and 4'-chalkonyl glycidyl ethers with an aromatic polyamine (aniline-formaldehyde linear resin) and a polyamide (condensation product of dimerized linseed oil and an aliphatic polyamine) are reported.

EXPERIMENTAL

Materials

4- and 4'-Chalkones were synthesized after Shriner and Kurosawa⁵ and characterized by their melting points, 173°C and 183°C , respectively.

The IR data in nujol for these compounds were
4-Hydroxychalkone:

$$\nu_{\text{OH}} = 3210 \text{ cm}^{-1} \text{ (s)}$$

$$\nu_{\text{C=O}} = 1648 \text{ cm}^{-1} \text{ (s)}$$

$$\nu_{\text{CH=CH}} = 1635 \text{ cm}^{-1} \text{ (sh)}$$

4'-Hydroxychalkone:

$$\nu_{\text{OH}} = 3130 \text{ cm}^{-1} \text{ (b)}$$

$$\nu_{\text{C=O}} = 1632 \text{ cm}^{-1} \text{ (s)}$$

$$\nu_{\text{CH=CH}} = 1622 \text{ cm}^{-1} \text{ (sh)}$$

Epichlorohydrin was obtained from Dr. Beck and Co., India, and used without further purification.

4- and 4'-Chalkonyl glycidyl ethers were synthesized by reacting the respective hydroxy chalkones with epichlorohydrin in 1:5 molar proportions using 1.5 moles of a 20% aqueous NaOH solution as the catalyst per mole of the hydroxy chalkone. The experimental details for synthesis and purification were the same as described by the author for the syntheses of diglycidyl ethers of dihydroxychalkones elsewhere. Attempts to distill these monoglycidyl ethers under reduced pressure were not successful. They were viscous materials that formed solid crusts when kept exposed to laboratory atmosphere. Characterization of the glycidyl ethers was done by comparing their IR spectra in CHCl_3 with those of their parent hydroxy chalkones.

4-Chalkonyl glycidyl ether (Durrans' melting point 40–43°C):

$$\nu_{\text{C=O}} = 1660 \text{ cm}^{-1} \text{ (s)} \quad \nu_{\text{CH=CH}} = 1632 \text{ cm}^{-1} \text{ (sh)}$$

$$\nu_{\text{C-O-C}} = 1250 \text{ cm}^{-1} \text{ (s)}, \quad \nu \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}-\text{CH}_2 \end{array} = 918 \text{ cm}^{-1} \text{ (s)}$$

λ_{max} (thin film) = 340 $m\mu$, m/e for the $\text{M}^+ = 280$ (a strong peak at $m/e = 92$ indicated that some toluene remained with the resin), soluble in carbon tetrachloride, chloroform, acetone, methyl ethyl ketone, cyclohexanone, benzene, and toluene and insoluble in methyl and ethyl alcohols at 20°C.

4'-Chalkonyl glycidyl ether (Durrans' melting point 30–35°C):

$$\nu_{\text{C=O}} = 1660 \text{ cm}^{-1} \text{ (s)} \quad \nu_{\text{CH=CH}} = 1632 \text{ cm}^{-1} \text{ (w)}$$

$$\nu_{\text{C-O-C}} = 1225 \text{ cm}^{-1} \text{ (s)}, \quad \nu \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}-\text{CH}_2 \end{array} = 918 \text{ cm}^{-1} \text{ (s)}$$

λ_{max} (thin film) = 318 $m\mu$, m/e for the $\text{M}^+ = 280$ (a strong peak at $m/e = 92$ indicated that some toluene remained with the resin), solubility same as that of 4-chalkonyl glycidyl ether.

Polyamine (aniline-formaldehyde linear resin) (No. AFC-M/4) was obtained in commercial packs in viscous form from Dr. Beck and Co.,

