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PHOTOCROSSLINKABLE VINYL ESTERS WITH α,β-UNSATURATED KETONE GROUPS IN THE BACKBONE

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ABSTRACT

Five vinyl esters with α,β-unsaturated ketone groups in their backbones have been synthesized from the corresponding diepoxides and acrylic acid with benzyltrimethylammonium methoxide as catalyst. The resins have been characterized by UV, IR, and mass spectral analysis, and their photoreactions have been studied under intense UV irradiation. The vinyl esters have been found to crosslink with UV light much faster than the parent diepoxides. On the other hand, a vinyl ester obtained from diglycidyl ether of Bisphenol A (VE) without the α,β-unsaturated ketonic group undergoes very slow photocrosslinking. Interestingly, the vinyl esters also cure chemically with styrene, methyl ethyl ketone (MEK) peroxide, and cobalt naphthenate within 30 min at 98°C, with the exception that VE does not crosslink under similar conditions. This leads to the conclusion that synergy in photo- and chemical curing can be obtained by symmetrically coupling the vinyl end groups of vinyl esters with the α,β-unsaturated ketonic moiety.

INTRODUCTION

In one of our recent publications [1], the synthesis, characterization, and photoreactions of a vinyl ester obtained from the diglycidyl ether of 4,4′-dihydroxychalcone by reaction with acrylic acid with *N,N*-dimethylaniline as catalyst was reported. It was found that the vinyl ester crosslinked faster than the parent diglycidyl ether, while remaining chemically curable with styrene, MEK peroxide, and cobalt naphthenate. Such resins are known to be tough, chemically resistant, and bond well to Kevlar fiber [2]. Thus they promise to be good matrix material for Kevlar fiber composites, intended for use as body armor against fragmentation attack. We therefore thought it worthwhile to extend our previous work to the synthesis of a number of vinyl esters and to study their photoreactions under UV irradiation. In this paper, five such resins are synthesized and characterized, and their photocrosslinking is investigated.

EXPERIMENTAL

Synthesis of Dihydroxy α,β-Unsaturated Ketones

4,4′-Dihydroxybenzylideneacetophenone (chalcone) was prepared after Sheik [3] and had a melting point of 205°C. 4,4′-Dihydroxydibenzalacetone, 2,5-bis(4-hydroxybenzylidene)cyclopentanone, 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone, and 2,6-bis(4-hydroxybenzylidene)cyclohexanone were synthesized after Borden [4] and had melting points of 235, 307 (319–321 in Ref. 4), 207 (214–215 in Ref. 4), and 280°C (282–288°C in Ref. 4), respectively. The purity of the dibenzylidene compounds was tested by mass spectral analysis.

Synthesis of Diglycidyl Ethers

Diglycidyl ether of Bisphenol A (DGEBA) (commercial grade) (I) was supplied by Dr. Beck and Company (India) Ltd., Pune, and was used as received. The diglycidyl ether of 4,4′-dihydroxybenzylideneacetophenone (III) was synthesized as reported earlier [1].

The diglycidyl ether of 4,4′-dihydroxydibenzalacetone (II), the diglycidyl ether of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (IV), the diglycidyl ether of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (V), and the diglycidyl ether of 2,6-bis(4-hydroxybenzylidene)-

cyclohexanone (VI) were synthesized after Lee and Neville [5] with some modification of the method. In a 1-L three-necked round-bottom flask immersed in a Gallenkamp thermostatic oil bath and fitted with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel, 0.05 mol unsaturated ketone, 0.5 mol epichlorohydrin, and 540 mL 2-methoxy ethanol were mixed and heated to 100°C to completely dissolve the solid ketone with stirring. The temperature was raised to 120 ± 1°C, and a 10% solution of sodium hydroxide in 2-methoxyethanol (0.1 mol) was added dropwise to the flask over a period of 3.5 h. After the addition was over, heating and stirring were continued for another hour. Unreacted epichlorohydrin, 2-methoxyethanol, and accumulated water were distilled off. Resins II, V, and VI were extracted with toluene, dried over anhydrous magnesium sulfate, and solvent was distilled out under vacuum to obtain pure products (yield: II, 86%; V, 84%; VI, 86%).

Resin IV was washed several times with hot water to free it from sodium chloride and dried in a vacuum oven for 5 h (yield, 86%).

Synthesis of Divinyl Esters

In a 250-mL three-necked round-bottom flask fitted with a mercury-sealed stirrer and a reflux condenser, and provided with thermostatic heating arrangements, the diglycidyl ethers, I–VI (0.1 mol), were reacted with acrylic acid (specific gravity 1.048, freezing point 13°C) (0.2 mol), in presence of benzyltrimethylammonium methoxide as catalyst (1 wt% of the total reaction mixture). Trace quantities (2–3 crystals) of hydroquinone were added to inhibit crosslinking during synthesis. The formation of the vinyl esters was followed by withdrawing samples of the reaction mixtures and recording the IR spectra at intervals of 30 min till the epoxy absorption at 915 cm^{-1} vanished completely. Thus, the temperature and the total reaction time for the formation of vinyl esters VII–XII were optimized as given in Table 1.

TABLE 1

Vinyl ester	Temperature, °C	Total reaction time, h
VII	120	2
VIII	90	4
IX	110	4.5
X	140	2
XI	120	2
XII	140	1

The reaction temperature was raised above 90°C in different cases to obtain a good reaction rate. The products were cooled and washed with methanol to free them from unreacted acrylic acid and dried. The resins were freely soluble in acetone, indicating the absence of any crosslinked product. *N,N*-Dimethylaniline can be used as a catalyst as reported earlier [1] for the synthesis of some of the resins, but it is not as versatile as benzyltrimethylammonium methoxide.

Spectral and Molecular Weight Measurements

The IR measurements were carried out on the solid and highly viscous samples in the form of KBr pellets and smears on the sodium chloride window, respectively, in a Perkin-Elmer double-beam 1330 IR spectrophotometer. The ultraviolet spectra were recorded for all samples by forming a thin coating on the outer transparent wall of a quartz cell, with a similar empty cell as the reference, in a Hitachi double-beam U-3200 spectrophotometer. The coatings were obtained from a 2% solution of the resins in either chloroform or acetone, whichever dissolved the resins better. The mass spectral measurements were carried out in a Finnigan Mat 1020 mass spectrometer operating at 70 eV.

The number-average molecular weights were measured in a Knauer vapor-pressure osmometer with universal probes in chloroform, dioxane, and tetrahydrofuran as solvent.

UV Irradiation

The quartz cells of the UV spectrometer, coated with resins as described above, were irradiated with intense UV light from a Hanovia high-pressure mercury arc lamp provided with a vertical quartz jacket to circulate water at room temperature. The samples were kept at the distance of 15 cm from the walls of the jacket with the coated surface vertically facing the lamp. The photocrosslinking of the resins was followed by the gradual disappearence of the *trans*-$CH=CH-CO-$ absorption in the resin and also by testing their insolubility in chloroform or acetone.

