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Synthesis of soft coating photocrosslinkable elastomers and study of their photoreactivity

Allal Challioui[1*], Abdelkader Oulmidi[1], Boufelja Bouammali[1], Rachid Mahy[1], Daniel Derouet[2], J. C. Brosse[2], and L. Fontaine[2].

1 - Laboratoire de Chimie Organique Macromoléculaire & Produits Naturels- Equipe Photochimie et Chimie Macromoléculaire, Université Mohammed Ier, Faculté des Sciences, Département de Chimie, 60000 Oujda - Maroc.
2- LCOM-Chimie des Polymères (UMR du CNRS UCO2M N° 6011), Université du Maine, Faculté des Sciences, Avenue Olivier Messiaen, 72085 Le Mans cedex 9, France.

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**Corresponding author. E-mail: allal.challioui@gmail.com; Tel: (+212536500601)*

Abstract

Soft coating photocrosslinkable elastomers were prepared by addition of photosensitive alcohol to epoxidized 1,4-polyisoprene (20% epoxidized units of 1,4-polyisoprene **E20** and 38% epoxidized units of 1,4-polyisoprene **E38**). The reaction was carried out in mild conditions in the presence of cerium ammonium nitrate **CAN** as catalyst and the yield in alkoxylated units averages 40% for 90% conversion of epoxidized units. The obtained polymers were characterized by **IR**, **^{1}H NMR** and **UV-Vis.** Spectroscopic techniques. Thin films obtained by casting technique were irradiated by UV light to undergo photocrosslinking reaction and the efficiency of the photocrosslinking process was monitored by UV-Vis analysis of the irradiated samples.

Keywords: photosensitive, photocroslinking, alkoxylation, chalcone, epoxidized polyisoprene.

Introduction

Photocrosslinkable polymers have attracted considerable interest in last decades owing to their potential applications in technological processes such as microlithography [1], printing materials [2] and photocurable coatings [3,4]. Recently, photocrosslinkable polymers have retained interest in the development of liquid crystalline polymers [5,6] and non-linear optic materials [7,8] where a strict control of the crosslinking process is required to obtain defined materials with particular properties.

In the case of natural and synthetic 1,4-polyisoprene rubbers, the photocrosslinking property is generally suitable for the preparation of soft coating materials. Among the synthetic routes extensively explored in the preparation of such polymers, cleavage of oxirane rings of epoxidized polyisoprene is a useful method due to the reactivity of the oxirane ring toward various nucleophilic and electrophilic reagents. Thus, addition of crosslinking dicarboxylic acids [9] acrylic acid [10,11], silica [12], phosphoric acid derivatives [13,14] and cationic photoinitiators [15-17] were studied over the last decades.

In earlier papers, we described the efficiency of cerium ammonium nitrate (CAN) in the catalysis of the alcoholysis of low molecular weight epoxidized 1,4-polyisoprenes [18-20] both in solution and in bulk. The purpose of this paper is to report the application of this procedure to the synthesis of photocrosslinkable polyisoprene by the addition of photosensitive alcohols to 20 and 38% epoxidized 1,4-polyisoprene in the presence of CAN as catalyst. The photochemical reactivity of the obtained elastomers is also discussed.

2. Materials and methods

2.1. Measurements, solvents and reagents

2.1.1.Measurements

NMR spectra were recorded on a Fourier transform spectrometer, Brucker AC 400, using $CDCl_3$ with tetramethylsilane (TMS) as internal standard for ^{1}H and ^{13}C NMR.

The molar masses determination was performed by size exclusion chromatography (**SEC**) using a double detection (UV, λ = 254 nm and Refractive Index) Water Associate 1500 apparatus fitted with 5 μ-styragel columns (100, 3 x 500, 1 000 Å) connected in series. THF was used as mobile phase at a flow of 1 ml/min and the column system was calibrated using monodisperse polystyrene standards.

FTIR spectra were recorded on a Perkin Elmer 1750 Fourier transform spectrometer. Polymer samples were analyzed in the form of thin films on NaCl plates.

DSC measurements were recorded on a TA Instrument SDT2960 apparatus at a constant heating rate of 20°C / min from –50°C to 150°C. The samples were scanned twice and the Tg values were kept from the second scan thermograms.

2.1.2. Solvents

Dichloromethane was dehydrated on calcium sulfate, then filtered and distilled on phosphoric anhydride after 1 h of reflux. Methanol was distilled on calcium sulfate after 2 h of reflux, then stored on molecular sieves 3 Å. THF was distilled under nitrogen in presence of sodium benzophenone complex, then stored on molecular sieves 3 Å. Toluene was dried on anhydrous calcium chloride, then filtered and distilled. Methanol was distilled on calcium sulfate after 2 h of reflux and then stored on molecular sieves 3 Å.

