



## Photocrosslinked Polymer Based on Pendant Extended Cinnamate as Photoreactive Moieties

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**Abstract** A monomer having a free-radical polymerizable methacryloyl group and a photocrosslinkable functional group (pendant cinnamate unit) was synthesized and polymerized at 65°C using AIBN as an initiator. The prepared monomer and polymer was characterized by UV, IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra. The molecular weights (Mw and Mn) of the polymer were determined by gel permeation chromatography.

The photoreactivities of the obtained polymers were examined in the solid state by irradiation of thin films.

**Keywords** Cinnamate derivates, photoreactivities, methacryloyl, irradiation, Photocrosslinkable polymers

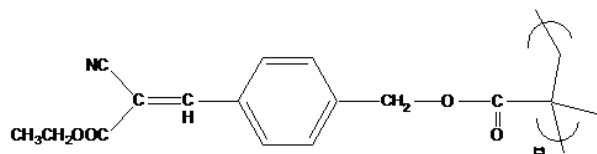
### 1. Introduction

The technological applications of the radiation sensitive polymers have attained considerable interest and have developed to a wide research area in different fields, such as, photolithography [1–3], printing materials [4-5], liquid crystalline [6–8] and non-linear optical materials [9–10].

The technological applications of many photoresists have been reviewed [11-15]. Many different photoresist systems are used in the manufacture of various industrial products such as integrated circuits [16], compact discs [17], cathode ray tubes [18] and printed circuit boards [19].

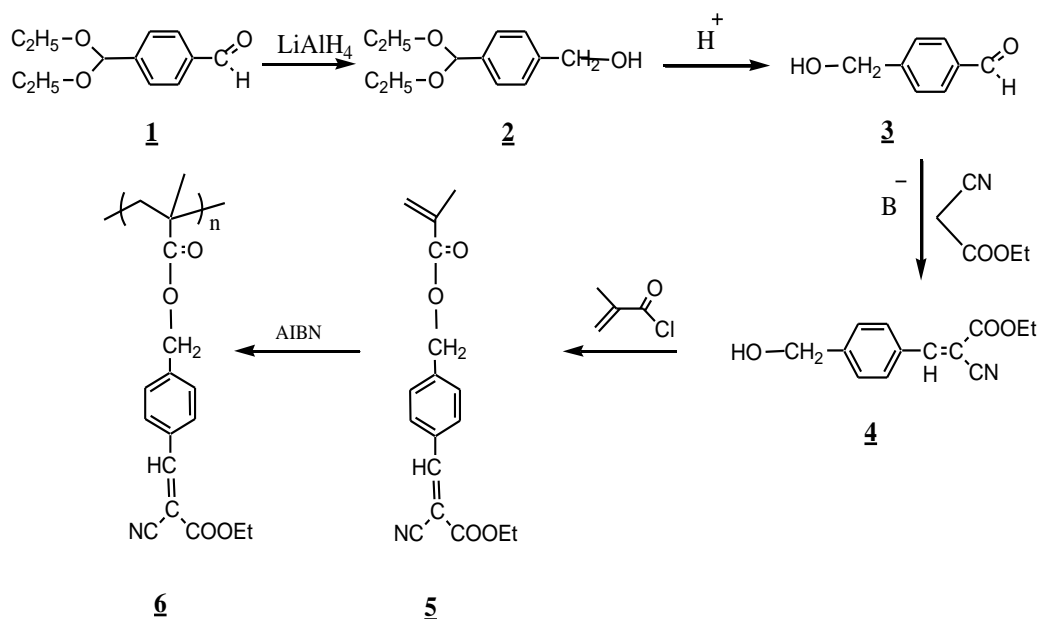
The polymers having  $\alpha,\beta$ -unsaturated carbonyl groups either in the backbone or in the pendant groups undergo crosslinking upon irradiation with UV light, and such polymers are regarded as negative type photoresists. High photosensitivity, thermal stability, and good solubility are essential requirements for the practical use of a polymer as a photoresist. The polymers with pendant photofunctional groups, such as cinnamoyl esters of poly(vinyl alcohol) [20–21], the Polymers with photosensitive groups, such as the cinnamic acid [22-25], and many other compositions, have been studied.

