

Photocrosslinkable Unsaturated Polyesters

D. S. SADAFULE and S. P. PANDA, *Institute of Armament Technology, Poona 411025, India*

Synopsis

Nine photocrosslinkable unsaturated polyesters containing pendent chalconyl and cinnamylidenemalonyl moieties have been synthesized by a route involving no water elimination. The resins are insolubilized by visible and UV irradiation. They can also be cured with styrene, MEK peroxide, and cobalt naphthenate. A study of the photoreactions reveals that the resins containing 4'-chalconyl groups crosslink and isomerize simultaneously, whereas those containing 4-chalconyl groups undergo crosslinking only, due to the steric suppression of isomerization. Photoinsolubility is also achieved by introducing the cinnamylidenemalonyl group into the resin structure. It is found that the resins containing both the chalconyl and cinnamylidenemalonyl groups in the repeat units do not exhibit any pronounced photofastness.

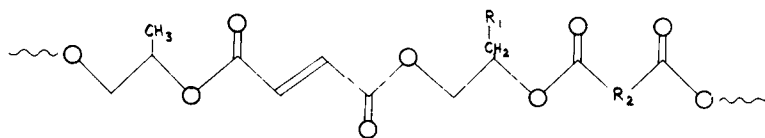
INTRODUCTION

Unsaturated polyesters are mostly used as matrix materials for glass-reinforced plastics, with styrene as the curing agent, MEK peroxide as the catalyst, and cobalt naphthenate as the accelerator.¹ We have been trying to make unsaturated polyesters which are also photocurable so that a layer of the gel coat can be uniformly crosslinked with visible or UV light to obtain better surface properties. In addition, we had two more applications in mind. Such polyesters can be used in photoduplication² processes and reduce the curing time of shipdeck paint primers to 3–4 hr making the painting schedule quicker. Besides, we were also interested in the synthesis of the resins and the study of the photoreactions of chalconyl and cinnamylidenemalonyl moieties occurring separately and together as pendent units of a polymeric chain. The synthesis and the photocrosslinkability of the following resins are reported in this paper (Scheme I).

