

Photosensitive Monomers and Polymers Derived from Glycidyl Cinnamate

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ABSTRACT

Compounds with photosensitive cinnamoyl groups were synthesized by reaction of glycidyl cinnamate with monomeric and polymeric carboxylic acid derivatives. These monomers and polymers were characterized by conventional analysis and spectrometry. Upon irradiation in solution the predominant reaction was found to be the *trans-cis* photoisomerization, while in film the photocrosslinking of cinnamate units occurs.

Key Words: glycidyl cinnamate, UV irradiation, photoisomerization, photocrosslinking, characterization

INTRODUCTION

The interest in photosensitive systems is considerable, because of their applications in various areas: microelectronics, photography, lithography, organic synthesis. Most of these systems are based on cinnamate derivatives. Esters of cinnamic acid and its analogous have been studied because of the technological importance of their photofunctionality. It is well known that cinnamate chromophore undergoes $[2\pi+2\pi]$ photocycloaddition, isomerization and photo-Fries rearrangement during UV irradiation.

Cinnamate based chromophores are incorporated into different monomeric and polymeric systems as potential cross-linking units by photoformation of cyclobutane ring systems. The cross-linking reaction, upon exposure to UV light, lowers the solubility of photosensitive system in the developing solvents. The

cycloaddition reaction has been used as photoresist mechanism and seem to serve as an interesting method for studying conformational states of macromolecules [1-6]. Polymers with cinnamoyl units have also been studied as material for optical wave-guides [7] or for their ability to regulate liquid crystal alignment [8, 9].

Oxiranes have drawn much attention as starting compounds in organic synthesis. Addition reactions and ring-opening polymerization of oxiranes are well known [10-15]. Also, the cationic photopolymerization of epoxy group can be initiated by triaryl-onium salts [16].

The glycidyl ester of cinnamic acid has a cinnamoyl group and an epoxy group. This compound combines the advantages of oxirane (reactive and photosensitive) and of α , β -unsaturated carbonyl groups (photosensitive). The glycidyl ester of

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cinnamic acid can be used in photosensitive systems. The literature data about this subject is very poor [17–19].

The purpose of the current work was the synthesis of new photosensitive esters derived from glycidyl cinnamate and the study of photochemical behaviour of synthesized cinnamate compounds.

These photosensitive compounds were obtained by reaction of epoxy group from glycidyl cinnamate with activated carboxyl units from derivatives of cinnamic acid and styrene-maleic anhydride copolymers.

EXPERIMENTAL

Materials

Cinnamoyl chloride (mp: 36 °C) was synthesized as reported earlier [20]. Styrene-maleic anhydride (S₁, S₂) alternating copolymers were prepared by radical polymerization in presence of benzoyl peroxide [21]. Epichlorohydrin was dried over Na₂SO₄ and fractionated (bp: 115–117 °C). Tetrabutyl ammonium bromide and triethylamine were purchased from Fluka and were reagent grades. Potassium cinnamate was obtained by neutralization of equimolar amounts of cinnamic acid and potassium hydroxide. All solvents were purified by usual methods before use.

Measurements

IR absorption spectra were performed using a SPECORD M80 spectrophotometer in KBr pellets, and ¹H NMR spectra were recorded in CDCl₃ on a Jeol CH 60L spectrometer (tetramethylsilane as internal standard). The electronic absorption spectra were measured on a SPECORD M42 spectrophotometer (Carl Zeiss Jena), using 10 mm quartz cells fitted with PTFE stoppers. The initial absorbance of the absorption band under the study was kept between 0.9–1.0. The photochemical studies were performed with a high-pressure mercury lamp (350 W) as radiation source, in combination with a 313 nm filter, at room temperature. Differential scanning calorimetry (DSC) analysis were carried out under dry nitrogen flow using a Mettler DSC 12E apparatus.

A sample of 5–7 mg was placed onto an Al pan and was heated at 20 °C/min from room temperature. Indium standard sample was used for calibration. The viscosity measurements were performed using an Ubbelohde viscometer with internal dilution.

Synthesis

Preparation of Glycidyl Cinnamate (Compound 1)

In a 150 mL three necked flash equipped with a reflux condenser, a thermometer and a mechanical stirrer 3.72 g (0.02 mol) potassium cinnamate and 19.6 mL (0.25 mol) epichlorohydrin were mixed. Then 0.034 g (0.001 mol) tetrabutyl ammonium bromide was added. The reaction mixture was stirred at 95–100 °C for 1 h. The product was diluted with CCl₄ and potassium chloride was filtered. The organic layer was twice washed with 5% aqueous NaHCO₃ and water and then it was distilled under reduced pressure (yield 68.3 %).