Chemical Curing

The vinyl esters were chemically cured by adding commercially available inhibited styrene as hardener (33.3 mL/100 g resin), methyl ethyl ketone peroxide (MEKP) as catalyst used for curing unsaturated polyesters (3 mL/100 g resin), and cobalt naphthenate as accelerator (3 mL/100 g resin) for 30 min at 98°C or 4 h at 50°C. At room temperature the curing was not appreciable for all the resins exposed to atmospheric oxygen. In addition, it is well known that MEKP with high dimer content is more reactive with vinyl polyesters than the low-dimer MEKP used by us in curing the vinyl esters [6].

RESULTS AND DISCUSSION

The diglycidyl ethers, I-VI (Scheme 1), and their vinyl esters, VII-XII (Scheme 2), were characterized by measurement of number-average molecular weight, mass spectral analysis for the M^+ ion, IR absorption of $>C=O$, $>C=C<$, and $>C-O-C<$ groups (Tables 2 and 3). The glycidyl ethers were further characterized by the epoxide absorption around 915 cm^{-1}. On the other hand, the vinyl esters were characterized by the disappearance of the absorption at 915 cm^{-1} and the appearance of the ester peak at 1720 cm^{-1}. In addition, the end vinyl group bending absorption consistently appeared at 985-980 cm^{-1} (Table 3) [7]. The $-OH$ absorption for the vinyl esters in the IR region was broad and could not be used to make any conclusive inference.

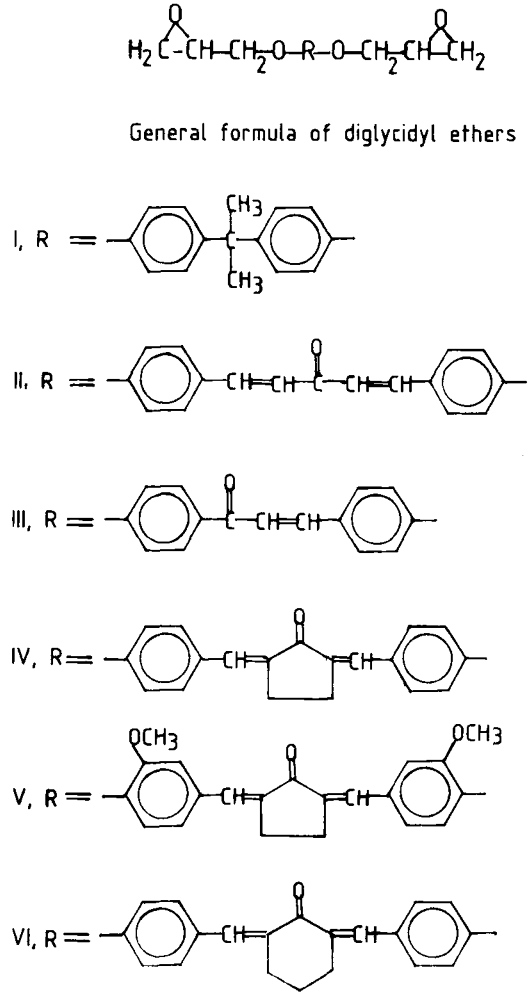
The maximum absorptions in the UV region observed at 340-365 nm for the glycidyl ethers (Table 2), which shifted to 340-395 nm for the vinyl esters (Table 3), were assigned to the $-CH=CH-CO-$ group.

The $\bar{m}_n$ measured by vapor pressure osmometry differed from the values of m/e for the M^+ ion of different resins (Tables 2 and 3), thereby indicating that the resins were not single compounds. The mass spectral peaks of measurable abundance beyond the M^+ ion shown in Tables 2 and 3 were observed but were not reported.

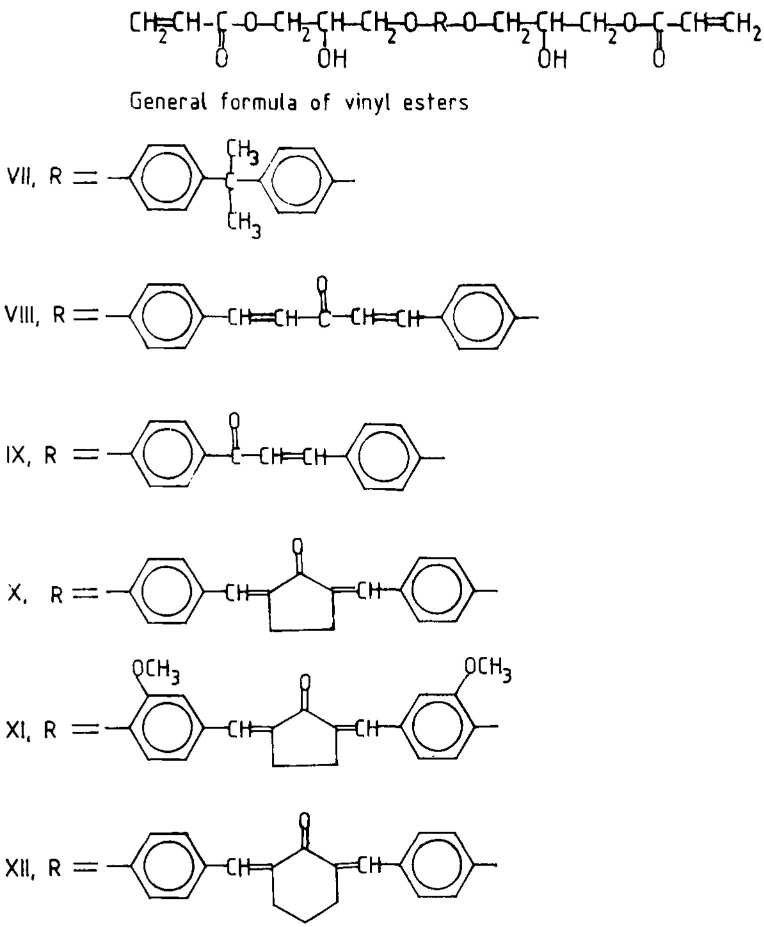
The solubility of the glycidyl ethers and the vinyl esters in several solvents was tested. All the resins were freely soluble in acetone, tetrahydrofuran, and dimethylformamide. Dioxane was also a good solvent at room temperature for most of the resins.

PHOTOREACTIONS

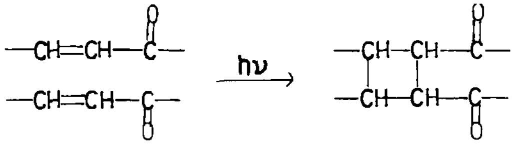
The photocrosslinking of the α,β-unsaturated ketones by (2+2) cycloaddition of the unsaturated bond is a very well-known phenomenon [8-11] (Scheme 3).