In continuation of our work on polymers containing pendant photocrosslinkable groups [26-27], we report in this article, the synthesis, characterization, and photocrosslinking property of a polymethacrylate having pendant cinnamate units (Scheme 1).



Scheme 1: Homopolymer

On the other hand the dimerization of the cinnamic function under irradiation would be affected by a functional group bonded on the  $\alpha$ -unsaturated carbone of the cinnamate group. So it was considered interesting to study these effects in case of the photocrosslinking of polymethacrylates support of cinnamate groups. Our purpose was to develop a general method to synthesize these types of photosensitive polymers (Scheme 2).



Scheme 2: Synthesis of photosensitive homopolymer

## 2. Material and Methods

### 2.1. Materials

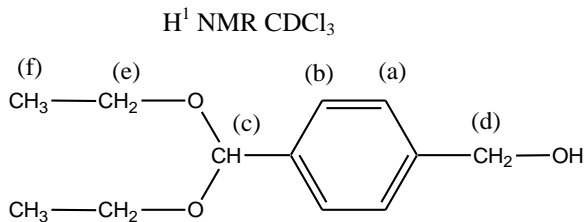
Solvents were distilled before use according to the procedures described by Perrin book. AIBN was recrystallized from methanol. Methacryloyl chloride was used after purification by vacuum distillation. The others compounds were used as received.

### 2.2. Apparatus

Melting points were determined on a Büchi apparatus. Infrared spectra were obtained on a Perkin-Elmer 1750 Fourier-transform spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on Avance DPX200 or Bruker AC 400 operating at 400.13 MHz for  $^1\text{H}$  and 100 MHz for  $^{13}\text{C}$ , in DMSO- $d_6$  with tetramethylsilane (TMS) as internal reference. The weight- and number-average molecular weights were determined by Size Exclusion Chromatography (SEC) on a Spectra SYSTEM AS1000 autosampler system, equipped with a guard column (Polmer Laboratories, PL gel 5  $\mu\text{m}$  Guard, 50x7.5 mm) and two columns (Polmer Laboratories, 2 PL gel 5  $\mu\text{m}$  MIXED-D columns, 300x7.5 mm) connected in series, and a Spectra SYSTEM RI-150 detector. Analyses were performed at 35°C, with THF used as mobile phase at a flow rate of 1 ml.min $^{-1}$ . The system was calibrated using low polydispersity polystyrene standards (580-483x103 g.mol $^{-1}$ ). The photocrosslinking studies were performed using a B100A Ultraviolet lamp emitting from 300 to 400 nm (100 w;  $k_{\text{max}} = 365$  nm).

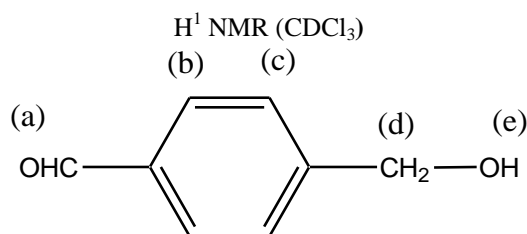
### 2.3. Synthesis diethyl acetal of 4-hydroxymethyl benzaldehyde **2**

In a tricolor equipped with a condenser, thermometer and dropping funnel are introduced 1g of  $\text{LiAlH}_4$  and 20ml of diethyl ether. The mixture is refluxed for 2 hours and a solution of 7g of diethylmonoacetal of terephthalaldehyde **1** in 20ml of diethyl ether is added dropwise. After the end of the addition, the mixture is refluxed for 16 hours. the reaction mixture is recovered in an ice-ether mixture.  $\text{LiAlO}_2$  formed is filtered and washed with water and with ether. The separated organic phase will be dried over  $\text{MgSO}_4$ . The product obtained is a colored liquid, the yield obtained is 92%.



