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Synthesis of novel photosensitive polymers and copolymers containing cinnamic groups as pendant photoreactive functions

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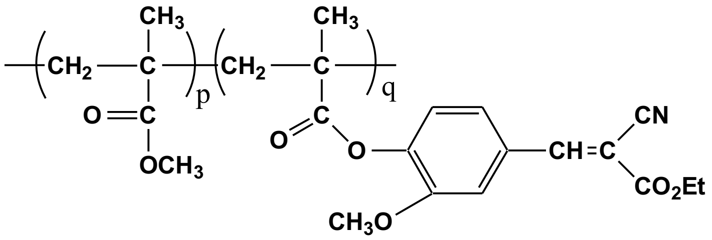
Abstract

A general method to synthesize photocrosslinkable (co)polymethacrylates support of pendant photosensitive cinnamate groups having the particularity to have a functional group bonded on its α unsaturated carbon was developed. The cyano group was selected as an example of functional group. Homopolymers of ethyl 2- cyano-3-(4-(methacrylate)-3-methoxyphenyl)prop-2-enoate and copolymers of this last monomer with methyl methacrylate were prepared in butanone solution at 65°C using AIBN as an initiator. They were characterized by IR, ^{1}H-NMR, and ^{13}C-NMR. Compositions of the copolymers were determined by ^{1}H-NMR spectroscopy. The photoreactivities of the obtained (co)polymers were examined in the solid state by irradiation of thin films

1. Introduction

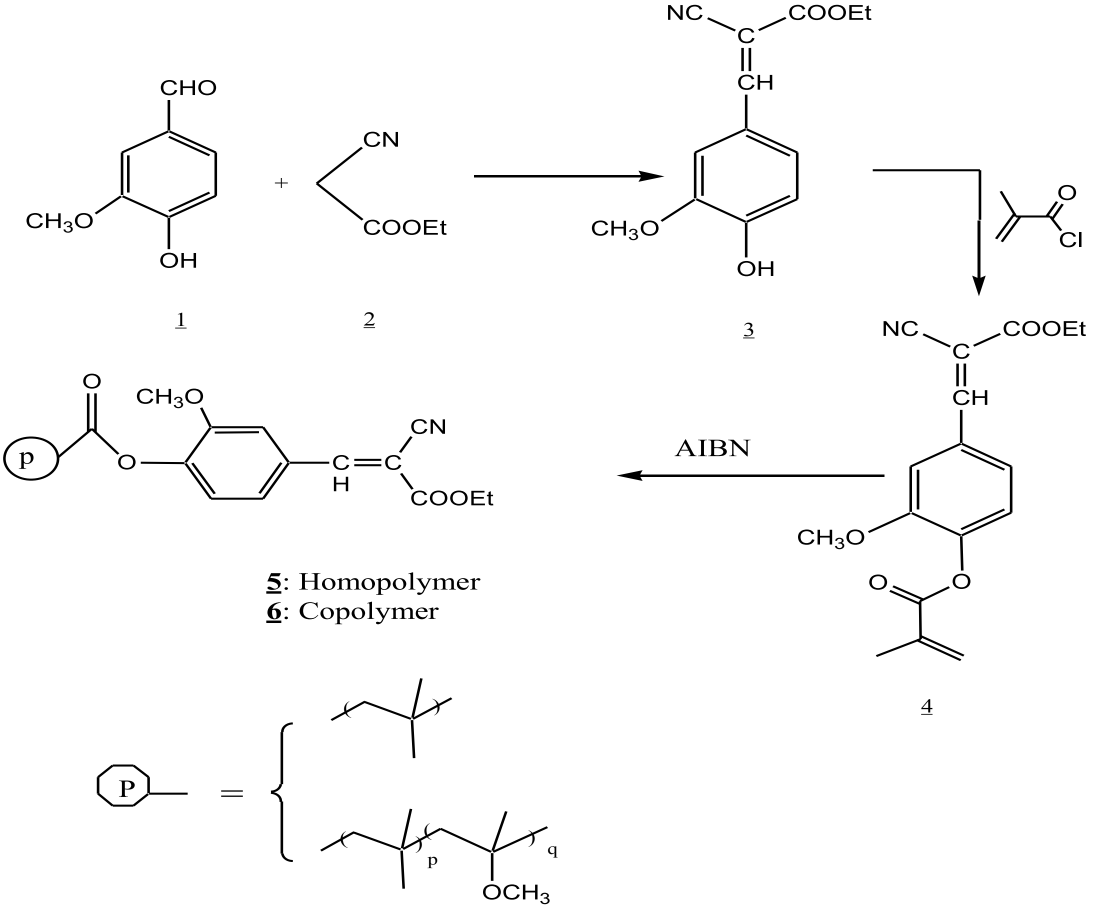
Photocrosslinkable polymers have attracted considerable interest in the last decades owing to their potential applications in photoresists for the manufacture of numerous industrial products, for instance, integrated circuits, printing materials, coatings, paint, compact discs, cathode ray tubes, etc.[1-5] Linear polymers having cinnamic groups either in the backbone or in side position of the chain undergo crosslinking after irradiation. The capability of these polymers to crosslink is due to the carbone-carbone double bonds of the α,β-unsaturated carbonyl groups, witch undergo [2π+2π] cycloaddition reactions under irradiation. These photosensitive polymers are regarded as negative-type photoresists [6-10]. For practical use as commercial negative-type photoresists materials [11-15], the properties of high photosensitivity, ability to form films, good solubility, thermal stability and resistance towards etching agents are very important[16-21]. The Polymers with photosensitive groups, such as the cinnamic acid [22-26], and many other compositions, have been studied.