SCHEME 1. General formula of diglycidyl ethers.



SCHEME 2. General formula of vinyl esters.



SCHEME 3. The photocrosslinking of the α,β-unsaturated ketones by (2+2) cycloaddition of the unsaturated bond.

In several cases the crosslinking is accompanied by *tran-cis* isomerization although it can be suppressed by putting steric barriers in the structure of the compounds, particularly when they are oligomeric or polymeric, rendering the *cis* structure labile [12–14]. In the present study, all the diglycidyl ethers (except I) contained α,β-unsaturated ketonic groups in their backbone, with the resin structure building up symmetrically from both ends. Such compounds are expected to undergo crosslinking and *cis-trans* isomerization, the latter occurring simultaneously to a lower degree. This has been observed in the crosslinking behavior of the glycidyl ethers, II–VI, as reproduced in Figs. 1 to 3 for Resins II, III, and VI.

The vinyl esters VII–XII contained two vinyl end groups in addition to the α,β-unsaturated ketonic moiety in their backbones (Scheme 2). We reported earlier [13, 14] that photo reactions of resins containing the $-CH=CH-CO-$ group are symmetry sensitive and that its loss inhibited photocrosslinking. In the vinyl esters VII–XII, symmetric juxtaposition of the vinyl end groups with the $-CH=CH-CO-$ group in the backbone is expected to increase the photocrosslinkability compared to that of the parent diglycidyl ethers. This expectation has been borne out by our experiments (e.g., Figs. 4–6). The vinyl ester of DGEBA, VII, having only the vinyl groups at the ends without a $-CH=CH-CO-$ group in the backbone, did not crosslink appreciably even after 15 h of irradiation.

To obtain a quantitative picture of the relative photofastness of the glycidyl ethers and their vinyl esters, the conversion of the $-CH=CH-CO-$ group with the (2+2) cyclic structure leading to crosslinking was plotted against the time of irradiation in Figs. 7–11. The percentage conversion of the $-CH=CH-CO-$ group was taken to be $[(A_t - A_0)/(A_\infty - A_0)] \times 100$, where A_0 is the absorbance at time zero, A_t is the absorbance at time t, and A_∞ is the absorbance at the completion of the reaction. It is seen from Figs. 7–11 that all the vinyl ethers photocrosslinked much faster than their parent diglycidyl ethers, indicating synergy,

TABLE 2. Spectral Characteristics of Diglycidyl Ethers[a]

No.	Name of the compound	Molecular weight	*m/e*, M^+	λ_{max} (*trans*- $-CH=CH-CO-$), nm	$\nu_{>C=O}$, cm^{-1}	$\nu_{>C=C<}$, cm^{-1}	$\nu_{\overbrace{CH_2-CH_2}^{O}}$, cm^{-1}	$\nu_{>C-O-C<}$, cm^{-1}
I	Diglycidyl ether of Bispherol A	359	361 (100%) 376 (22.8%) 397 (43.8%), 412 (8.7%)				915(s)	1245(s)
II	Diglycidyl ether of bis(4-hydroxybenzylidene)acetone	364	378 (100%)	360	1640(s)	1620(sh)	915(s)	1250(s)
III	Diglycidyl ether of 4,4′-dihydroxybenzylidene-acetophenone	380	352 (100%)	340	1650(s)	1630(sh)	915(s)	1250(s)
IV	Diglycidyl ether of 2,5-bis(4-hydroxybenzylidene)cyclopentanone	400	404 (65.4%)	342	1680(s)	1620(w)	925(w)	1250(s)
V	Diglycidyl ether of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone	504	464 (50.4%)	365	1670(m)	1615(s)	915(w)	1240(s)
VI	Diglycidyl ether of 2,6-bis(4-hydroxybenzylidene)cyclohexanone	433	418 (26%)	345	1655(s)	1625(w,sh)	915(s)	1250(s)

[a] s = strong, m = medium, w = weak, sh = shoulder.

TABLE 3. Spectral Characteristics of Vinyl Esters[a]

No.	Name of the compound	Molecular weight	*m/e*, M^+	λ_{max} (*trans*- $-CH=CH-CO-$), nm	ν_{-CO-O-}, cm^{-1}	$\nu_{>C=O}$, cm^{-1}	$\nu_{>C=C<}$, cm^{-1}	$\nu_{>C-O-C<}$, cm^{-1}	$\delta_{-CH=CH_2}$, cm^{-1}
VII	Divinyl ester of diglycidyl ether of Bisphenol A	524	505 (13%) 520 (4.2%) 541 (3.3%) 556 (1.6%)	287 278	1720(s)			1245(s)	985(m)
VIII	Divinyl ester of diglycidyl ether of bis(4-hydroxybenzylidene)acetone	502	522 (4.4%)	380	1720(s)	1635(m)	1620(w)	1255(s)	985(s)
IX	Divinyl ester of diglycidyl ether of 4,4′-dihydroxybenzylideneacetophenone	551	496 (3%)	340	1720(s)	1650(m)	1620(sh)	1255(s)	980(m)
X	Divinyl ester of diglycidyl ether of 2,5-bis(4-hydroxybenzylidene)cyclopentanone	584	548 (5.3%)	375	1720(s)	1680(sh)	1620(w)	1250(s)	985(s)
XI	Divinyl ester of diglycidyl ether of 2,5-bis(4-hydroxy-3-methoxybenzylidene)-cyclopentanone	556	608 (29.1%)	395	1720(s)	1680(sh)	1620(w)	1250(s)	980(s)
XII	Divinyl ester of diglycidyl ether of 2,6-bis(4-hydroxybenzylidene)cyclohexanone	554	562 (43.3%)	365	1720(s)	1650(w)	1630(w)	1250(s)	980(s)

[a] s = strong, m = medium, w = weak, sh = shoulder.