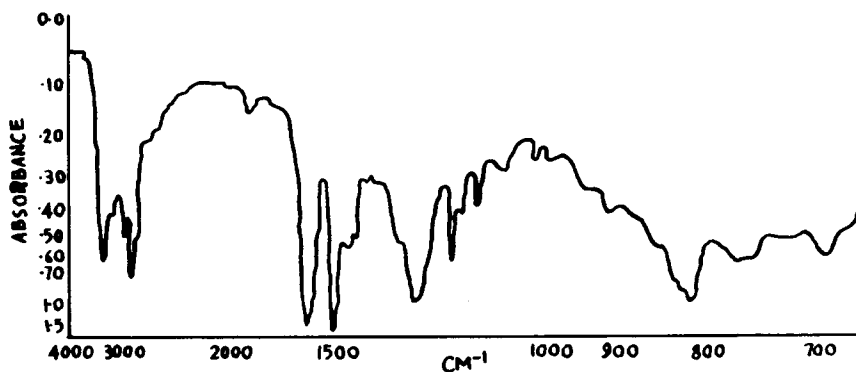


Fig. 1. IR spectrum of commercial polyamine curing agent, taken in a Perkin-Elmer infrachord spectrometer as smear on sodium chloride window.

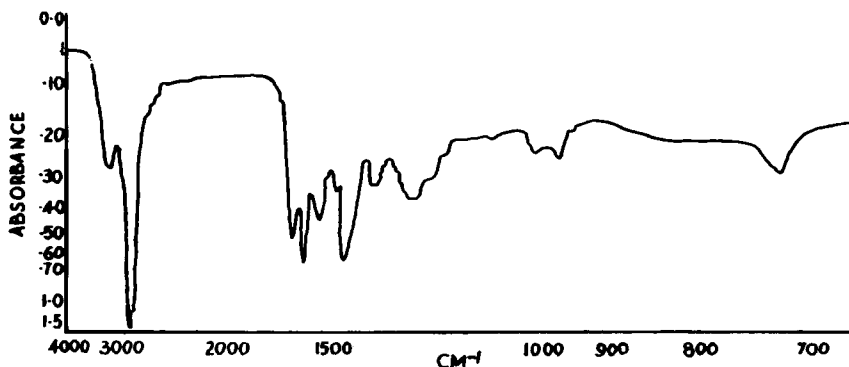


Fig. 2. IR spectrum of commercial polyamide curing agent taken in a Perkin-Elmer infrachord spectrometer as smear on sodium chloride window.

India, and used as received. The IR spectrum of the substance is shown in Figure 1. The resin composition is soluble at 20°C in carbon tetrachloride, chloroform, benzene, and toluene and insoluble in methyl and ethyl alcohols, acetone, methyl ethyl ketone, cyclohexanone, and dimethylformamide.

Polyamide (condensation product of dimerized linseed oil and an aliphatic polyamine) (*No. 771*) was obtained in commercial packs in viscous state from Dr. Beck and Co., India, and used as received. The IR spectrum of the substance is shown in Figure 2. The resin composition is soluble at 20°C in chloroform, acetone, methyl ethyl ketone, cyclohexanone, dimethylformamide and insoluble in methyl- and ethyl alcohols, carbon tetrachloride, benzene, and toluene.

Equipment and Procedures

Synthesis of Polymers with Chalkone Structure in Side Chains. 4- and 4'-Chalkonyl glycidyl ethers were grafted onto the polyamine and poly-

TABLE I
Experimental Details of 4- and 4'-Chalkonyl Glycidyl Ethers Cured with Polyamine and polyamide*

Polymer no.	Name of polymer	Durrans' melting point, °C	$\nu_{C=O}$, cm^{-1}	ν_{CH-CH} in cm^{-1}	ν_{C-O-C} in cm^{-1}	$\nu_{\begin{array}{c} \diagup \\ CH-O \\ \diagdown \end{array}}$ in cm^{-1}	λ_{max} , $m\mu$	Soluble at room temperature in	Insoluble at room temperature in
1	4-Chalkonyl glycidyl ether cured with polyamine	45-47	1656(s)	(—)	1248(s)	none	340 252	chloroform, MEK, cyclohexanone, DMF	carbon tetrachloride, trichloroethylene, methanol, ethanol, acetone, benzene, toluene
2	4-Chalkonyl glycidyl ether cured with polyamide	58-62	1660(s)	1632(sh)	1252(s)	none	340 245	chloroform, DMF, cyclohexanone, trichloroethylene	carbon tetrachloride, acetone, MEK, methanol, ethanol, benzene, toluene
3	4'-Chalkonyl glycidyl ether cured with polyamine	80-85	1658(s)	(—)	1248(s)	none	320	chloroform, MEK, cyclohexanone, DMF	carbon tetrachloride, trichloroethylene, methanol, ethanol, acetone, benzene, toluene
4	4'-Chalkonyl glycidyl ether cured with polyamide	70-73	1658(s)	1632(vw)	1250(s)	none	315	chloroform, cyclohexanone, DMF	carbon tetrachloride, trichloroethylene, acetone, MEK, methanol, ethanol, benzene, toluene

