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NOTE
A PHOTOCROSSLINKABLE VINYL POLYESTER

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INTRODUCTION

Vinyl polyesters combine the advantages of epoxy and unsaturated polyester resins [1, 2]. They are tough and adhere well to the substrate surface. With acrylic end groups, these resins turn photocrosslinkable [1]. However, photocurable vinyl polyesters are not as well reported as photocurable epoxy resins [3, 4] and unsaturated polyesters [5, 6]. Crosslinking with UV light is an excellent method for obtaining articles with thick cross sections, with or without reinforcement, without large heat build-up in the interior, which would damage the plastic [7]. We, therefore, thought of preparing a vinyl polyester resin from a photocurable diepoxide, such as the diglycidyl ether of 4,4′-dihydroxychalcone with acrylic end groups, and test its photofastness compared to that of the parent diepoxide. The results obtained are interesting, and the method of synthesis can be extended to a large number of photocrosslinkable vinyl polyesters.

EXPERIMENTAL

Synthesis of 4,4′-Dihydroxychalcone

4,4′-Dihydroxychalcone was prepared after Sheik [8] by reacting a mixture of *p*-hydroxyacetophenone (0.8 mol) with *p*-hydroxybenzaldehyde (0.8

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mol) dissolved in 1 L absolute alcohol saturated with HCl gas and maintained at 5°C for 5 h. The reddish violet crystals formed were filtered, washed thoroughly with distilled water, and dried in a vacuum oven at 100°C. The crude product was recrystallized in ethanol-water to obtain the pure product with a melting point of 208°C.

Synthesis of Diglycidyl Ether of 4,4′-Dihydroxychalcone

The above-mentioned diepoxide was prepared after Sheik [8] by dissolving 4,4′-dihydroxychalcone (2.5 mol) and epichlorohydrin (20 mol) in 1 L isopropanol and heating the solution to 75°C. A 50% aqueous solution of NaOH (5.5 mol) was added slowly over 6 h, maintaining a gentle reflux. Then the reaction mixture was stirred at 83°C for another 2 h. On cooling, the product crystallized out as a fine yellow powder which could be recrystallized from alcohol-chloroform mixture (2:1 v:v); mp, 116°C; m/e (M^+), 352 (100%); $\nu_{\text{epoxy gp}}$, 912 cm^{-1}; $\nu_{C=O}$, 1650(s) cm^{-1}; λ_{max} (*trans* $-CH{=}CH-\overset{O}{\overset{\|}{C}}-$), 340 nm.

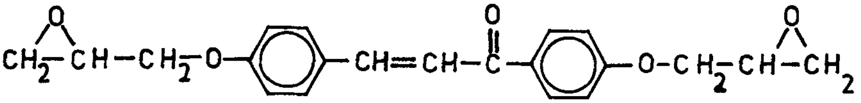
Synthesis of the Divinyl Polyester of Diglycidyl Ether of 4,4′-Dihydroxychalcone

The diglycidyl ether of 4,4′-dihydroxychalcone (1 mol) was reacted with acrylic acid (sp.gr. 1.048; fp, 13°C) (2 mol) in the presence of dimethylaniline (0.1 mL) under nitrogen at 90°C for 2 h [9]. These reaction conditions were arrived at after several trials at higher temperatures and longer reaction time, which led to crosslinking of the product. However, reaction at 90°C for 2 h ensured complete reaction of the epoxy groups, which was followed by IR spectral measurements. The product was cooled and washed with methanol to make it free from unreacted acrylic acid. The resin thus prepared was completely soluble in acetone and dimethylformamide and, unlike the parent diepoxide, was insoluble in chloroform. Yield 95%; $\bar{M}_n$ (VPO) 708; ν_{ester}, 1720 cm^{-1} (s); $\nu_{C=O}$, 1650 cm^{-1}; λ_{max} ($CH{=}CH-\overset{O}{\overset{\|}{C}}-$), 340 nm. Mass spectral analysis of the resin revealed that it contained products obtained from two acrylic acid monomers reacting with one molecule of the diglycidyl ether of 4,4′-dihydroxychalcone, m/e (M^+), 496 (25%), along with the products in which a dimerized acrylic acid molecule has reacted with the glycidyl ether at one end with monomeric acrylic acid reacting at the other or with dimerized acrylic acid at both ends. Similarly, reaction of tri- and tetramerized acrylic acid with the diglycidyl ether was also indicated at one or both the ends.