The present paper deals with the synthesis and the characterization a by selected photosensitive methacrylate monomer (Scheme 1) and the (co)polymers derived from it. Studies on the photosensitivity in the solid state of the obtained (co)polymers are also reported.



Scheme 1 : *Homopolymers (p=0, q≠0) et Copolymers (p≠0, q≠0) Homopolymers (p=0, q#0) and Copolymers (p=0, q#0)*

On the other hand the dimerzation of the cinnamic function under irradiation would be affected by a functional group bonded on the α-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. For that, (co)polymethacrylates support of cinnamate groups bearing an α -cyano substituent were considered (Scheme 2).



Scheme 2 : *Synthesis of photosensitive homo-co-polymer*

2. Material and Methods

2.1. Materials

Solvents were distilled before use according to the procedures described by Perrin book. AIBN (2,2′-Azobis(2-methylpropionitrile), 2-(azo(1-cyano-1-methylethyl))-2-methylpropane nitrile) was recrystallized from methanol. Methylmethacrylate was washed twice with an aqueous solution of $NaHCO_3$ (5%), and twice with water then dried over Na_2SO_4, and finally the dried filtrate was distillated under reduced pressure.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 Bütchi apparatus. Infrared spectra were obtained using a Perkin-Elmer 1750 Fourier-transform spectrometer. ^1H and ^{13}C-NMR spectra were recorded on Avance DPX200 or Bruker AC 400 operating at 400.13 MHz for ^1H and 100 MHz for ^{13}C, in DMSO-d_6 with tetramethylsilane (TMS) as internal reference. The weight- and number-average molecular weights were determined by Size Exlusion Chromatography (SEC) on a Spectra SYSTEM AS1000 autosampler system, equipped with a guard column (Polmer Laboratories, PL gel 5 µm Guard, 50x7.5 mm) and two columns (Polmer Laboratories, 2 PL gel 5 µm 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 dispersity polystyrene standars (580-483x103 $g.mol^{-1}$). The photocrosslinking studies were peformed with Hanovia mercury lamp (365 nm, 300W).

*2.3. Synthesis of ethyl 2-cyano-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoate **3***

A pyridne solution (7.5 ml) of 4-hydroxy-3-metoxybenzaldehyde **1** (25 mmol), ethyl cyanoacetate **2** (25 mmol) and piperidine (2 drops) was refluxed for 1h in a round bottom flask fitted with a condenser. Then, the solution was poured drop by drop into a flask containing 100 ml of water 25 g of and ice. The mixture was stirred until a product suspension was obtained. The precipitated material was filtered, washed with water and then recristallized in ethanol.

Yield: 85%; Bp = 110°C

IR (KBr) : 3375 (OH); 2220 (CN) ; 1702 (C= O) ; 1608 (C= C).