* s = Sharp; sh = shoulder; v.w. = very weak; (—) = cannot be read. The IR data are for $CHCl_3$ solutions, and the uv data are for thin coatings, room temp. = 20°C. All the polymers are light-yellow to brownish-yellow in color.

amide backbones by a simple curing reaction. 4- or 4'-Glycidyl ether, 5.6 parts by weight, was thoroughly mixed with 1.8 and 1.6 parts by weight of polyamine and polyamide curing agent, respectively, at 50°C after heating them separately to the same temperature to increase ease of mixing. The reactions were carried out under a 10-mm vacuum at 50°C for 3 hr and then for 1/hr at 100°C to ensure complete consumption of the glycidyl ethers. The cured products were solids, stable at room temperatures, and could be kept exposed to dull light for short durations. They were characterized by their melting points, solubilities, and IR and UV spectra as recorded in Table I.

IR Spectral Measurement. These were carried out in a Perkin-Elmer No. 221 spectrometer in chloroform solutions.

Preparation of Samples. Polymer coatings were obtained from 2% solutions of the polymers in chloroform on glass slides for insolubility test after irradiation. They were dried at room temperature for 15 min, followed by drying for 5 min at 50°C. All the slides used were degreased in trichloroethylene before any coating was done.

For recording UV spectra of polymer samples before and after irradiation, coatings of suitable thickness were obtained from 2% solutions of polymers in CHCl_3 on one of the outer walls of a required number of 1-cm quartz cells. They were dried as described above.

UV Irradiation. A Hanovia 100-watt high-pressure mercury arc lamp provided with a suitable transformer to strike the arc was used as the UV source. To cut off all the effects of heat produced by the source, it was surrounded with a quartz jacket provided with inlet and outlet tubes for circulation of ice-cold distilled water with the help of a water circulating pump. The source and the jacket were kept at the center of a circular cabinet provided with a lid having a central hole to hold the jacket with the source at its center. Irradiation was carried out by keeping the slides and the cells with their coated surfaces facing the source in suitable holders inside the cabinet at a distance of 6 cm from the source.

UV Spectral Measurements. These were carried out in a Beckmann DK-2 UV visible spectrophotometer. The coated cells were kept in the sample beam with an empty cell in the reference beam.

Insolubility Test for Irradiated Samples. Glass slides having known weights (*A*) of polymer coatings, taken out of the irradiation cabinet after various periods of irradiation, were kept immersed in a chloroform bath for 5 min each, removed, rinsed by three more quick dips, and dried to constant weight (*B*) at room temperature and finally for 5 min at 50°C. From the differences ($A - B$), the per cent insolubles were calculated.

RESULTS AND DISCUSSIONS

Characterization

The reactions between the chalconyl glycidyl ethers and the polyamine or polyamide curing agents were effectively followed by IR spectral measure-