IR spectrum (KBr): 680 cm⁻¹ (C=C *cis*), 770 cm⁻¹ (C=C-Ph), 860 cm⁻¹ and 915 cm⁻¹ (epoxy), 980 cm⁻¹ (C=C *trans*), 1640 cm⁻¹ (C=C-Ph), 1715 cm⁻¹ and 1170 cm⁻¹ (ester).

¹H NMR (CDCl₃) δ (ppm) = 7.25 and 7.6 (*m*, aromatic protons), 6.4 and 7.7 (*d*, CH=CH), 3.95–4.65 (*dd*, CH₂), 3.15–3.40 (*m*, CH), 2.7–2.9 (*m*, CH₂).

UV (C₂H₄Cl₂): λ_{max} = 280 nm.

Epoxy equivalent weight = 233 ; Epoxy value found/calculated = 0.428/0.490.

Reaction of Glycidyl Cinnamate with Cinnamoyl Chloride (Compound 2)

The glycidyl cinnamate 2 g (0.01 mol) was dissolved in 20 mL dry dioxane and 0.034 g (0.001 mol) tetrabutyl ammonium bromide was added. Then cinnamoyl chloride 2.1 g (0.0125 mol) in 10 mL dry dioxane was added dropwise under stirring at room temperature. The reaction mixture was heated at 100 °C for 15 h and then it was filtered. The solvent was evaporated and the crude product (**2**) was twice precipitated from acetone into methanol and dried in vacuo at 40 °C (yield 64%).

IR spectrum (KBr) 710 cm⁻¹ (C-Cl), 980 cm⁻¹ (C=C *trans*), 1640 cm⁻¹ (C=C-Ph), 1720 cm⁻¹ (ester).

$^1\text{H NMR}$ (CDCl_3) δ (ppm) = 3.8 (*d*, CH_2Cl), 4.2–4.6 (*t*, CH_2), 5.2–5.6 (*m*, COOCH), 6.4 and 7.65 (*d*, $\text{CH}=\text{CH}$), 7.25–7.6 (*m*, aromatic protons).

%Cl found/calculated = 9.56/9.59

Synthesis of Tricinnamate (Compound 3)

The toluene solution of chloromethylated compound 2 (1 g) containing potassium cinnamate (0.9 g) and tetrabutyl ammonium bromide (0.09 g) was heated at 70 °C for 24 h. The reaction mixture was filtered and the solution was washed with 5% aqueous NaCl and water. Then the solvent was evaporated and the product was dried in vacuo at 40 °C (yield 52%).

UV ($\text{C}_2\text{H}_4\text{Cl}_2$): λ_{max} = 280.5 nm; %Cl = 5.82

Reaction of Glycidyl Cinnamate with Styrene Maleic Anhydride Copolymers (Copolymers 4.1 and 4.2)

Styrene maleic anhydride copolymers (S_1 and S_2) were synthesized by copolymerization of an equimolar mixture of styrene and maleic anhydride in benzene solution (5.0 g monomers per 25 mL of solution) in presence of benzoyl peroxide (0.2 wt % related to the monomers).

Elemental analysis for copolymer S_1 .

| Copolymer | C % | H % |
|-----------|------|------|
| calcd | 72.3 | 5.08 |
| found | 71.3 | 5.20 |

Elemental analysis for copolymer S_2 .

| Copolymer | C % | H % |
|-----------|------|------|
| calcd | 72.3 | 5.08 |
| found | 71.6 | 5.40 |

The general procedure for obtaining the copolymers 4.1 and 4.2 is illustrated by the following example: styrene-maleic anhydride copolymer (1 g) was dissolved in 10 mL dimethylformamide (DMF). Then 0.56 g glycidyl cinnamate in 5 mL DMF, 0.5 mL triethylamine and 0.2 mL of methyl alcohol were added. The mixture was stirred at 80 °C for 2 h, and poured into chloroform. The solution was washed with diluted hydrochloric acid and water. The solvent was evaporated and the copolymer was redissolved in

DMF. A clear film was obtained from DMF solution of copolymer 4.1 or 4.2.

RESULTS AND DISCUSSION

The synthetic pathway of the compounds under this study is outlined in Scheme 1.

Compound 1, glycidyl cinnamate, was obtained from potassium cinnamate and epichlorohydrin. In order to obtain the compound 1 in good yield it is necessary to use the phase-transfer catalyst ($\text{R}_4\text{N}^+\text{X}^-$) and to apply an excess of epichlorohydrin. Addition of a quaternary ammonium halide was reported to increase the rate of reaction of epichlorohydrin with carboxylic acid salts [10, 13]. The rate determining step is the formation of chlorohydrin alcoholate by nucleophilic attack of the carboxylate anion at the epoxy group [13].