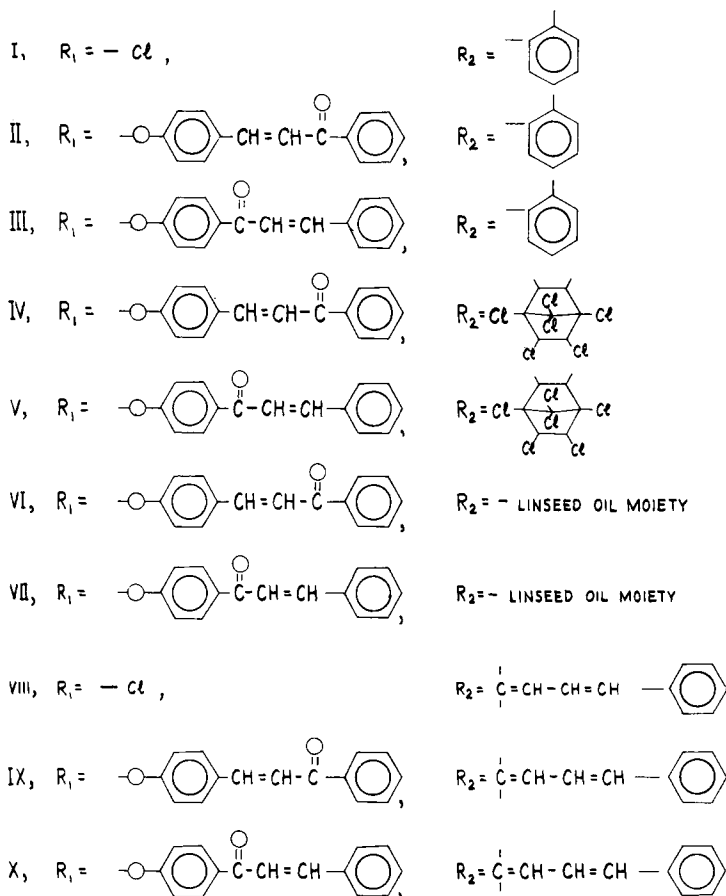
EXPERIMENTAL

Materials

4-Chalconyl and 4'-chalconyl glycidyl ethers were synthesized by reacting the respective hydroxy chalcones with epichlorohydrin in 1:5 molar proportions using 1.5 mole of a 20% aqueous NaOH solution as the catalyst per mole of the hydroxy chalcone.³ Cinnamylidenemalononic acid was synthesized after Bansal and Pandya⁴ by reacting cinnamaldehyde (0.01 mole, 1.32 g), malonic acid (0.01 mole, 1.04 g), and pyridine (0.0015 mole, 0.13 ml) as the catalyst. The reaction mixture was heated on a water bath for 1 hr. The reaction started immediately, and the mixture changed into a homogeneous liquid in 5 min. In another 15 min a yellow solid began to separate. The entire reaction mixture turned solid after 1/2 hr of heating. The heating was continued for another 1/2 hr. The reaction product was cooled, crushed, and dissolved in aqueous sodium carbonate solution. Unreacted cinnamaldehyde was extracted out with ether.



GENERAL POLYESTER CHAIN



Scheme I

The sodium carbonate solution of the reaction product was acidified with 1:1 HCl and ice when a yellow solid precipitated. It was filtered under suction, washed with distilled water several times to make it free from acid, and washed with hot benzene to remove cinnamylidene acetic acid formed during the reaction in small percentage. The product thus purified was dried and crystallized from alcohol thrice to obtain bright-yellow needles, mp 206–208°C.

Synthesis of the Unsaturated Polyester Resins

The unsaturated polyester resins were synthesized by the method of Sikorski and Puszyn'ski⁵ that did not involve any elimination of water. The method was slightly modified to suit our system as follows. In a round-bottom flask of 100

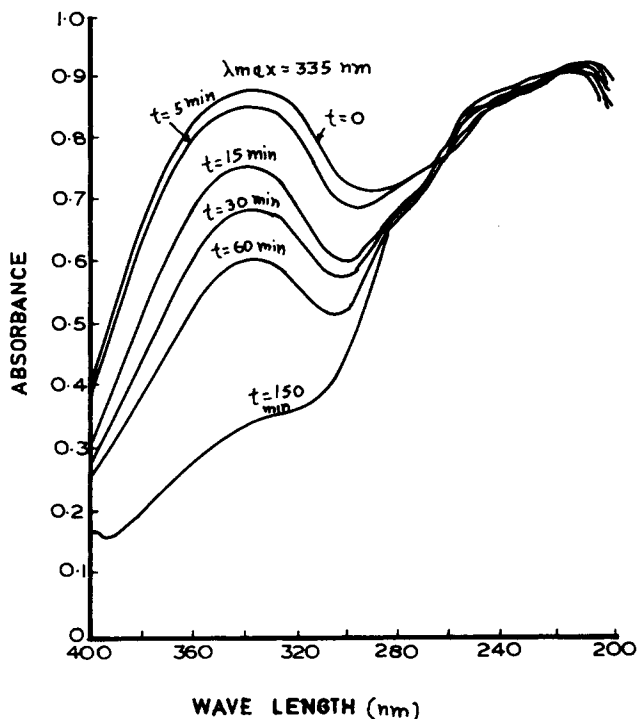


Fig. 1. UV spectra of polyester IV made from propylene glycol, maleic anhydride, glycidyl 4-chalconyl ether, and chlorendic acid after different periods of irradiation (t).

ml capacity equipped with a mechanical stirrer and a reflux condenser were placed an epoxide (epichlorhydrin, 4- or 4'-chalconyl glycidyl ether, 0.04 mole), propylene glycol (0.01 mole), maleic anhydride (0.02 mole), and an anhydride or acid (phthalic anhydride, chlorendic acid, linseed oil, or cinnamylidenemalonic acid, 0.02 mole) and heated for a period of 36 hr at 150°C in a liquid paraffin bath. When cinnamylidenemalonic acid was one of the reactants, to avoid decomposition of the acid to its monocarboxylic derivative and thermal crosslinking of the polyester resin, the heating schedule was modified to 18 hr at 100°C, 15 hr at 120°C, 2 hr at 150°C, and 1 hr at 180°C. Resin I was colorless, whereas all others were yellowish, translucent materials. All the resins were readily soluble in acetone, chloroform, and ethyl acetate and insoluble in alcohol, carbon tetrachloride, and toluene. The number-average molecular weight of the resins were measured in acetone solutions with the help of a Mechrolab vapor phase osmometer Model 301 A. The results are recorded in Table I.