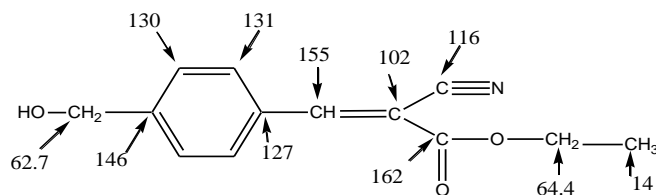
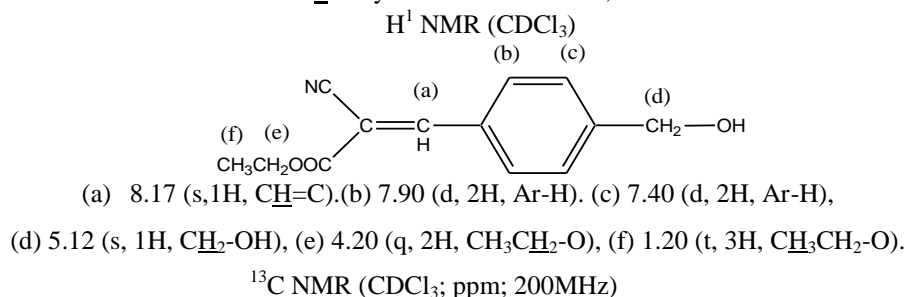
#### 2.4. Synthesis of 4-hydroxymethylbenzaldehyde **3**

We introduced 3.3 g of **2**, 30 ml of THF and 14 ml of HCl(3N). The mixture is stirred for 24 hours. The solvent is removed. The residue is dissolved in dichloromethane. The organic phase is washed with water and a saturated solution of Na<sub>2</sub>CO<sub>3</sub> and then dried over MgSO<sub>4</sub>. After filtration and evaporation we obtained **3**, the yield obtained is 42%, Bp = 42°C.



#### 2.5. Synthesis of cyano 4-hydroxymethylcinnamate ethyl **4**

A mixture of 4-hydroxymethylbenzaldehyde **3** (0.025 mol), ethyl cyanoacetate (0.038 mol), pyridine (7.5 ml) and piperidine (0.1 ml) are refluxed for 1 hour. Then, the solution is poured into a beaker containing water (100 ml) and crushed ice (25 g). After filtration we obtained **4** the yield obtained is 55%, Pf = 122°C.

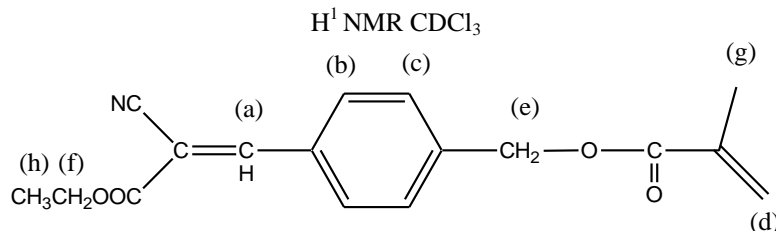


#### 2.6. Synthesis of cyano 4-methylmethacrylate methylcinnamate ethyl **5**

A solution of **4** (0.018 mol) in dichloromethane (12 ml) was introduced in a three necked round-bottom flask and cooled at 0°C using an ice bath. Solutions of methacryloyl chloride (0.018 mol) in dichloromethane (6 ml) and triethylamine (0.018 mol) in dichloromethane (6 ml) were added simultaneously and dropwise from two dropping funnels into the stirred mixture. At the end of addition, the ice bath was removed and the stirring was maintained for 24h at room temperature. The resulting triethylammonium chloride was filtered off and the filtrate was washed twice

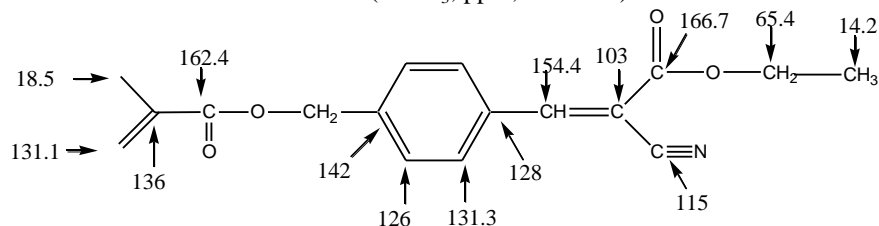


with a solution sodium bicarbonate, then water. After drying with the natrium sulfate, the solution was filtered, the solvent was evaporated under reduce pressure and the crude product was recrystallized in ethanol. yield = 50%; Bp = 74°C.