It is known that a gel compound is produced when the reaction takes place between epichlorohydrin and carboxylic acid. It is considered that the best method is the reaction of epoxides with acid chloride. The compounds with an ester group and a reactive chloromethyl group are formed. These compounds can be further modified by nucleophilic substitution [11, 22].

The compound 2 was obtained from glycidyl cinnamate and cinnamoyl chloride using quaternary ammonium salt as catalyst. The synthesis of compound 2 was monitored by IR spectroscopy. The disappearance of absorption band at 915 cm^{-1} assigned to terminal epoxide group was observed.

The compound 3 has 2.2–2.4 cinnamate ester group in molecule. It is known that molecules containing more than one cinnamoyl moiety are potential photocrosslinking agents [23].

In the $^1\text{H NMR}$ spectrum the decrease of the signals for $-\text{CH}_2\text{Cl}$ group at 3.7–3.8 ppm was noticed.

The light sensitive copolymers 4.1 and 4.2 were prepared by modification of alternating styrene-maleic anhydride copolymers with glycidyl cinnamate. The reaction is initiated by activation with triethylamine [12, 15, 24 and 25]. Methyl alcohol is added for opening the anhydride ring. The anhydride

Table 1. Characteristics of copolymers 4.1 and 4.2.

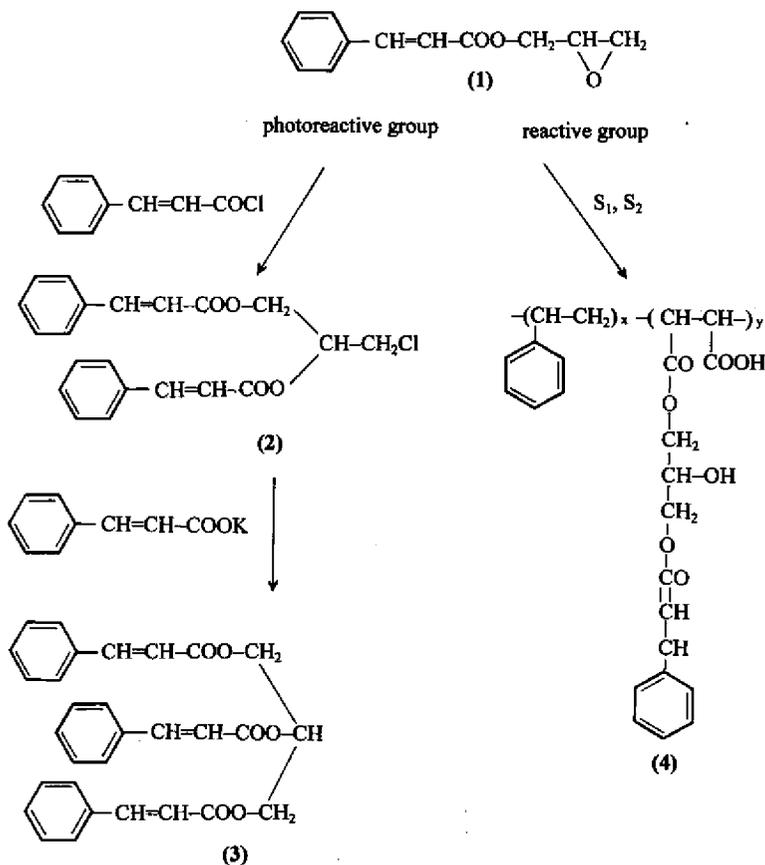
| Sample | M_n^* | Degree of esterification** (%) | T_g^{DSC} (°C) | λ_{max} (DMSO) (nm) | Product (g) |
|--------|---------|--------------------------------|------------------|-----------------------------|-------------|
| 4.1 | 38000 | 18 | 146 | 281 | 0.97 |
| 4.2 | 82000 | 22 | 152 | 281 | 1.06 |

* M_n – viscometric average molecular weight of styrene-maleic anhydride copolymers S_1 and S_2 , respectively; ** determined from the UV spectra.

units are reactive towards epoxy group from glycidyl cinnamate and in this case styrene confers mechanical properties of copolymers. The characteristics of co-

polymers 4.1 and 4.2 are presented in Table 1.