RESULTS AND DISCUSSION

IR Spectra of the Resins

The IR spectral measurements were carried out by smearing the resins on a sodium chloride window or preparing mulls in Nujol, using a Perkin-Elmer No. 221 double-beam spectrometer. The results are given in Table I. The resins

TABLE I
Molecular Weight and Spectral Characteristics of Copolyesters^a

No.	Copolyesters	Molecular weight	λ_{\max} , nm	ν -OH, cm^{-1}	$\nu > \text{C}=\text{C}$, cm^{-1}	ν -C(=O)-O-, cm^{-1}	$\nu > \text{C}-\text{O}-\text{C}$, cm^{-1}
I	Propylene glycol + maleic anhydride + epichlorohydrine + phthalic anhydride	540	—	3450(b,vw)	1640(w)	1725(s)	1300-1200(b,s), 1200-1100(b,s)
II	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + phthalic anhydride	617	345	3370(b,vw)	1660(m)	1730(s)	1260(m), 1220(m), 1180(m)
III	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + phthalic anhydride	602.6	320	3400(b,m)	1660(m)	1730(s)	1265(m), 1225(m), 1130(m)
IV	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + phthalic anhydride	912.6	333	3420(b,w)	1652(s)	1725(s)	1250(m), 1215(m), 1175(m)
V	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + chlorendic acid	1305	315	3440(b,m)	1652(s)	1725(s)	1260(s), 1220(s), 1175(s)

VI	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + linseed oil	681	335	3420(b,m)	1652(w)	1725(s)	— ^b
VII	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + linseed oil	817.6	315	3430(b,m)	1655(w)	1725(s)	— ^b
VIII	Propylene glycol + maleic anhydride + epichlorohydrine + cinnamylidenemalonic acid	867	330	3450(b,m)	1650(sh)	1715(s)	1300–1210(b,s), 1200– 1160(b,s)
IX	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + cinnamylidenemalonic acid	539	335	3440(b,s)	1655(m)	1725(s)	1260(s), 1220(s), 1175(s)
X	Propylene glycol + maleic anhydride + glycidyl 4'-chalconyl ether + cinnamylidenemalonic acid	566	315	3430(b,s)	1650(w)	1710(s)	— ^b

^a s = strong; m = medium; w = weak; vw = very weak; b = broad; sh = shoulder.

^b Strong flat absorption without any peak.

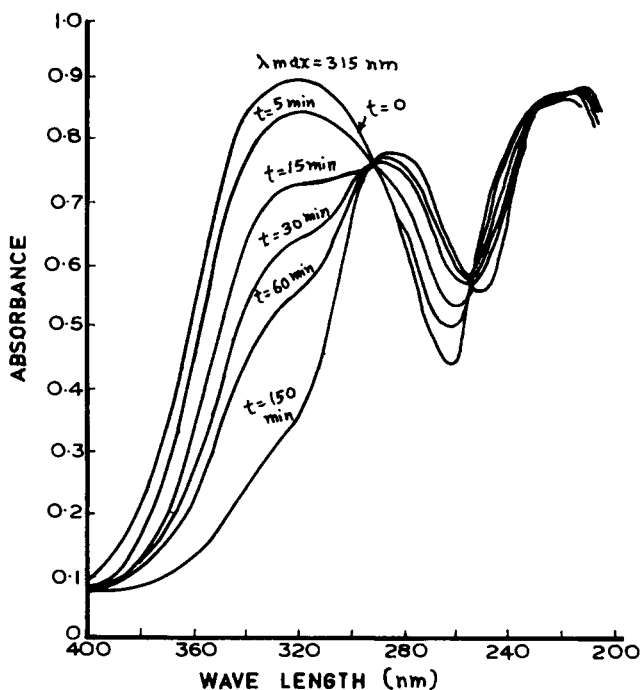
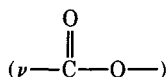


Fig. 2. UV spectra of polyester V made from propylene glycol, maleic anhydride, glycidyl 4'-chalconyl ether, and chlorendic acid after different periods of irradiation (t).