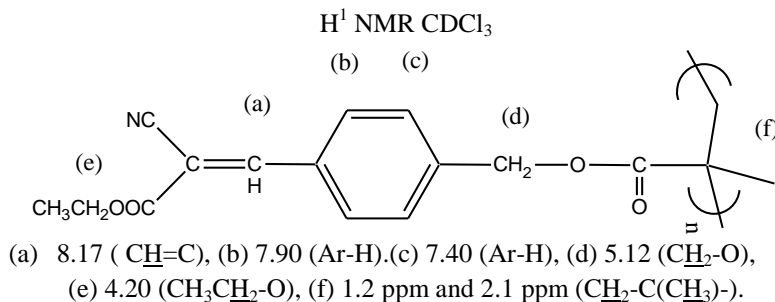
- (a) 8.17 (s, 1H,  $\text{CH}=\text{C}$ ), (b) 7.90 (d, 2H, Ar-H), (c) 7.40 (d, 2H, Ar-H), (d) 6.10 (s, 1H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ), 5.50 (s, 1H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ), (e) 5.12 (s, 1H,  $\text{CH}_2-\text{OH}$ ), (f) 4.20 (q, 2H,  $\text{CH}_3\text{CH}_2-\text{O}$ ), (g) 2.06 (s, 3H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ), (h) 1.20 (t, 3H,  $\text{CH}_3\text{CH}_2-\text{O}$ ).

<sup>13</sup>C NMR (CDCl<sub>3</sub>; ppm; 200MHz)



### 2.7. Synthesis of Homopolymer **6**

In a round-bottom flask fitted with a condenser were introduced 0.23 mmol of monomer **5**, 5 ml of butanone and AIBN (1% compared to monomer **5**). The mixture was swept by nitrogen, then heated at 65°C. After the required time (8 h), the obtained mixture was poured in an excess of methanol (20 ml). The product was washed with methanol, then purified by reprecipitation into methanol from solution in chloroform and finally dried in vacuum. yield = 95%.



### 2.8. Photoreactivity measurements

The photochemical reactivity of the synthesized polymers was measured as follows:

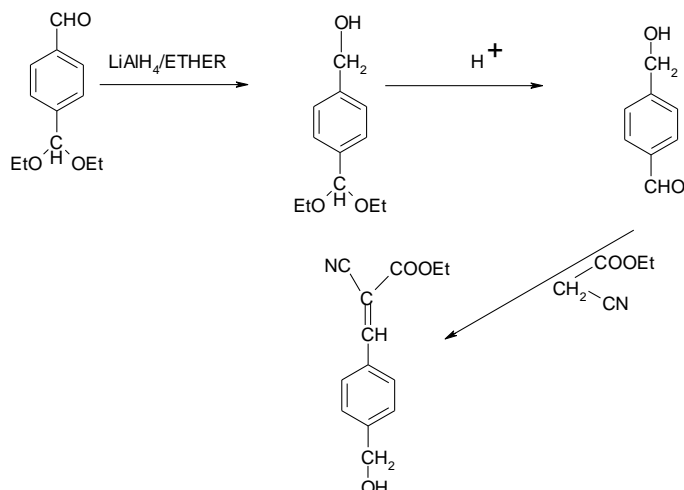
The polymer solution in THF was cast on a quartz plate and dried under vacuum at 40 °C for 1 h. After drying, the film formed on the plate was irradiated using the B100A Ultraviolet lamp placed at a distance of 5 cm for different time intervals. After each exposure interval, UV spectra of the sample were recorded, and the photocrosslinking rate was determined by following the intensity decrease of the cinnamate absorption band 340 nm.

## 3. Results and Discussion

### 3.1. Preparation of cyano 4-hydroxymethylcinnamate ethyl **4**

We have realised the synthesis of the cinnamic derivative **4**. This compound can be obtained by two methods: The first method consists in first condensing the malonic derivative on terephthalaldehyde diethylmonoacetal **1** by the Knoevenagel reaction, then regenerating the aldehyde function by unblocking diethylmonoacetal with hydrochloric acid solution, and finally reducing the aldehyde function to alcohol by alumina (Scheme 3).