^{1}H -NMR (400MHz, DMSO-d_6) : 8.17 (s, 1H, $\underline{H}C{=}C$), 7.87 (s, 1H, Ar-H_2), 7.42 (s, 1H, Ar-H_6), 7.02 (s, 1H, Ar-H_5), 4.38 (q, 2H, CH_3-$C\underline{H_2}$-O), 3.99 (s, 3H, CH_3-O), 1.40 (t, 3H, CH_3-$C\underline{H_2}$-O).

^{13}C-NMR (MHz, DMSO-d_6) **:** δ 162.8 (CO_2Et), 150.5 (C_4), 154.5 ($\underline{C}H{=}C$), 146.3 (C_3), 128.4 (C_1), 123.8 (C_6), 114.5 (C_5), 110.5 (C_2), 116 (CN), 98.5 ($CH{=}\underline{C}$), 62.1 (CH_3-$\underline{C}H_2$-O), 55.7 ($\underline{C}H_3O$), 13.8 ($\underline{C}H_3$-CH_2-O).

*2.4. Synthesis of ethyl 2-cyano-3-(4-(meyhacrylate)-3-methoxyphenyl)prop-2-enoate **4***

A solution of **3** (0.012 mol) in dichlormethane (12 ml) was introduced in a three necked round-bottom flask and cooled at 0°C using an nice bath. Solutions of methacryloyl chloride (0.018 mol) in dichlormethane (6 ml) and triethylamine (0.018 mol) in dichlormethane (6 ml) were added simultaneously and dropwise from tow dropping funnels into the stirred mixture. At the end of addition, the ice bath was removed and the stirring was maintained for 12h 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 filtred, the solvent was evaporated under reduce pressure and the crude product was recrystallized in ethanol.

Yield= 70%; Bp= 80°C.

IR (KBr) **:** 2222 (C≡N) , 1731 et 1712 (CO), 1627 and 1595 (C=C)

^{1}H-NMR (400MHz, $CDCl_3$): 8.21 (s,1H, -$C\underline{H}{=}C(CO_2Et)$), 7.82 (s, 1H, Ar-$H_2$), 7.48 (d, 1H, Ar-H_6), 7.22 (d, 1H, Ar-H_5), 6.39 (s, 1H, $C\underline{H_2}{=}C(CH_3)$-), 5.82 (s,1H, $C\underline{H_2}{=}C(CH_3)$-), 4.42 (q, 2H, (O-$C\underline{H_2}$-$CH_3$), 3.85 (s, 3H, $C\underline{H_3}$-O), 1.98 (s, 3H, $CH_2{=}C(C\underline{H_3})$-), 1.40 (t, 3H, O-$CH_2$-$C\underline{H_3}$).

^{13}C-NMR (MHz, $CDCl_3$) : δ 164.8 (CO_2Et), 162.5 (CO-methacrylate), 154.2 ($\underline{C}H{=}C$), 151.8 (C_4), 144.1 (C_3), 135.2 ($H_2C{=}\underline{C}$- methacrylate), 130 ($H_2\underline{C}{=}C$- methacrylate), 128 (C_1), 125.7 (C_6), 123.7 (C_5), 113.2 (C_2), 115.6 (CN), 102.6 ($CH{=}\underline{C}$), 62.8 (CH_3-$C\underline{H_2}$-O), 56.2 (CH_3O), 18.4 (CH_3- methacrylate), 14.2 ($\underline{C}H_3$-CH_2-O-).

*II-5- Homopolymerization of **4***

In a round-bottom flask fitted with a condenser were introduced 0.23 mmol of monomer **4**, 5 ml of butanone and AIBN (1% compared to monomer **4**). 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 = 85%.

IR (KBr): 2220 (C≡N) , 1745 and 1710 (C=O), 1608 (C=C).

^{1}H -NMR (400MHz, $CDCl_3$):8.20(s,1H, -$CH{=}C(CO_2Et)$), 7.83 to 7.25(3H, Ar-H_2, Ar-H_5 ,Ar-H_6), 4.42 (2H, (O-$C\underline{H_2}$-CH_3)), 3.90 (s, 3H, $C\underline{H_3}$-O), 0.8 to 2.40 (4H, chaine carbon) and (3H, $C\underline{H_3}$-CH_2-O-).