were characterized by the absence of anhydride peaks at 1820 and 1760 cm^{-1} and the epoxy asymmetrical stretching absorption around 915 cm^{-1} . The ester peak



at 1710 – 1730 cm^{-1} was the most characteristic of the resins. It was supported by the presence of the asymmetrical ether stretching peaks ($\nu > \text{C}-\text{O}-\text{C} <$) coming around 1180 and 1250 cm^{-1} .⁶ In the case of resins I and VIII (Table I), these peaks were broad and strong. For resins VI, VII, and X, the asymmetrical ether peaks could not be read due to the absorption becoming almost flat in this region. All the resins having the chalconyl moiety retained the carbonyl absorption coming at 1650 – 1660 cm^{-1} . Resins VIII had no chalcone group. It showed only a shoulder at 1650 cm^{-1} assigned to the carbonyl group of the cinnamylidenemalonyl structure. However, resin I had a weak peak at 1640 cm^{-1} due to the carbonyl group of the maleic anhydride residue in its structure. This absorption, though expected to be present in all the resins, was completely blurred by strong to medium carbonyl absorptions arising from the chalconyl and cinnamylidenemalonyl structures.

Broad absorptions in the $-\text{OH}$ stretching region were the most irregular making any conclusion difficult. However, the peak absorptions in this range are given in Table I, which may be due to the terminal hydroxyl and carboxyl

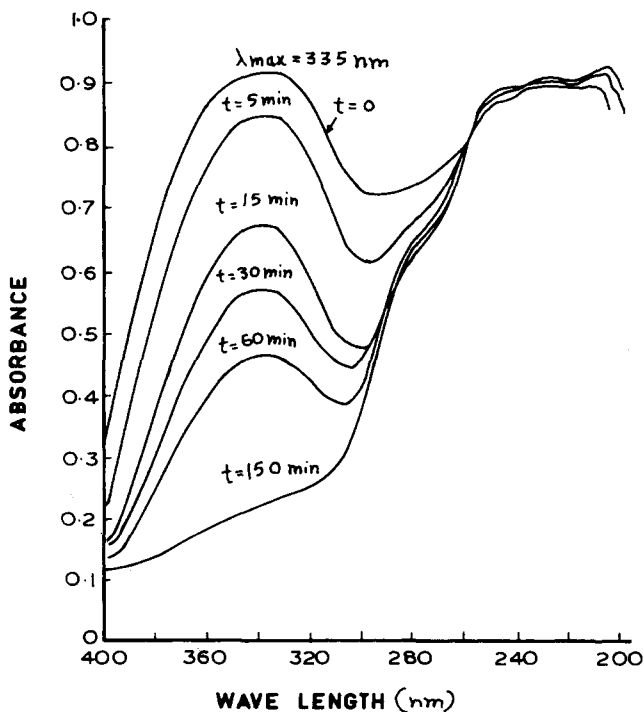


Fig. 3. UV spectra of polyester VI made from propylene glycol, maleic anhydride, glycidyl 4-chalconyl ether, and linseed oil after different periods of irradiation (t).

groups. It was not possible to characterize the resins with the help of the specific IR absorption of their double bonds. The presence of maleic anhydride unsaturations was confirmed by crosslinking all the resins at room temperature using styrene (0.3 part by weight per 1 part of the resin), MEK peroxide (0.03 ml per 1 part of the resin), and cobalt naphthenate (0.03 ml per 1 part of the resin). The resins having chalconyl and cinnamylidenemalonyl moieties can be readily cured by sunlight and UV light, indicating the presence of photosensitive unsaturation. Further, the trans nature of chalconyl and cinnamylidenemalonyl double bonds was evidenced by their λ_{max} values given in Table I.

Photoreactions

Photocrosslinkability of the resins were tested by obtaining coatings from acetone or chloroform solutions or by smearing the molten resins on glass slides to 0.002 cm thickness and exposing them to sunlight between 9 AM to 1 PM during the period March to July. All the resins except resin I turned hard and insoluble in chloroform or acetone after 3–4 hr of exposure. For UV irradiation, a Hanovia 100-W high-pressure mercury arc lamp was used as the source. Details of the irradiation procedure have been described elsewhere.³ Thin coatings of the resins from a 2% solution in chloroform were obtained on one of the transparent sides of quartz cells used for UV spectrophotometers. The crosslinking of the