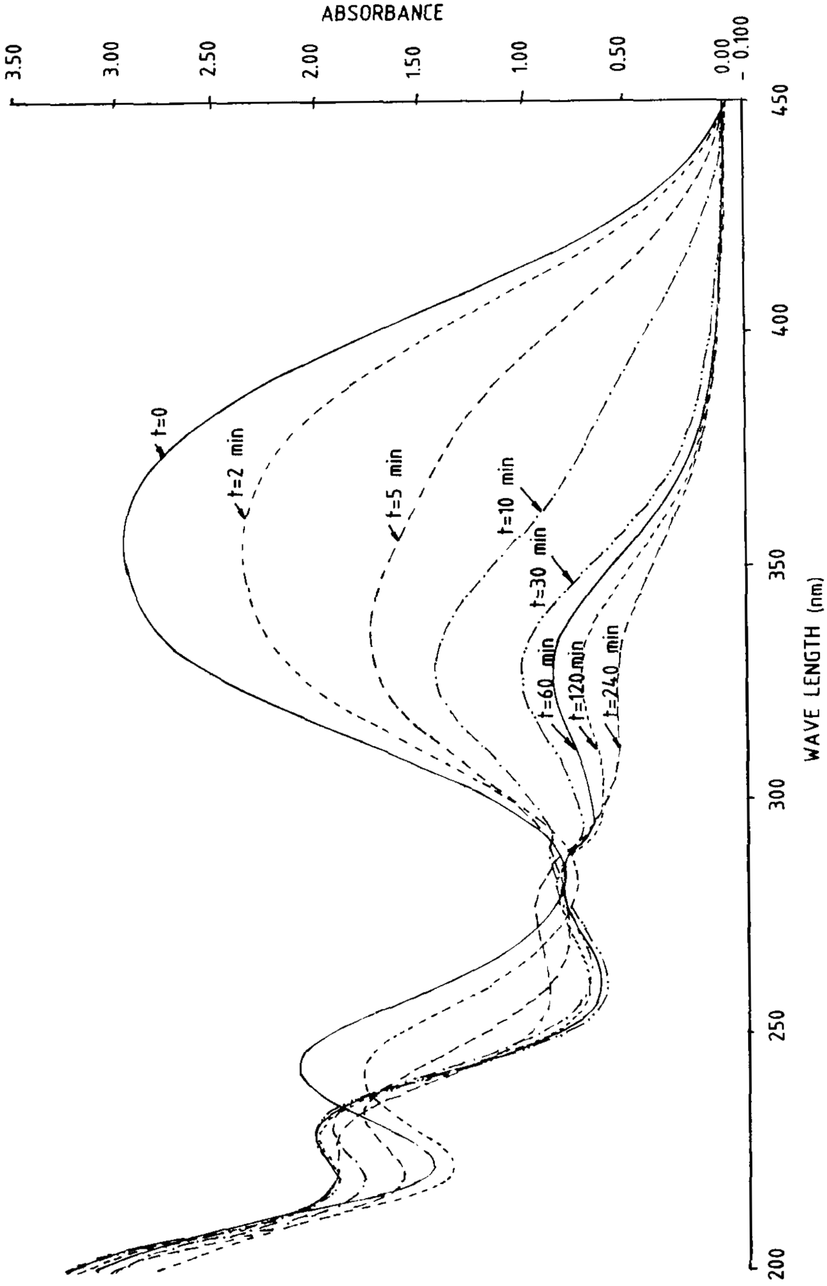


FIG. 1. UV spectra of diglycidyl ether of bis(4-hydroxybenzylidene)acetone (II) after different times of irradiation, *t*.

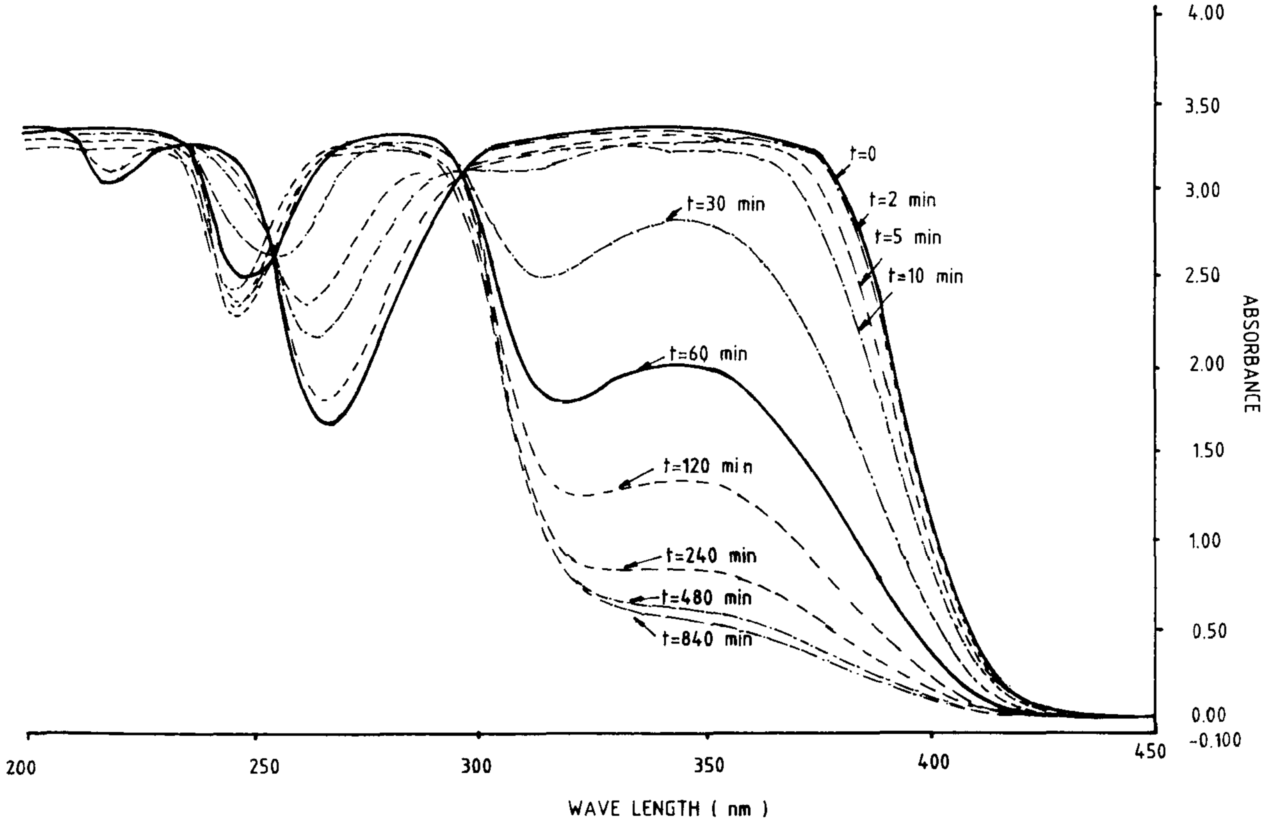


FIG. 2. UV spectra of diglycidyl ether of 4,4′-dihydroxybenzylideneacetophenone (III) after different times of irradiation, *t*.