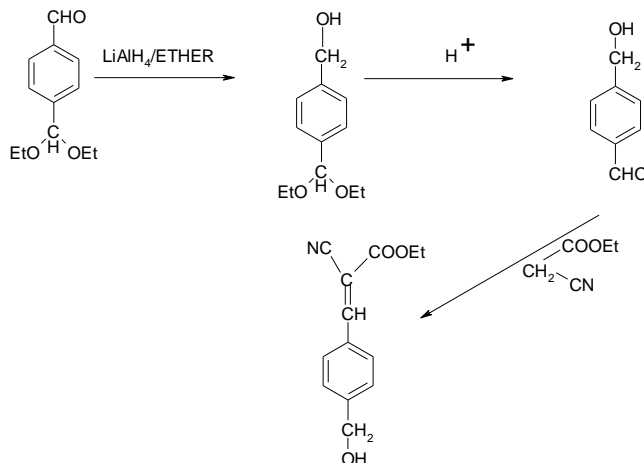




**Scheme 3:** Synthesis of cyano 4-hydroxymethylcinnamate ethyl **4**

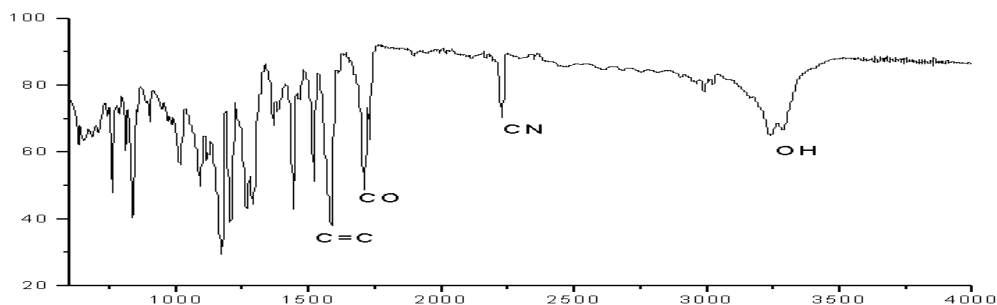
The product **4** is obtained but mixed with other products probably coming from the acid hydrolysis of the ester and nitrile functions.

The second method consists of reducing the aldehyde function of diethylmonoacetal with lithium tetrahydride and aluminum then condensing the product obtained on ethyl cyano malonate at the reflux of pyridine and in the presence of piperidine (Scheme 4).



**Scheme 4:** Synthesis of cyano 4-hydroxymethylcinnamate ethyl **4**

The product **4** white solid is obtained after repeated recrystallizations in a pentane-dichloromethane mixture. Melting point is 122 °C-124 °C, the structure of which is confirmed by the spectroscopic: IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR.