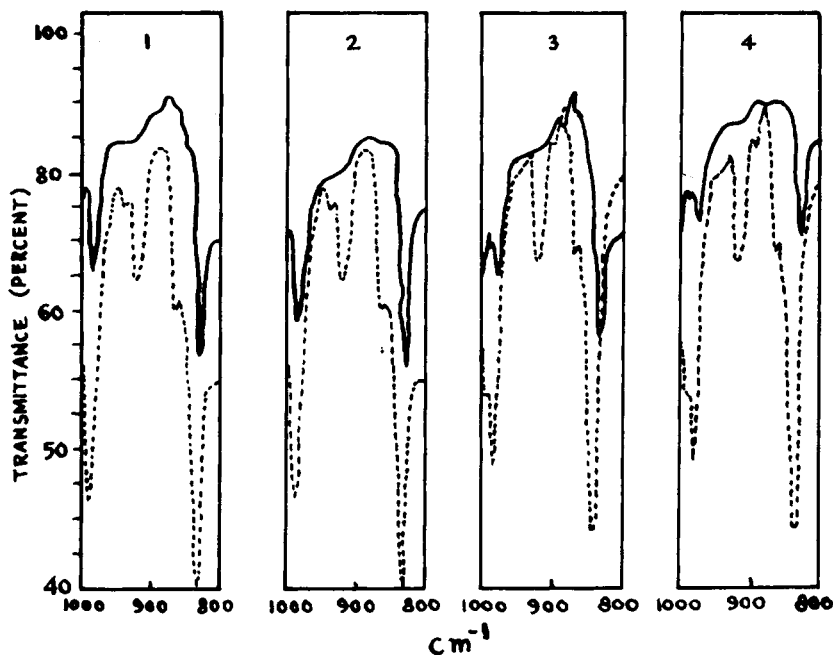


Fig. 3. IR spectra in CHCl_3 for epoxide absorption of (1) 4-chalconyl glycidyl ether cured with a polyamine; (2) 4-chalconyl glycidyl ether cured with a polyamide; (3) 4'-chalconyl glycidyl ether cured with a polyamine; (4) 4'-chalconyl glycidyl ether cured with a polyamide. Dotted lines are for the respective chalconyl glycidyl ethers.

ments in chloroform solutions. The epoxide groups absorbing at 918 cm^{-1} in the glycidyl ethers completely vanished when all the epoxide groups reacted out with the polyamine or polyamide (Fig. 3). This also provides a strong support to the author's earlier assignment of the peak around 915 cm^{-1} to epoxide groups in diepoxides obtained from the condensation of dihydroxychalcones with epichlorohydrin.⁶

Absence of epoxide absorption with polymers 1 and 3 (Table I) was also coupled with appearance of ketonic and ether absorptions originally absent in the polyamine. In the polyamide-cured products such as polymers 2 and 4, the carbonyl and the ether absorptions were not similarly important as the polyamide curing agent also possessed absorption peaks at the same wavelengths.

The only region of some interest in case of polymers 2 and 4 was the $-\text{OH}$ absorption region. Broad absorptions of low intensity starting from 3600 cm^{-1} to 3100 cm^{-1} were consistently obtained with these polymers and also with polymers obtained by curing the two glycidyl ethers with various amounts of polyamide curing agent. Though the glycidyl ethers, owing to presence of traces of water as impurity, and the polyamide curing agent, owing to its $>\text{NH}$ absorption, exhibited narrow and weak peaks in this region, the peaks for polymers 3 and 4 were distinctly different. Poly-

amine-cured products like polymers 1 and 2 had absorptions in this region comparable to those of the polyamine curing agent.

As to the hydroxy chalcones, their glycidyl ethers, and polymers 1-4, the CH=CH absorptions came as weak shoulders after the carbonyl absorptions. In polymers 1 and 3, they could not be clearly read. The CH=CH absorption assignment was done after Bellamy⁷ and two of the author's earlier publications.⁶

The structure-spectrum correlations for the UV spectra are shown in the next section.

Melting points and solubilities of polymers 1-4 (Table I) were helpful for their characterization. Unlike the starting materials, the polymers were solids having Durrans' melting points fairly above room temperature. The melting points of the polyamide-cured products, however, could be increased by using more amounts of polyamide for curing. In case of polyamine-cured products, the increases in the melting points were not equally pronounced when more amounts of polyamine were used for curing. It is also interesting to note that all the polymers (1-4) were insoluble in CCl₄ while the two glycidyl ethers and the polyamide were soluble in CCl₄. Other differences are noted in Table I.

Photo-reactions

It is well known that 4- and 4'-chalcones dimerize or polymerize when irradiated with UV light. In addition to crosslinking reactions, isomerization from the *trans* to the *cis* form had been detected by Unruh¹ for poly(vinyl-*trans*-4'-benzylideneacetophenone) and other related compounds under UV irradiation. He had established that λ_{\max} at 308 m μ in poly(vinyl-*trans*-4'-benzylideneacetophenone) was due to the *trans*-benzylideneacetophenone structure. *Trans*-benzylideneacetophenone itself absorbs at 307 m μ . As an alkyl substituent in the benzene ring does not affect its absorptions to any appreciable extent, as evident from the following data,⁹ Unruh's inference in this regard seems valid:

Compound	Frequency of predominant absorption in UV region
benzene	204 m μ
toluene	207 m μ
ethylbenzene	208 m μ