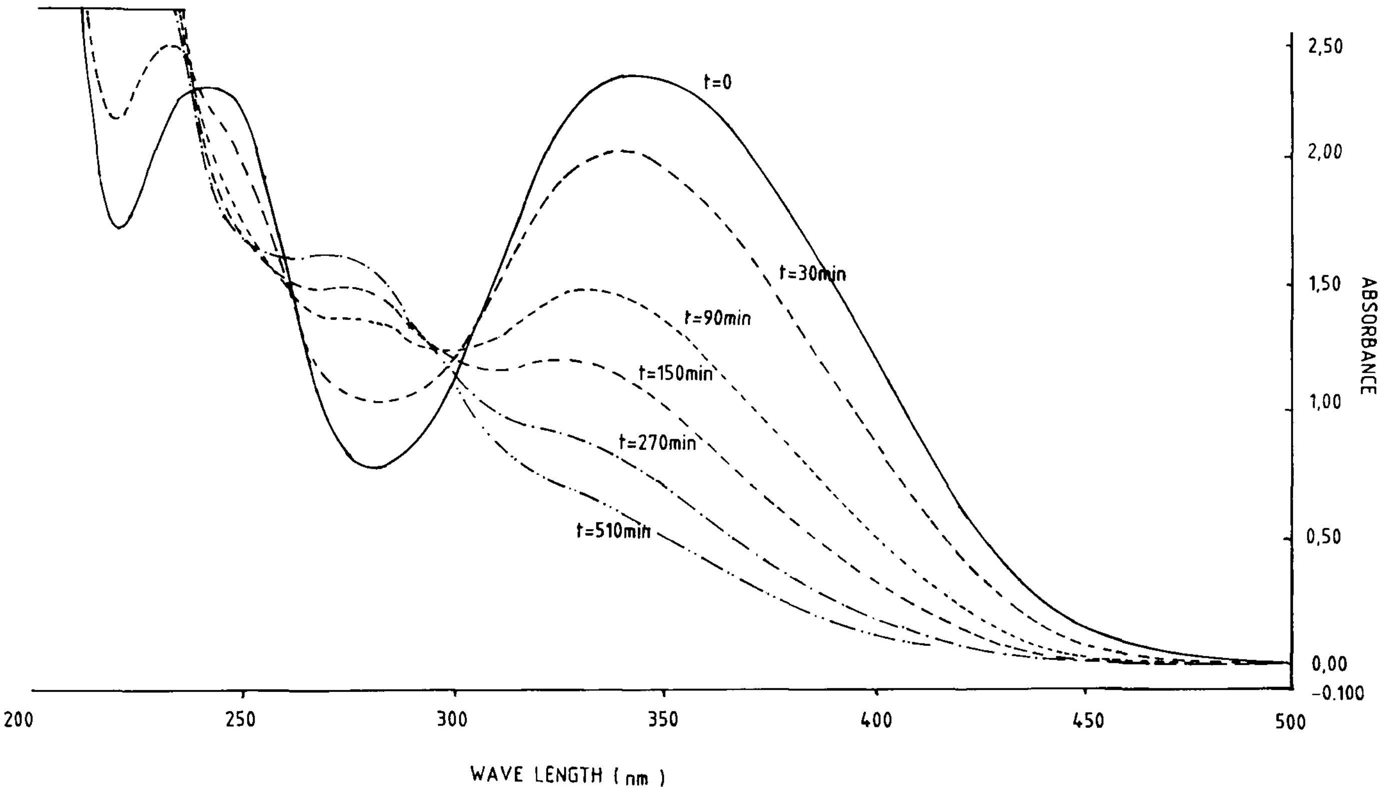


FIG. 3. UV spectra of diglycidyl ether of 2,6-bis(4-hydroxybenzylidene)cyclohexanone (VI) after different times of irradiation, *t*.

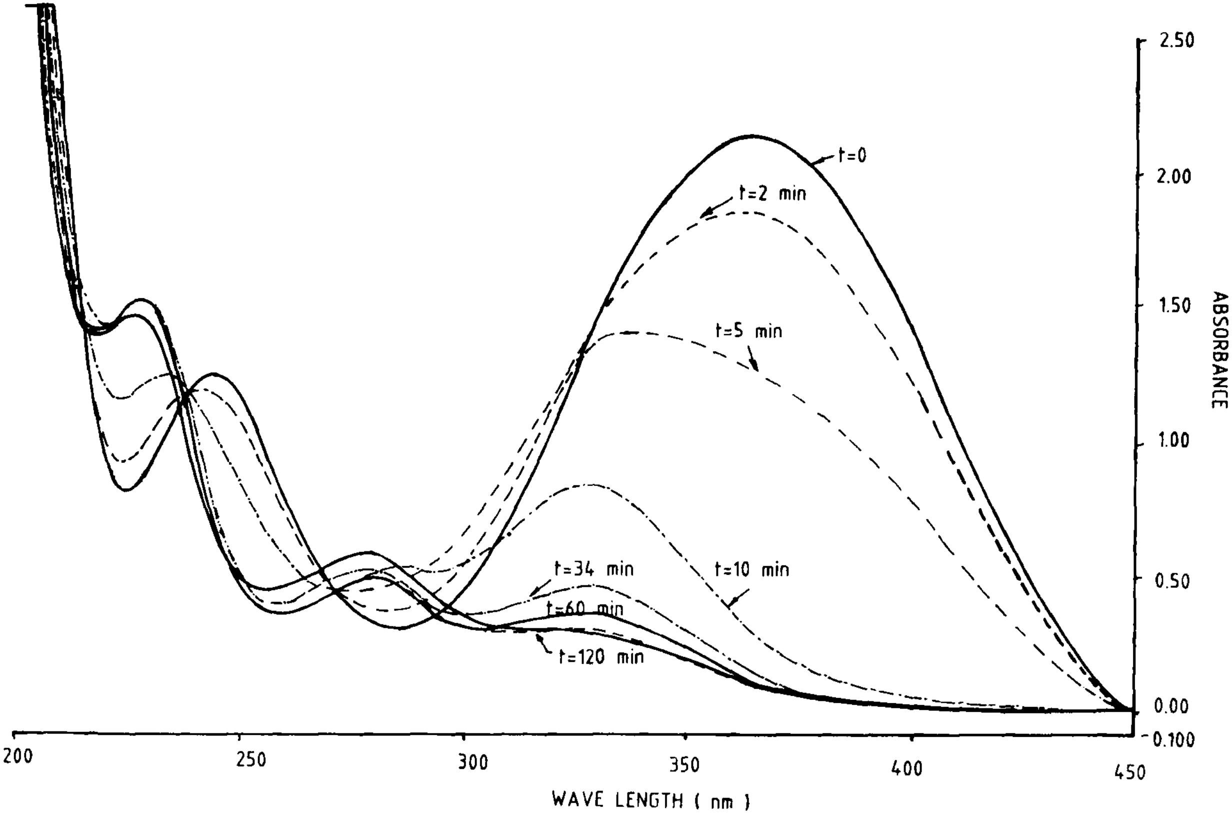


FIG. 4. UV spectra of divinyl ester of diglycidyl ether of bis(4-hydroxybenzylidene)acetone (VIII) after different times of irradiation, *t*.