**Figure 1:** IR of cyano 4-hydroxymethylcinnamate ethyl **4**



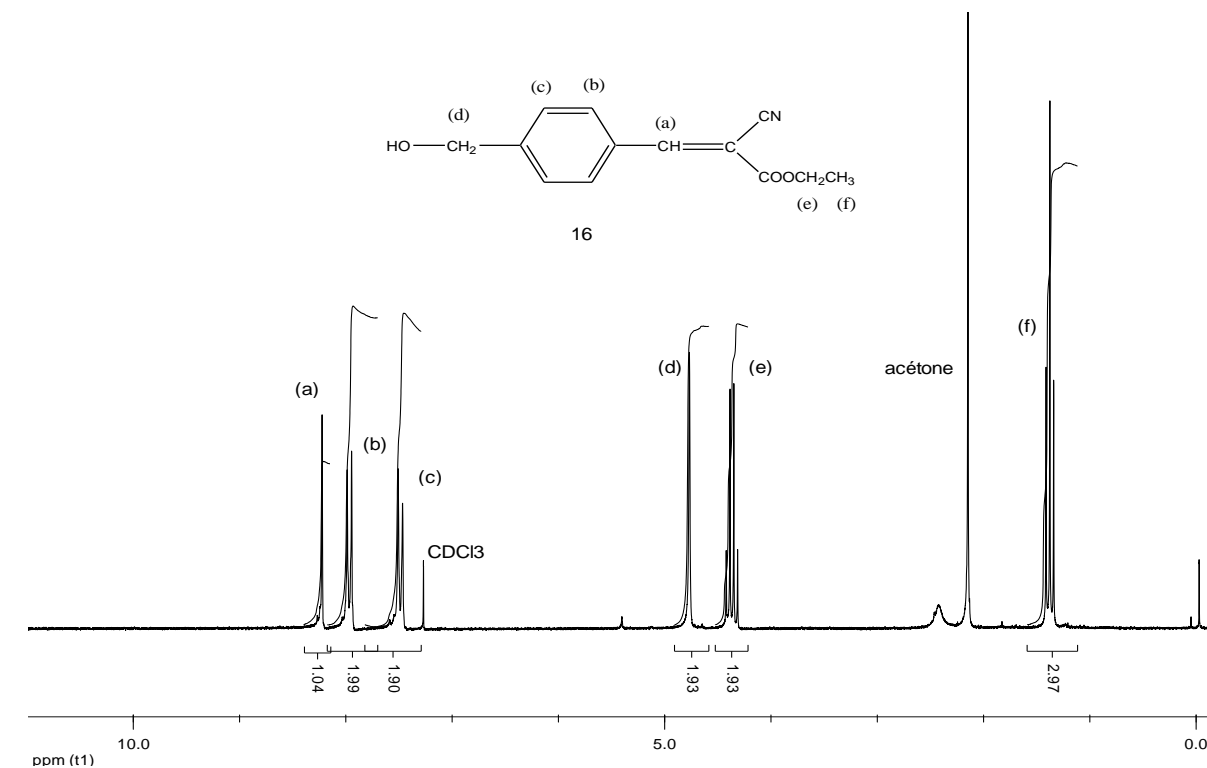


Figure 2:  $^1\text{H-NMR}$  of cyano 4-hydroxymethylcinnamate ethyl **4**

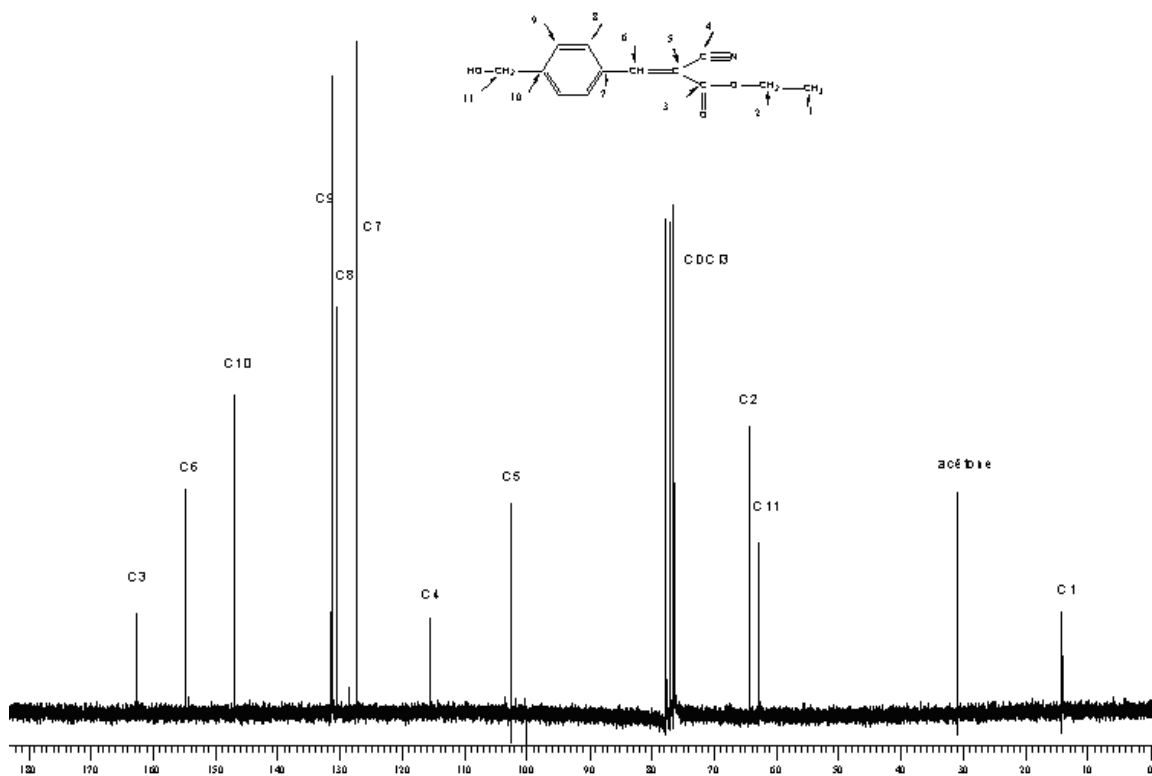


Figure 3:  $^{13}\text{C-NMR}$  of cyano 4-hydroxymethylcinnamate ethyl **4**

### 3.2. Preparation of cyano 4-methylmethacrylatemethylcinnamate ethyl **5**

The product **4** was esterified by methacryloyl chloride in presence of triethylamine to give the methacrylate monomer **5** (Scheme 2).