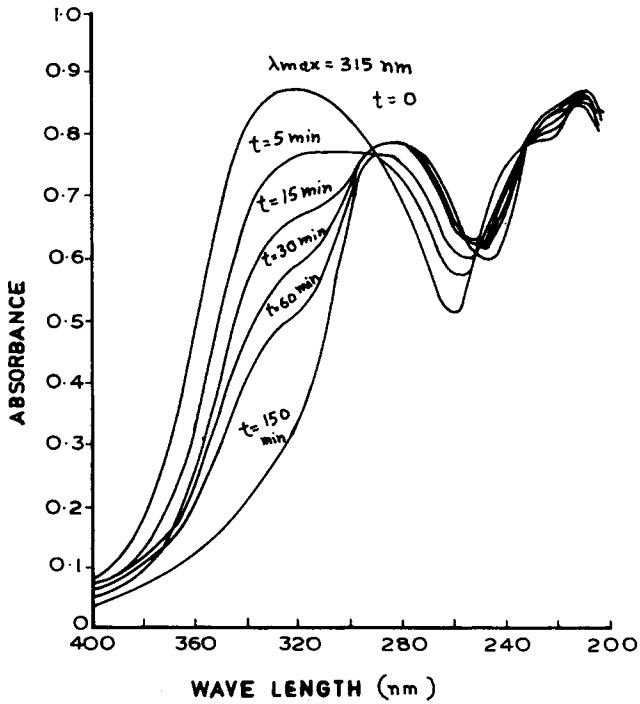


Fig. 4. UV spectra of polyester VII made from propylene glycol, maleic anhydride, glycidyl 4'-chalconyl ether, and linseed oil after different periods of irradiation (t).

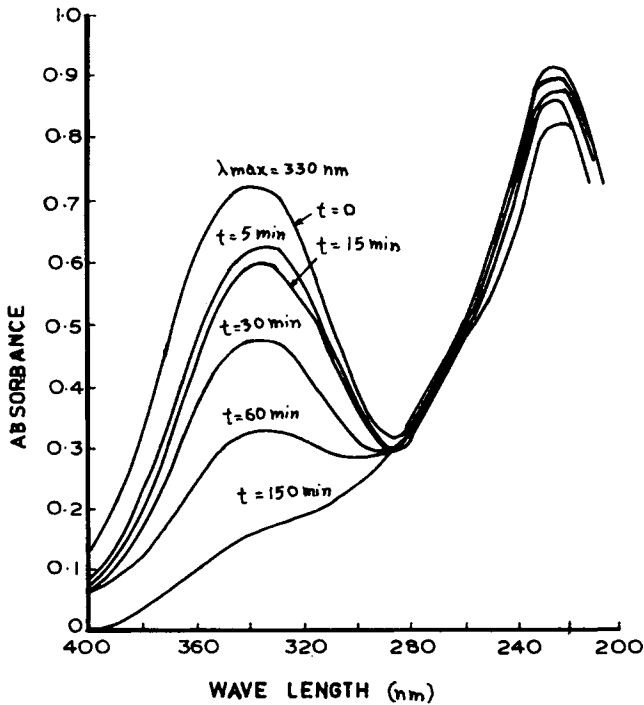


Fig. 5. UV spectra of polyester VIII made from propylene glycol, maleic anhydride, epichlorohydrin, and cinnamylidenemalonic acid after different periods of irradiation (t).

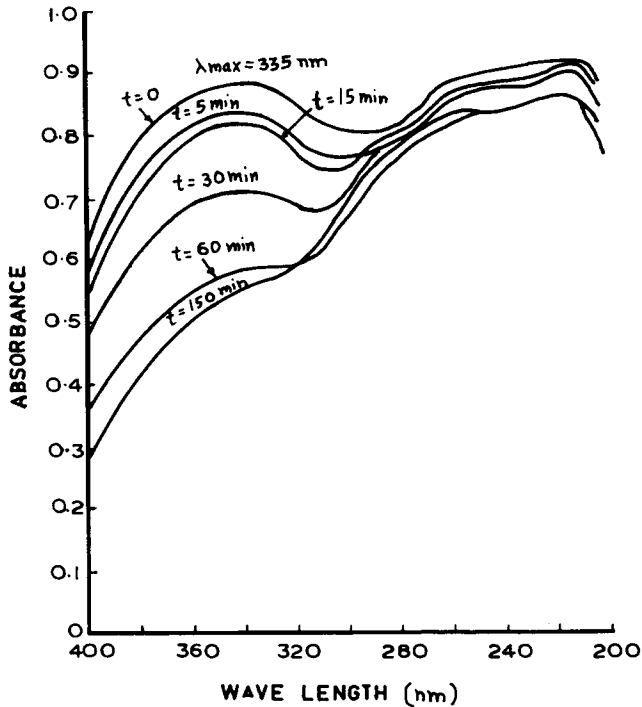
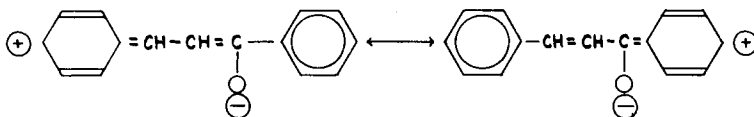