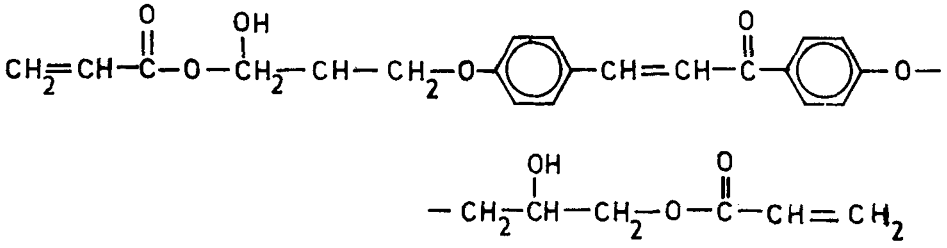
The disappearance of the absorption, i.e., the conversion, was taken to be equal to $[(A_t - A_0)/(A_\infty - A_0)] \times 100$, where A_0 is the absorbance at time $t = 0$, A_t is the absorbance at $t = t$, and A_∞ is the absorbance at $t = 60$ min. The UV spectra were recorded with a Hitachi 220A double-beam spectrophotometer.

PHOTOREACTIONS

The diglycidyl ether of 4,4′- dihydroxychalcone (I) and its vinyl polyester (II) (with products of higher molecular weights) was irradiated as a solid coating on a quartz surface deposited from a 2% solution in chloroform and acetone, respectively, using a Hanovia high-pressure mercury arc lamp. The quartz plates were placed 15 cm from a vertical lamp with a quartz jacket with cold water circulating in it. The reaction was followed by measuring the UV spectra after different periods of irradiation with the resin coated on the transparent side of the quartz cell. Figure 1 shows the UV spectra of the vinyl polyester (II) irradiated for various times.



I



II

Both Resins I and II were crosslinked by the well-known (2+2) cycloaddition of the α,β-unsaturated ketonic group:

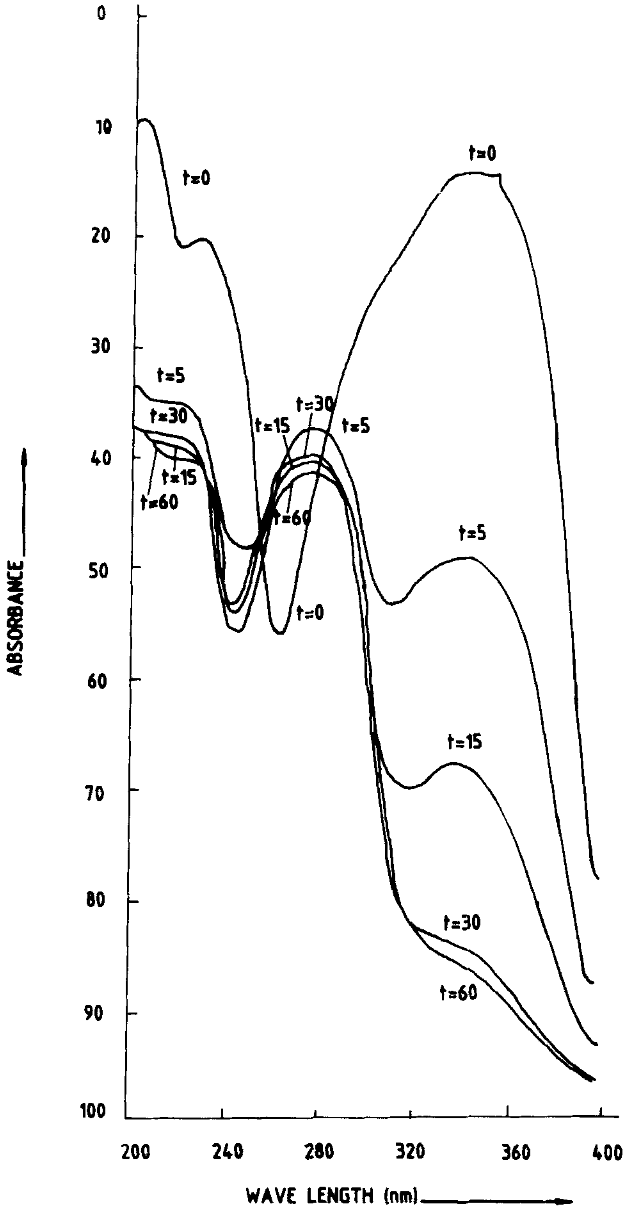
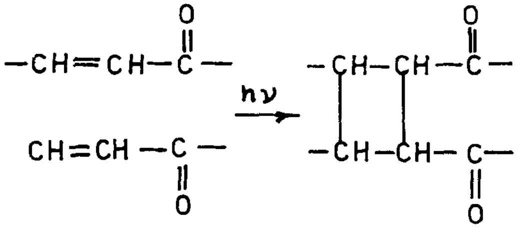