The product **5** is obtained after recrystallization in a ethanol. yield 50%, melting point is 74°C, the structure of which is confirmed by the spectroscopic : IR, <sup>1</sup>H-NMR and <sup>13</sup>C NMR. In IR, strong absorption bands characteristic of the carbonyles of methacrylate and cinnamate functions were noted at 1756 cm<sup>-1</sup> and 1716 cm<sup>-1</sup>, respectively and absence weak absorption band at 3250 cm<sup>-1</sup> to HO-. The <sup>1</sup>H NMR spectrum of **5** shows resonances at 7.90 and 7.40 ppm due to aromatic protons, the proton of the CH=C unsaturations is noted at 8.17 ppm, signal at 6.10 ppm correspond to CH<sub>2</sub>=C(CH<sub>3</sub>)-, signal at 5.50 ppm correspond to CH<sub>2</sub>=C(CH<sub>3</sub>)-, signal at 5.12 ppm correspond to CH<sub>2</sub>-OH, quadriplet at 4.20 ppm correspond to CH<sub>3</sub>CH<sub>2</sub>-O, signal at 2.06 ppm correspond to CH<sub>2</sub>=C(CH<sub>3</sub>)- and triplet to 1.20 ppm correspond to CH<sub>3</sub>CH<sub>2</sub>-O. The monomer prepared is characterized by the presence of two sites, a photosensitive site and a polymerizable site. It is essential that the two sites do not interact with each other during the polymerization and during photocrosslinking.

### 3.3. Preparation of Homopolymer **6**

Radical homopolymerization of **5** was initiated with azoisobutyronitrile (AIBN). It was performed at 65°C in butanone (Scheme 2). After 8 h of reaction, polymer **6** was obtained in 90% yield. It showed good solubility in butanone, THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, benzene, toluene, DMF.

The weight- and number-average molecular weights of 12155 and 6034, respectively, were determined by SEC. The value of dispersity index (Đ = 2.014) which is close to 2, suggests a tendency for chain termination by dispropotionation. Homopolymer **6** was characterized by IR and <sup>1</sup>H NMR. In IR, strong absorption bands characteristic of the carbonyles of methacrylate and cinnamate functions were noted at 1770 at 1725 cm<sup>-1</sup> respectively. An absorption band at 1595 cm<sup>-1</sup> was assigned to aromatic CH=C stretching vibration.

The <sup>1</sup>H NMR spectrum of **6** shows resonances at 7.90 to 7.40 ppm due to aromatic protons. The proton of the CH=C unsaturations is noted at 8.17 ppm, Signal at 5.12 ppm corresponds to CH<sub>2</sub>-O protons, Signal at 4.20 ppm corresponds to CH<sub>2</sub> protons of ethoxy groups, the CH<sub>3</sub> protons of ethoxy groups and the backbone protons rise at 1.2–2.1 ppm. In figure 4 we represent the principal parts characterizing the synthesized products