*II-6- Copolymerization of **4** with MMA*

Copolymers of (4) with MMA of different compositions were prepared in butanone solution at 65°C using AIBN as initiator. Appropriate amounts of monomers, intiator (1 % compared to monomer **4**) and butanone (5 ml) were mixed in round-bottom fitted with a condenser. The mixture was swept by nitrogen and kept at the required temperature (65°C) for 8h. The obtained copolymers were purified according to a same procedure as for the homopolymer.

Yield = 90%.

IR (KBr): 2224 (C≡N) , 1750 and 1710 (C=O), 1608 (C=C).

^{1}H -NMR (400MHz, $CDCl_3$): 8.20(s,1H, -$CH{=}C(CO_2Et)$), 7.83 (s, 1H, Ar-H_2), 7.46 (1H, Ar-H_6), 7.25 (1H, Ar-H_5), 4.42 (2H, (O-$C\underline{H_2}$-CH_3)), 3.90 (s, 3H, $C\underline{H_3}$-O), 3.62ppm (3H, $COOC\underline{H_3}$), massif 0,8 to 2,40 ppm of -$\underline{CH_2}$-C, methyl $OCH_2\underline{CH_3}$ of ester and $\underline{CH_3}$-.

3. Results and discussion

*3-1- Preparation of ethyl 2-cyano-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoate **3** and ethyl 2-cyano-3-(4-(methacrylate)-3-methoxyphenyl)prop-2-enoate **4***

Compound **3** was prepared by Knoevenagel condensation of 4-hydroxy-3-metoxybenzaldehyde **1** with ethyl cyanoacetate **2** in presence of piperidine as a basic catalyst. Then **3** was esterified by methacryloyl chloride in presence of triethylamine to give the methacrylate monomer **4** (Scheme 2).

3 and **4** were obtained in good yields (85% and 80%, respectively) and the analytical data (see Section 2, figure 1 and figure 2) fully supported the structure of **3** and **4**.