However, anisole has its predominant absorption at 217 m μ . The marked bathochromic shift is due to the *p*- π conjugation of the methyl ether auxochrome with the benzene ring. Similarly, when a glycidyl ether group was introduced at the 4- and 4'-positions of *trans*-chalcone, the absorptions shifted to 340 m μ and 318 m μ , respectively (the spectra were recorded for thin coatings of the glycidyl ethers on quartz surfaces). However, a glycidyl ether group at the 4-position caused a bigger shift than when it was placed at the 4'-position in *trans*-chalcone. Based on this, it is ex-

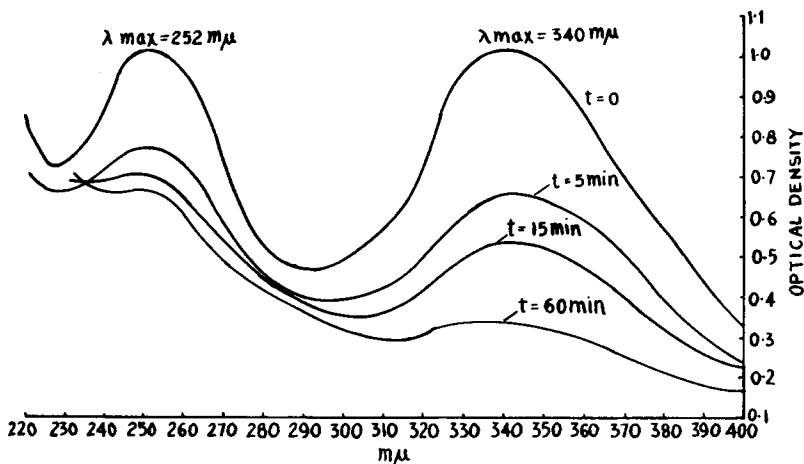


Fig. 4. UV spectra recorded for thin coats of 4-chalkonyl glycidyl ether cured with polyamide before and after various periods of irradiation (t).

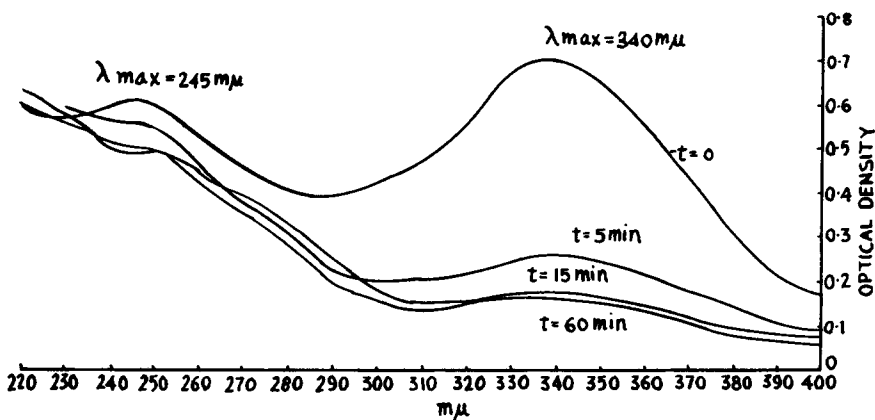


Fig. 5. UV spectra recorded for thin coats of 4-chalkonyl glycidyl ether cured with polyamide before and after various periods of irradiation (t).

pected that the λ_{\max} at 340 $m\mu$ for polymers 1 and 2, 320 $m\mu$ for polymer 3, and 315 $m\mu$ for polymer 4 in Table I (Figs. 4-7) were due to the trans configuration of the chalkonyl structures in the side chains.

After irradiation, if we assume in the line of Unruh's findings¹ that both crosslinking and isomerization reactions were proceeding simultaneously in case of polymers 3 and 4 (Figs. 6 and 7) which have 4'-chalkonyl structure in their side chains, the λ_{\max} of the lower wavelength side of the original peaks might be due to *cis*-chalkonyl structures. These absorptions suffered from bathochromic shifts from the absorption at 266 $m\mu$ of poly(vinyl-*cis*-4'-chalkone) due to the p - π conjugation of the ether oxygen with the benzene ring. In this isomeric configuration, Unruh has argued that the phenyl