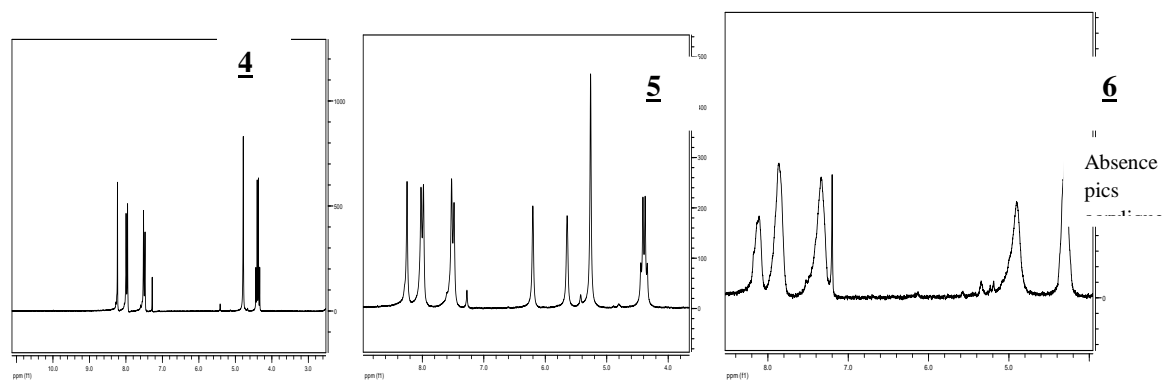


Figure 4: The principal parts characterizing the synthesized products

### 3.4. Photoreactivity of the synthesized polymer

A first approach of the photoreactivity in solid state of the synthesized polymer was carried out. The film were irradiated using a B100A Ultraviolet lamp emitting from 300 to 400 nm (100 w; λ<sub>max</sub> = 365 nm).

UV spectra of the polymer **6** recorded after various times of irradiation are given in Figure 5. The UV analyses show that the intensity of absorbance at λ = 340 nm due to cinnamate moieties decreases during exposure. While that at λ = 270 nm due to the cyclobutane formation increases gradually. The insolubility of the studied films in organic solvents after the irradiation confirms that photocrosslinking took place.



More detailed studies on the ability of homopolymer **5** to crosslink under UV irradiation are under investigation. The results of these studies will be reported elsewhere.

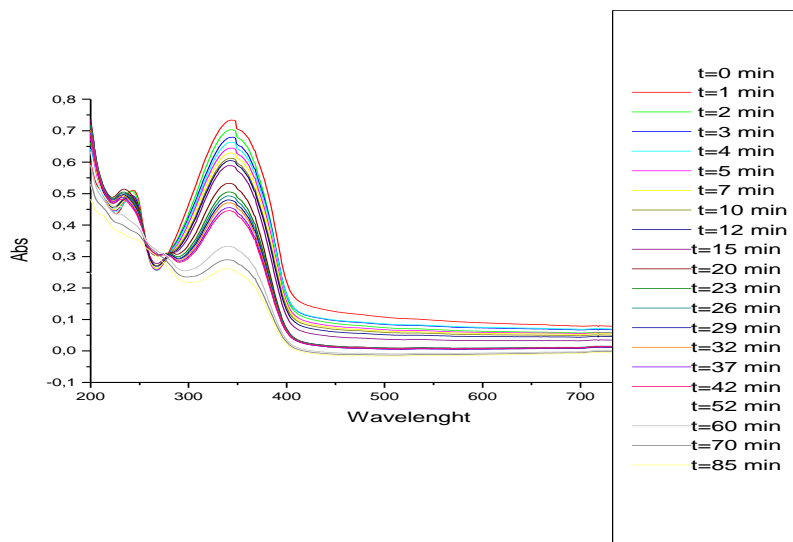


Figure 5: UV spectra of polymer **6** recorded after each exposure interval

## Conclusion

The purpose was to develop a general method to synthesize new photocrosslinkable polymethacrylates support of pendant photosensitive cinnamate having the particularity to have a functional group bonded on its  $\alpha$  unsaturated carbon. The cyano group was selected as an example of functional group. From that, the objective was to synthesize the photosensitive methacrylate monomer **5**. It was prepared in two steps with good yields:

- First, the intermediate **4** was prepared by Knoevnagel condensation.
- Then **4** was reacted with methacryloyl chloride to form the intended monomer **5**.

Afterwards radical polymerization initiated with AIBN was used to prepare homopolymer of **5**. Homopolymerization are performed at 65°C in butanone as solvent. homopolymer of medium molecular weights were obtained with good yields. They showed good solubility in most of the organic solvents. Their structures were confirmed by using various spectroscopic methods.

The photoreactivity in solid state of the synthesized polymer was carried. The film were irradiated using a B100A Ultraviolet lamp emitting from 300 to 400 nm (100 w;  $\lambda_{\text{max}} = 365$  nm). The insolubility of the studied films in organic solvents after the irradiation confirms that photocrosslinking took place.

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