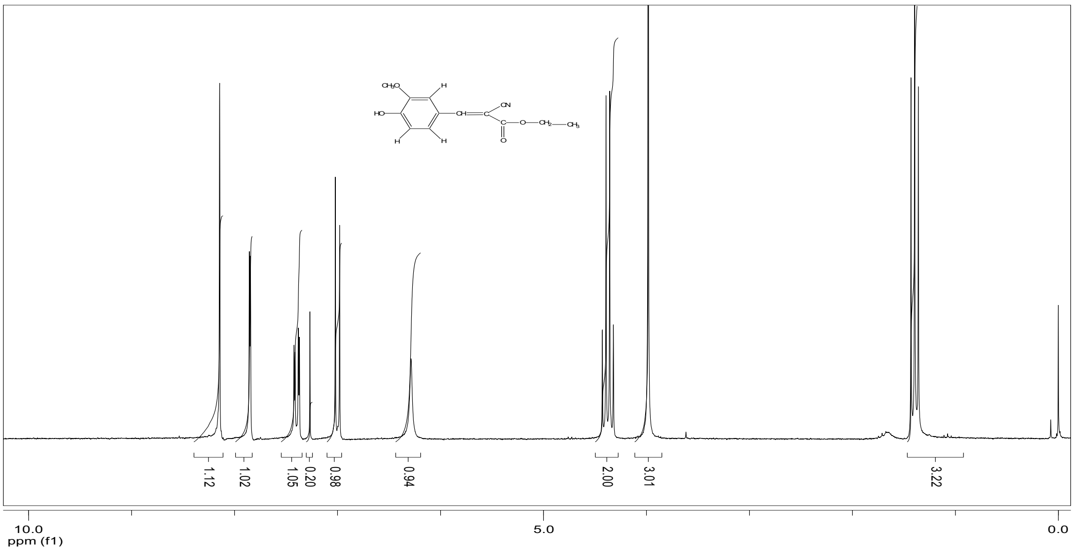


Figure 1: Spectre ^{1}H-NMR of **3**

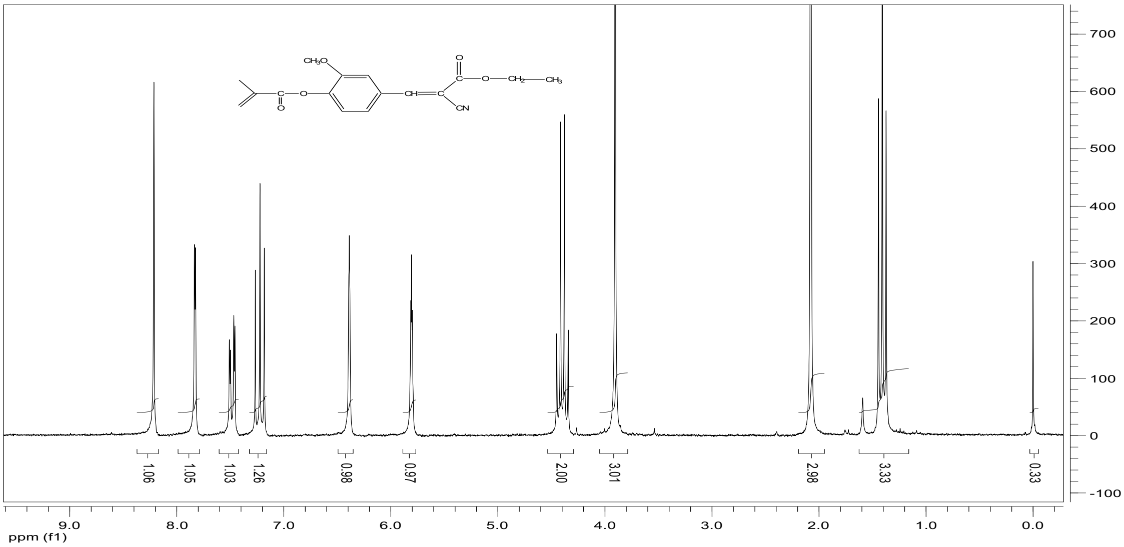


Figure 2: Spectre ^{1}H-NMR of **4**

*3-2- Homopolymerization of **4***

Radical homopolymerization of **4** was initiated with azoisobutyronitrile (AIBN). It was performed at 65°C in butanone (Scheme 2). After 8 h of reaction, polymer **5** was obtained in 92% yield. It showed good solubility in butanone, THF, CH_2Cl_2, $CHCl_3$, benzene, toluene, DMF.

The weight- and number-average molecular weights of 20300 and 10800, respectively, were determined by SEC. The value of dispersity index (Đ = 1.9) which is close to 2, suggests a tendency for chain termination by dispropotionation. Homopolymer **5** was characterized by IR and ^{1}H NMR. In IR, strong absorption bands characteristic of the carbonyles of methacrylate and cinnamate functions were noted at 1770 et 1725 cm^{-1} respectively. An absorption band at 1595 cm^{-1} was assigned to aromatic CH=C stretching vibration.

The ^{1}H NMR spectrum of **5** shows resonances at δ= 7,83 to 7.25 ppm due to aromatic protons. The proton of the CH=C unsaturations is noted at δ = 8.21 ppm. Signal at δ= 4,42 ppm corresponds to CH_2 protons of ethoxy groups. The proton of $C\underline{H}_3$-O at δ= 3,90 ppm, the CH_3 protons of ethoxy groups and the backbone protons rise at 0.8–2.4 ppm (Figure 3).