The electronic absorption spectra of monomers and polymers synthesized are characterized by a

**Scheme 1**

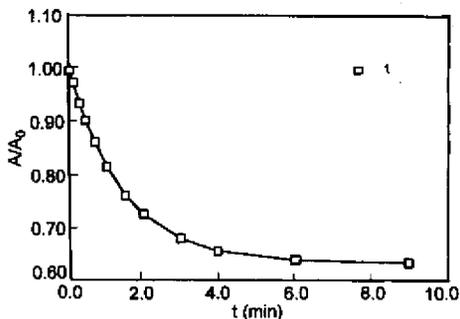


Figure 1. Dependence of relative absorption of compound 1 on irradiation time.

strong absorption band at about 280 nm attributable to the cinnamate ester group.

UV irradiation of the monomeric compounds 1 and 2 in dichloromethane solutions leads to a significant decrease with the irradiation time of the intensity of absorption band centered at 280 nm, as is shown in Figures 1 and 2.

The successive spectral changes in the electronic absorption spectra of compound 3 are characterized by two isosbestic points at 250 and 316 nm. The presence of the isosbestic points and the linear plot of absorbance differences suggests that the *trans-cis* photoisomerization is the predominant photoreaction

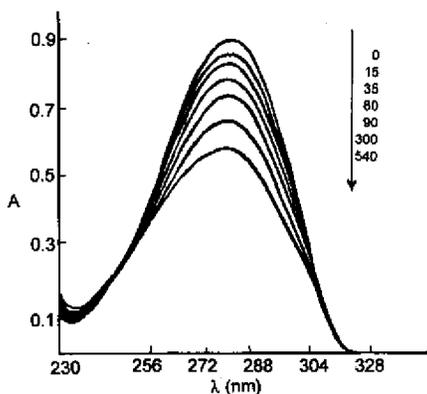


Figure 2. Changes in electronic absorption spectrum of compound 3 during UV irradiation.

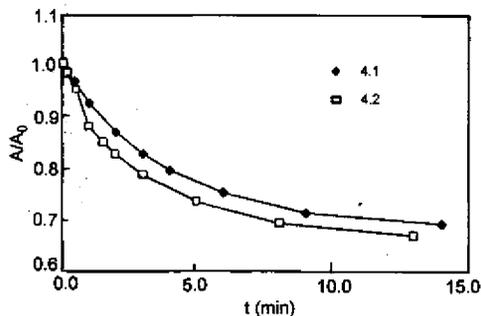


Figure 3. Dependence of relative absorption on irradiation time for polymers 4.1 and 4.2.

in solution.

Upon irradiation of the polymers 4.1 and 4.2 in solution the absorbance of cinnamate moiety at 280 nm is decreased as shown in Figure 3. In the same manner as compounds 1 and 3, the kinetics of the photoreaction are characterized by an initial fast decrease of the cinnamate absorbance, followed then by a slow decrease on further exposure, the photoisomerization being also the predominant process in this case.

However, on continued irradiation the isosbestic points disappear. The change of the absorbance can be caused by [2+2] photocycloaddition reaction [1, 6].

Analysis of this decrease in intensity of the absorption band at 280 nm shows that in the first minute of irradiation the process is linear for all

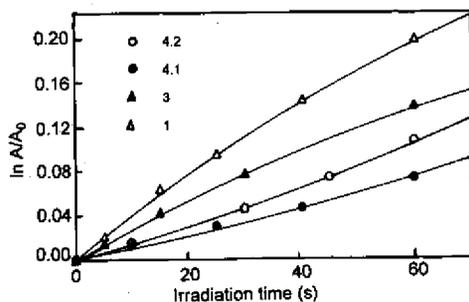


Figure 4. Relative photostability of cinnamate compounds.

compounds considered (Figure 4). We observe that the compound 1 is much more sensitive to UV exposure than other compounds. Also, the polymer 4.2 exhibits a higher photoreactivity to UV than compound 4.1.

In films of polymers 4.1 and 4.2 obtained from DMF solutions a continuous decrease of cinnamate absorption band at 280 nm is observed on irradiation. Also, the IR-absorption band at 980 cm^{-1} , associated with *trans* -C=C- double bond, from cinnamate moieties decreased quickly during photoirradiation. After 2 min the irradiated polymer films became insoluble in organic solvents due to the photocrosslinking of cinnamate groups most probably by interchain cyclodimerization.

CONCLUSION

Photosensitive compounds with cinnamoyl units were synthesized from glycidyl cinnamate and active carboxylic acid derivatives (cinnamoyl chloride, potassium cinnamate and maleic anhydride units from styrene-maleic anhydride copolymers).

Upon irradiation of synthesized compounds in solution the absorption band due to cinnamoyl chromophore positioned at 280 nm is decreased and the *trans-cis* photoisomerization is the predominant photoreaction. The films of polymers 4.1 and 4.2 become insoluble in organic solvents upon 2 min of exposure at UV light due to the photocyclodimerization of cinnamate moieties.

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