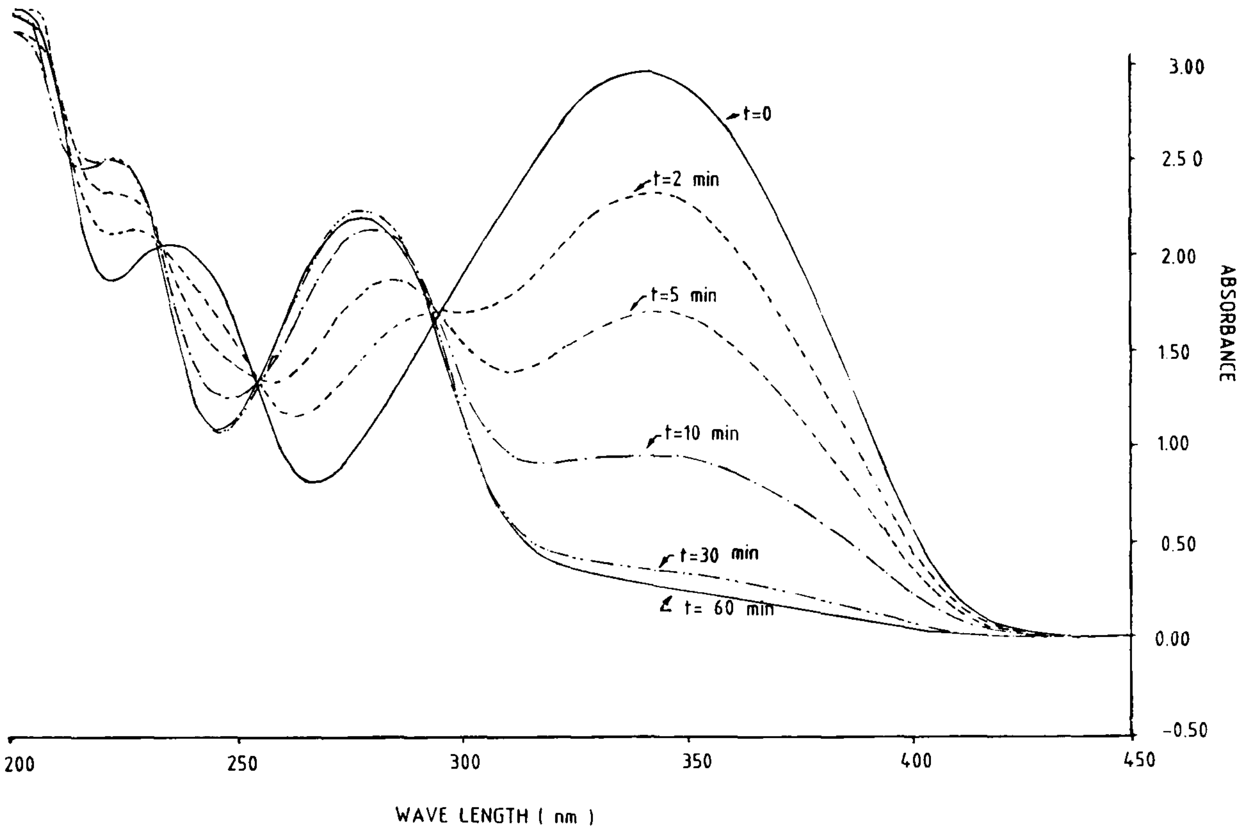


FIG. 5. UV spectra of divinyl ester of diglycidyl ether of 4,4′-dihydroxybenzylideneacetophenone (IX) after different times of irradiation, *t*.

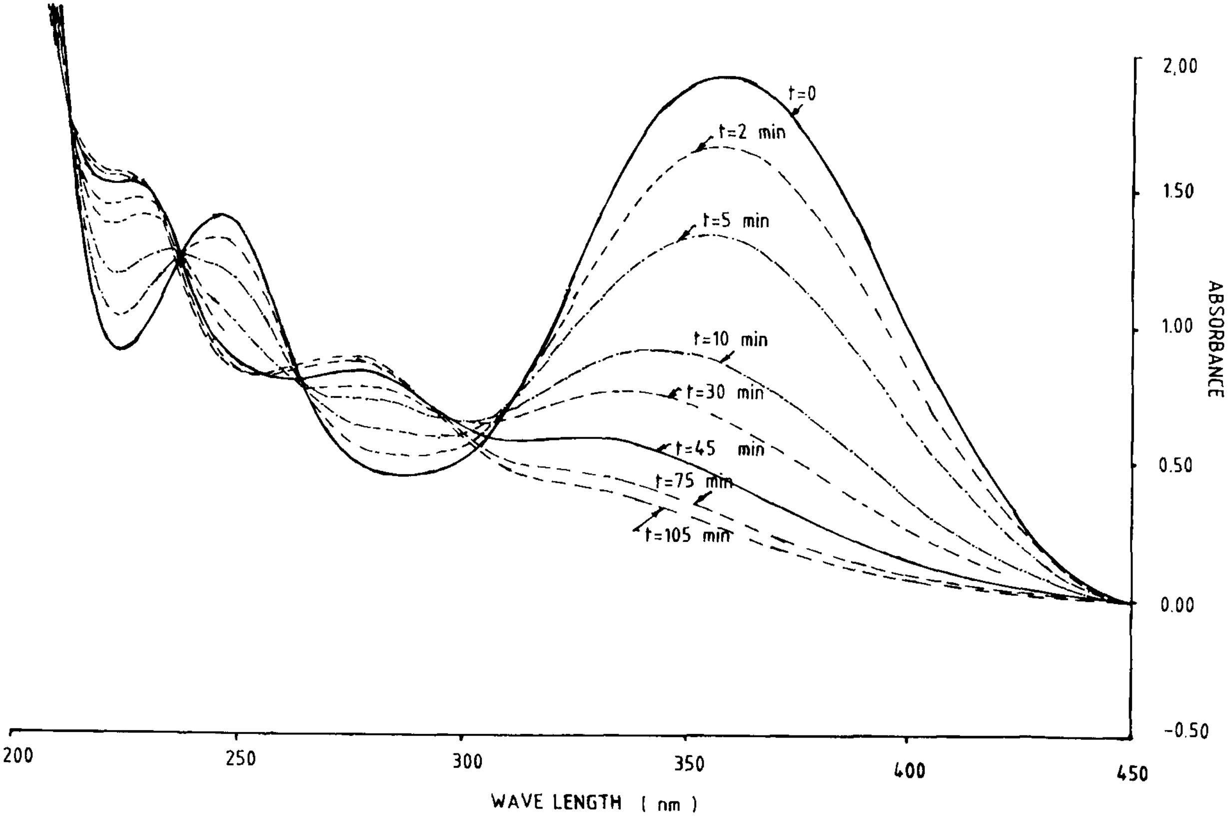


FIG. 6. UV spectra of divinyl ester of diglycidyl ether of 2,6-bis(4-hydroxybenzylidene)cyclohexanone (XII) after different times of irradiation, *t*.