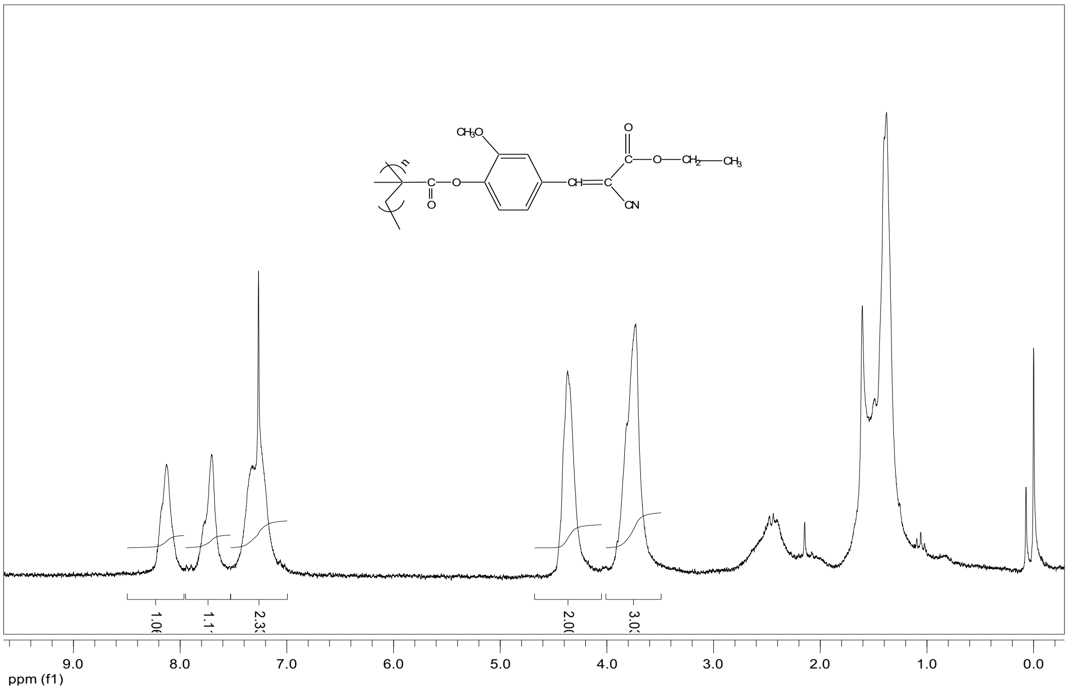


Figure 3 : Spectre ^{1}H-NMR of homopolymer **5**

A progress of **4** polymerization performed in deuterated chloroform was followed by 1H NMR (Figure 4). The incorporation of monomer **4** in polymer was determined form 1H NMR spectre by comparing the relative intensities of the methacrylic methylene protons of the residual monomer (δ = 6.39 and 5.80 ppm) to protons at δ = 7.8 and 8.21 ppm (CH=C and aromatic protons) of both residual monomer and monomer incorporated in polymer.

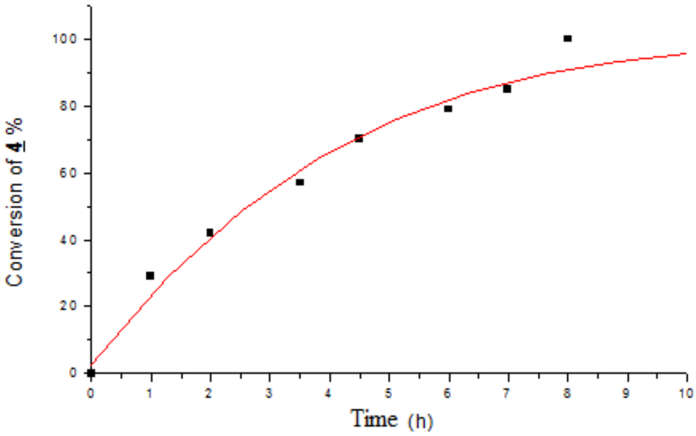


***Figure* 4 :** Progress of radical polymerisation of **4** versus time.

3-3- Copolymerization of 4 with methylmethacrylate

The free radical copolymerization of **4** with MMA was conducted in butanone for 8 h at 65°C using AIBN as an initiator (Scheme 2). Various monomer ratios were considered (Table 1). The copolymers **6** were obtained with good yields .They were easily soluble in most of the organic solvents such as butanone, THF, CH_2Cl_2, $CHCl_3$, benzene, toluene and DMF.

The weight and number-average molecular weights were determined by SEC. The value of dispersity index (**Đ**= 1.9) which is close to 2, suggests a tendency for chain termination by dispropotionation.

Table 1 : Results of radical copolymerisation of monomer **4** with MMA

Copolymer	**f**	**Conversion (%)**	$\overline{\text{W}}$**n**	$\overline{\text{M}}$**n**	**Đ**
6a	0.25	90	24400	12500	1,9
6b	0.50	92	13700	7700	1,8
6c	0.75	95	10300	5400	1,9

The ^{1}H NMR spectrum of **6** (figure 5) shows resonances at δ= 7.83 to 7.25 ppm due to aromatic protons. The proton of the CH=C unsaturations is noted at δ = 8.20 ppm. Signal at δ= 4.42 ppm corresponds to CH_2 protons of ethoxy groups. The proton of $C\underline{H}_3$-O at δ= 3.90 ppm, The proton of $COOC\underline{H}_3$ at δ= 3.62 ppm, the CH3 protons of ethoxy groups and the backbone protons rise at 0.8–2.4 ppm.