FIG. 1. UV spectra of vinyl polyester of diglycidyl ether of 4,4′-dihydroxychalcone at different times of irradiation, *t*.



Resin II has an extra site for photoreaction at the vinyl end group in addition to the crosslinking of the α,β-unsaturated ketonic double bond, indicated by the progressive decrease in intensity of the 340 nm band. Some *cis*-transformation of the *trans*-double bond took place with an absorption appearing at 280 nm as well. It can be seen from Fig. 2 that the vinyl polyester (II) crosslinks faster than the diepoxide (I).

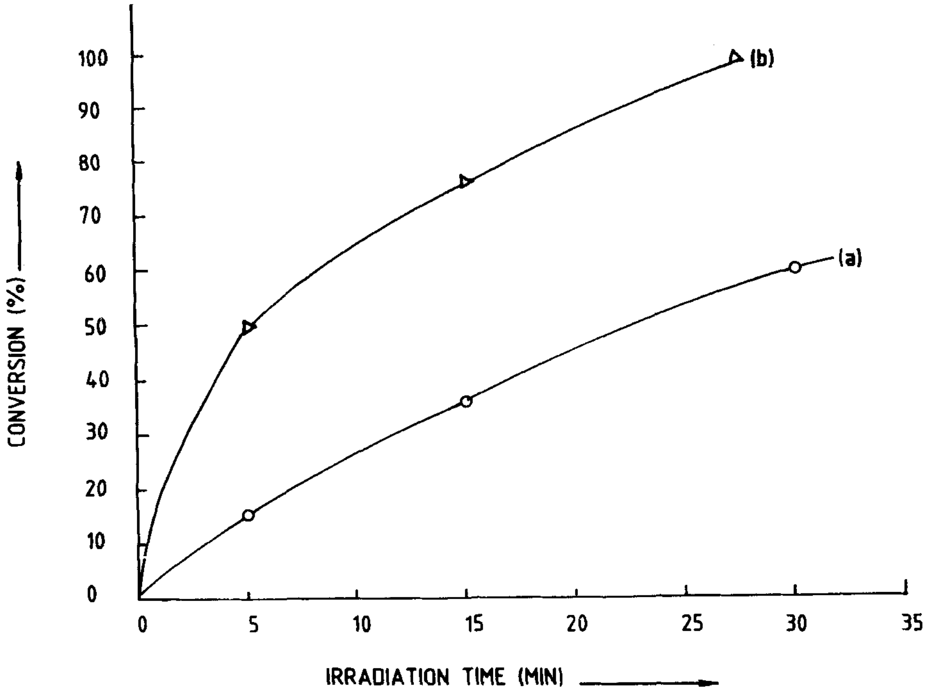


FIG. 2. Rate of disappearance of photoreactive double bond in (a) diglycidyl ether of 4,4′-dihydroxychalcone and (b) vinyl polyester of diglycidyl ether of 4,4′-dihydroxychalcone.

The vinyl polyester, being an unsaturated polyester resin, was also cured at room temperature for a period of 3 h with styrene as hardener (33.3 mL/100 g resin), methyl ethyl ketone peroxide as catalyst (3 mL/100 g resin), and cobalt naphthenate as accelerator (3 mL/100 g resin). The cure of the resin is extremely sensitive to atmospheric oxygen, and hence, the resin surface was kept covered and pressed with a glass plate coated with wax during the cure. Thus the exothermal curing can be avoided by photocrosslinking, and a second layer can be grafted onto the first by chemical curing.

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