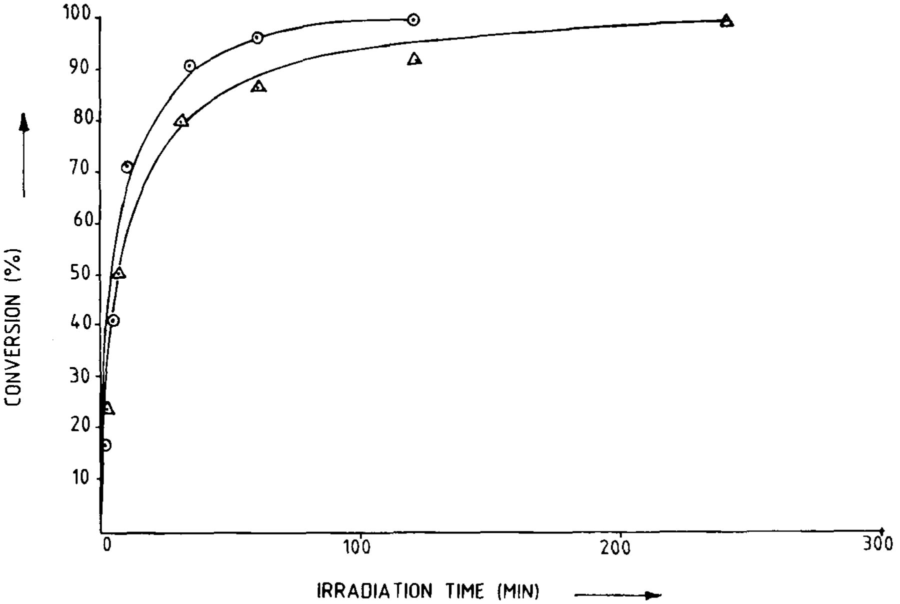


FIG. 7. Rate of disappearance of photoreactive double bond of diglycidyl ether of bis(4-hydroxybenzylidene)acetone (△) and its divinyl ester (⊙).

the fastest being Resin IX which reached 100% conversion within 60 min of irradiation. The order of their ease of photocrosslinkability is IX > XII > VIII > X > XI.

The relative photofastness of the vinyl esters may be of some research curiosity but loses most of its significance in thick films, 1 mm or above, in different applications. We found that the resins could not be cured even after 2-3 h of irradiation in thick films.

In addition to crosslinking with UV light, the vinyl esters were also tested for their chemical curability by the addition of styrene as hardener, MEKP as catalyst, and cobalt naphthenate as accelerator, as described earlier. All the resins crosslinked completely within 30 min at 98°C, with the exception of VII, which did not crosslink at all under similar conditions. The chemical crosslinking is expected to proceed via free-radical polymerization of the unsaturated end groups of the vinyl esters because the $-CH=CH-CO-$ does not copolymerize with styrene. It appears that in vinyl esters with α,β-unsaturated ketone groups in the backbone and

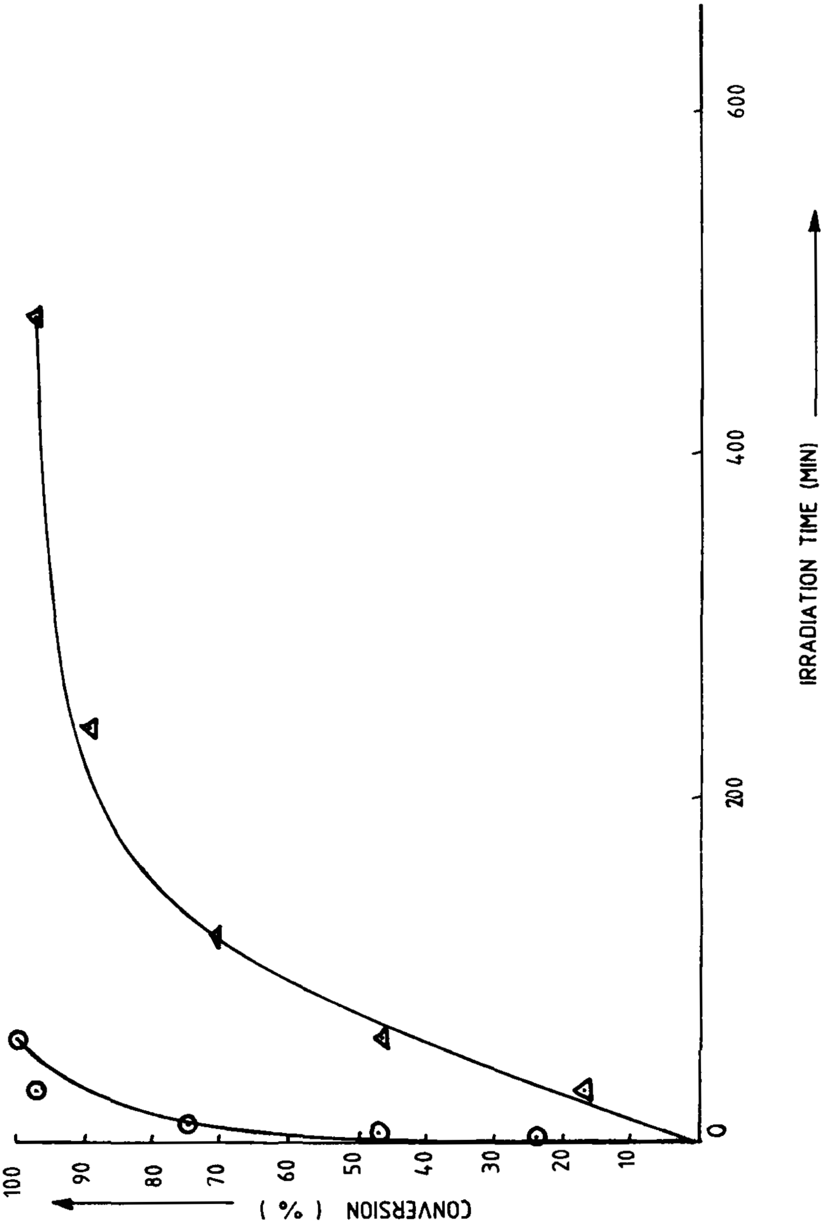


FIG. 8. Rate of disappearance of photoreactive double bond of diglycidyl ether of 4,4'-dihydroxybezylideneacetophenone (△) and its divinyl ester (⊙).