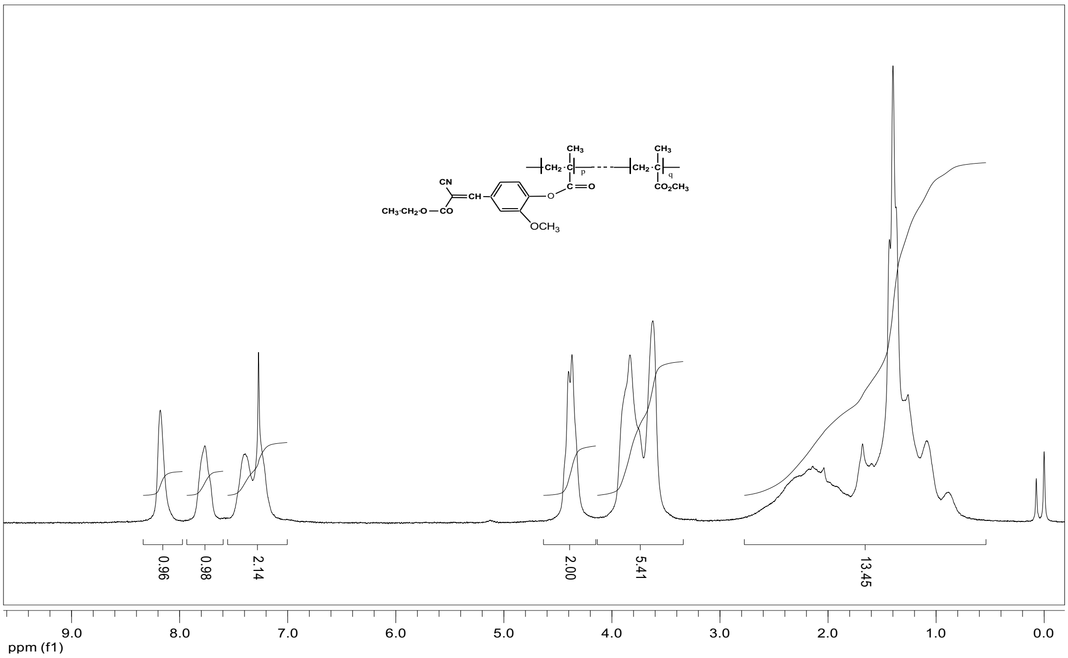


Figure 5 : RMN H ^{1} of poly(**4**-co-MMA)

3-4- Photoreactivity of the synthesized polymer and copolymers

A first approach of the photoreactivity in solid state of the synthesized polymer and copolymers was carried out. Thin films were irradiated using Hanovia mercury lamp (365 nm, 300W).

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** and copolymers **6** to crosslink under UV irradiation are under investigation. The results of these studies will be reported elsewhere.

Conclusion

The purpose was to develop a general method to synthesize new photocrosslinkable (co)polymethacrylates support of pendant photosensitive cinnamate having the particularity to have a functional group bonded on its α unsaturated carbon. The cyano group was selected as an example of functional group. From that, the objective was to synthesize the photosensitive methacrylate monomer, that is *ethyl 2-cyano-3-(4-(methacrylate)-3-methoxyphenyl)prop-2-enoate* 4. It was prepared in two steps with very good yields :

- Firstly the intermediate *ethyl 2-cyano-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoate* **3** was prepared by Knoevnagel condensation reaction between 4-hydroxy-3-metoxybenzaldehyde **1** and ethyl cyanoacetate.

- Then **3** was reacted with methacryloyl chloride to form the intended monomer **4**.

Afterwards radical polymerization initiated with AIBN was used to prepare homopolymer of **4** and various copolymers derived from it. Homopolymerization and copolymerization were performed at 65°C in butanone as solvent. Homo- and copolymers 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 and copolymers was carried. Thin films were irradiated using Hanovia mercury lamp (365 nm, 300W).

The insolubility of the studied films in organic solvents after the irradiation confirms that photocrosslinking took place.

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