Fig. 6. UV spectra of polyester IX made from propylene glycol, maleic anhydride, glycidyl 4'-chalconyl ether, and cinnamylidenemalonic acid after different periods of irradiation (t).

photosensitive double bonds was followed by recording the UV absorption curves at different periods of irradiation in a Beckman spectrophotometer. Some of the results are given in Figures 1 to 7. Resin I did not turn insoluble on exposure to sunlight and UV light. This indicated that the maleic anhydride unsaturation did not interfere with the photoreactions of other resins having the chalconyl and cinnamylidenemalonyl moieties.

It was observed that photocrosslinking of the resins made with glycidyl 4'-chalconyl ether as one of the monomers was accompanied by *trans*-*cis* isomerization. The *cis* formation was characterized by the peaks occurring toward the lower wavelength side of the original absorption ($t = 0$) after different periods of irradiation, as seen in Figures 2, 4, and 7. The resins containing the glycidyl 4'-chalconyl structure underwent photocrosslinking without any isomerization (Figs. 1, 3, and 6). This may be due to the large aplanarity of the styrylbenzene ring in the *cis*-chalcone structure arising from the steric interaction with the bulky benzoyl group with a large *para* linkage that inhibited the resonance:



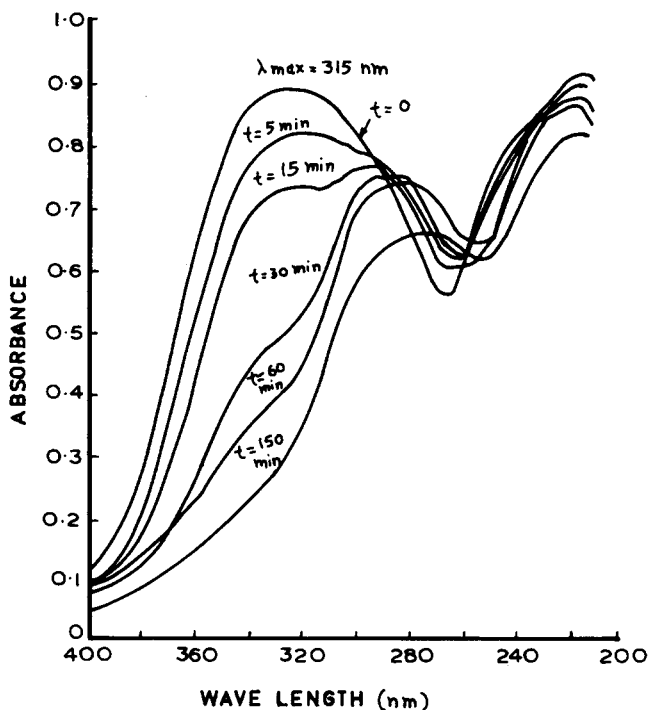
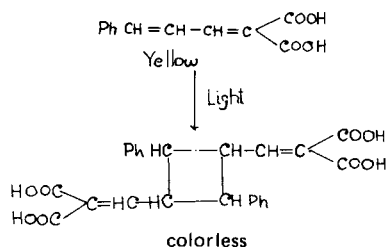


Fig. 7. UV spectra of polyester X made from propylene glycol, maleic anhydride, glycidyl 4'-chalconyl ether, and cinnamylidenemalonic acid after different periods of irradiation (t).

This suppressed the formation of the *cis* isomer. Such observations were also made by the authors in some of their earlier publications.^{3,7-9}

Cinnamylidenemalonic acid is known to undergo photodimerization through a four-center reaction forming a cyclobutane ring.¹⁰



Resin VIII, having cinnamylidenemalonyl group as its only photosensitive moiety, crosslinked without undergoing isomerization (Fig. 5). It was interesting to note that resins IX and X, which contained both the chalconyl and cinnamylidenemalonyl groups in their repeat units, did not exhibit any enhanced photoinsolubility. This indicated that the advantages of the two photosensitive groups were not being realized. Four-center solid-state photopolymerization is known to be lattice controlled over the whole reaction process.¹¹ Therefore, it was likely that resins IX and X, having two photosensitive side chains of unequal volume and structure in their repeat units, did not crosslink efficiently.

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