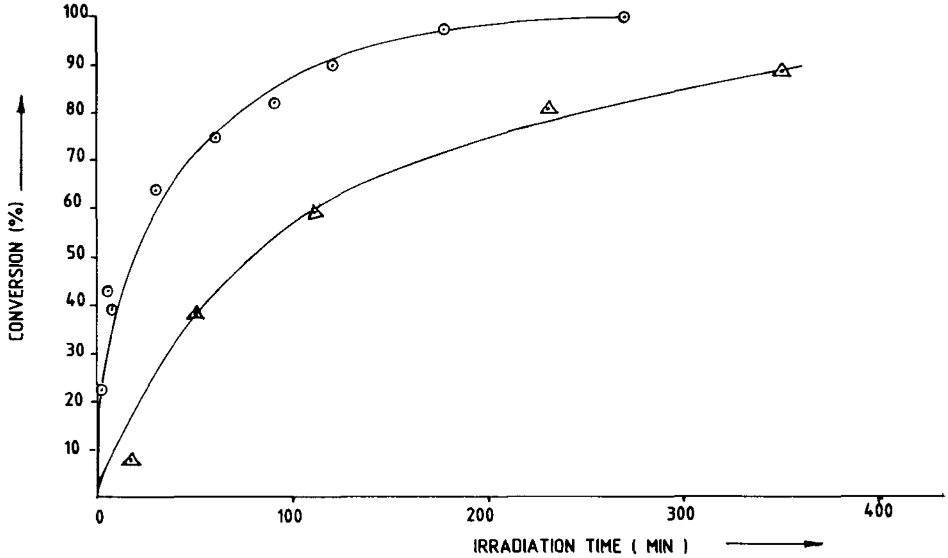


FIG. 9. Rate of disappearance of photoreactive double bond of diglycidyl ether of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (△) and its divinyl ester (⊙).

vinyl end groups symmetrically placed, there is some synergy in chemical curing as well. This can be exploited by curing vinyl esters for several applications by UV irradiation to decrease the exothermicity of curing, followed by chemical crosslinking of the residual vinyl end groups obtained by heating with the hardener system that was added to the resins at the outset.

Vinyl esters without α,β-unsaturated ketone groups in their backbones are reported to crosslink very fast under UV irradiation with the addition of triplet-state sensitizers like benzophenone or benzoin ethers [15]. Our work carried out along similar lines will be reported shortly.

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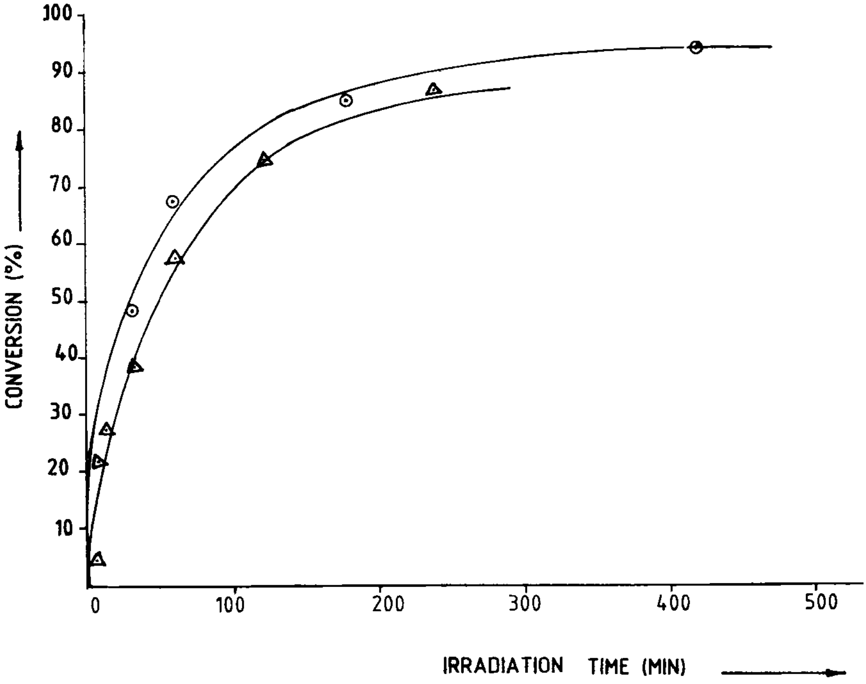

FIG. 10. Rate of disappearance of photoreactive double bond of diglycidyl ether of 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (△) and its divinyl ester (⊙).

Panda, under which the present work was carried out. Dr. E. Bhagiratharao, Director and Dean, I.A.T., is warmly thanked for his kind interest and permission to publish this paper.

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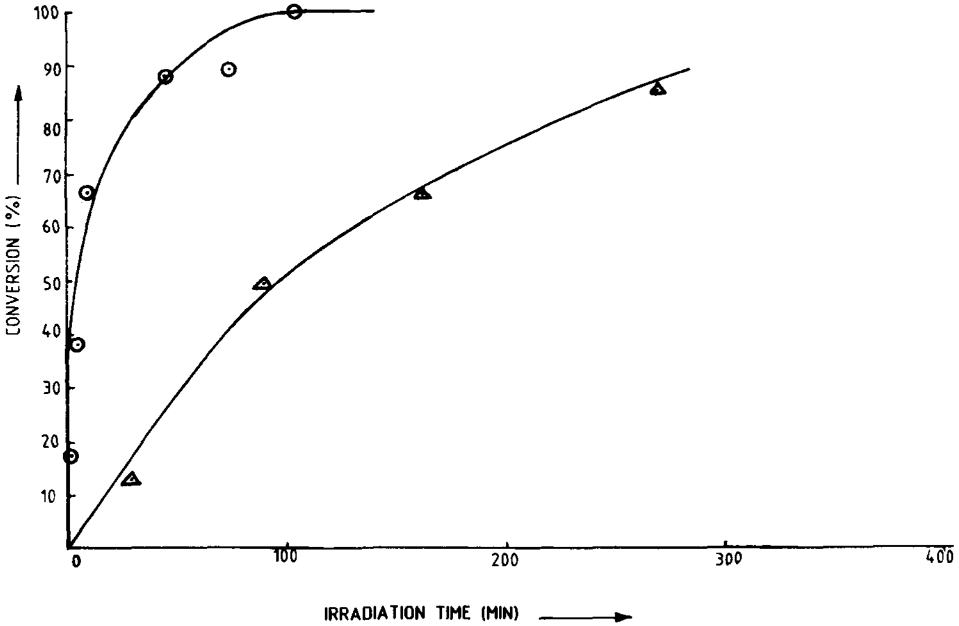

FIG. 11. Rate of disappearance of photoreactive double bond of diglycidyl ether of 2,6-bis(4-hydroxybenzylidene)cyclohexanone (△) and its divinyl ester (⊙).

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