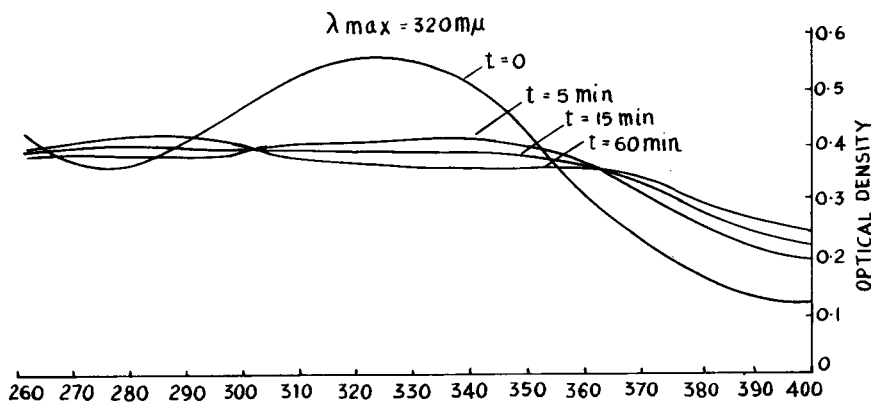


Fig. 6. UV spectra recorded for thin coats of 4'-chalkonyl glycidyl ether cured with polyamine before and after various periods of irradiation (t).

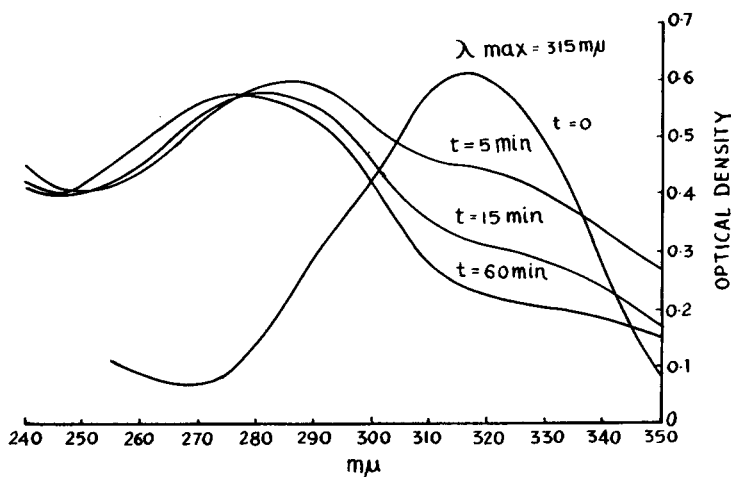
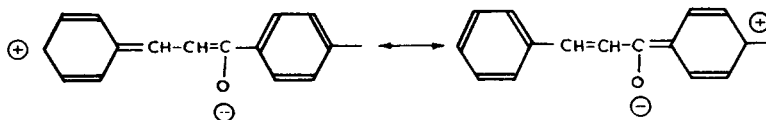


Fig. 7. UV spectra recorded for thin coats of 4'-chalkonyl glycidyl ether before and after various periods of irradiation (t).

ring attached to the double bond is out of the plane of the chalcone skeleton, particularly when the bulky benzoyl group has a large para substituent:



This contracts the resonance, as signalled by an appreciable low wavelength shift of the cis absorption (266 $m\mu$) from that of the trans absorption (308 $m\mu$). This argument is likely to hold good for a large low-wavelength shift of the cis absorptions from their corresponding trans absorptions with polymers 3 and 4.

The situation becomes more difficult when the styryl group acquires a bulky *p*-substituent. In the *cis* configuration, the aplanarity of the styrylbenzene ring is expected to be large enough to inhibit the *trans*-*cis* isomerization reaction. This argument may hold for the complete suppression of isomerization reaction for polymers 1 and 2 with 4-chalkonyl structures in the side chains. As a result, the crosslinking reactions predominated (Figs. 4 and 5).

Crosslinking reactions were also followed by determining the polymer insolubilities in chloroform, as previously described, after various periods of irradiation. In all cases, the polymers exhibited high insolubilities after 5 min of irradiation, when the coatings were very thin in thickness.

CONCLUSIONS

The polymers described in this paper can be called UV-sensitive, one-component epoxy resins. In addition to their use as resists for photo-mechanical processes, they may find applications in the manufacture of special (e.g., antibacterial) paints. The synthesis also can be extended to more such polymers using various polymeric curing agents used for opening the epoxide group.

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