2.1.3. Reagents

a) Liquid 1,4-polyisoprene : liquid 1,4-polyisoprne is a synthetical polyisoprene (LIR-30) supplied by Siber Hegner Company. It was purified by re-precipitation from chloroform to methanol. It showed the following physico-chemical characteristics: $\overline{Mn}$ = 15 000, Ip = 1.5. Its content in 1,4-units was 93.2% as determined by ^{1}H NMR spectroscopy.

IR (ν cm^{-1}) : 3035 : =C-H ; 2960-2966 : -C-H, -CH$_2$-, and -CH$_3$; 1667 : C=C ; 1150 : -CH$_3$ *cis* ; 1130 : -CH$_3$ *trans* ; 890 : =CH$_2$ of 3,4- units ; 839 : =C-H of 1,4- units.

b) Epoxidation of 1,4- polyisoprene (general procedure)

Partial epoxidation of 1,4-polyisoprene was performed using *m*-chloroperbenzoic acid (amount used in relation with the desired rate of epoxidation). Thus, to prepare 20% epoxidized 1,4-polyisoprene E20, 7.20 g (4.20*10^{-2} mol.) of m-chloroperbenzoic acid (70% purity) in 100 ml of dichloromethane was added dropwise to a solution of 10 g of 1,4-polyisoprene (14.71*10^{-2} mol. in polyisoprene units) in 300 ml of dichloromethane cooled at 0°C and magnetically stirred. After addition, the mixture was stirred for 6 h at 25°C, filtered on a filter paper and concentrated to 50 ml by evaporation of dichloromethane under reduced pressure. E20 was precipitated twice from dichloromethane to methanol, and then dried under reduced pressure for 48 h at 40°C. E38 was prepared according to the same experimental procedure by using 13.7 g of *m*-chloroperbenzoic acid.

The rates of epoxidation were calculated from ^{1}H NMR spectra by area comparison of the signal at 2.7 ppm corresponding to the proton on oxirane rings of the epoxidized units to that at 5.2 ppm characteristic of the proton of the carbon - carbon double bounds of 1,4-polyisoprene units.

IR (ν cm^{-1}) : 3035 : =C-H ; 2960-2966 : -C-H, -CH$_2$- and -CH$_3$; 1667 : C=C ; 1250 : -C-O of oxirane rings ; 1150 : -CH$_3$ *cis* ; 1130 : -CH$_3$ *trans* ; 890 : =CH$_2$ of 3,4- units ; 839 : =C-H of 1,4- units.

2.2. Synthesis of photosensitive alcohols

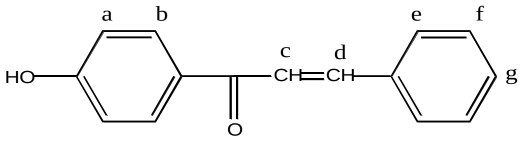
Synthesis of 4-(6-hydroxyhexyloxy) chalcone **HHC**: this product was prepared by the addition of 4-hydroxychalcone PHC to 6-chlorohexanol according to procedure described below.

a) *synthesis of 4-hydroxychalcone [3-(4-hydroxyphenyl)-1-phénylpro-2-enone]* ***PHC*** :

In a 500 mL three necked flask equiped with a mechanical stirrer, reflux condenser and dropping funnel are introduced successively 25 g of sodium hydroxyde, 200 mL of water and 200 mL of ethanol. The flask is immersed in a bath of crushed ice and, then 30 g (0.25 mol.) of *p*-hydroxyacetophenon are added.

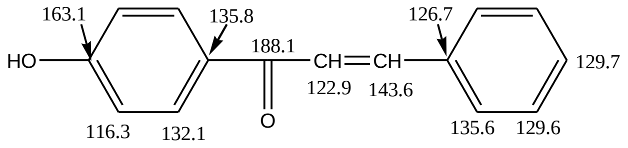
A solution of benzaldehyde is prepared by addition of (0.25 mol.) of benzaldehyde to 100 mL of ethanol (0.25 mol.). The solution is placed in a dropping funnel and added to p-hydroxyacetophenone alcaline solution. The mixture is stirred for 3 h at room temperature and, then kept to reflux of ethanol for 72 h. The reaction is followed by TLC using dichloromethane/ethyl acetate (9:1, v: v) as *eluent*. The reaction is stopped by addition of concentrated aqueous HCl solution until pH = 1. A yellow solid product precipitate which is washed until neutral pH, dried and crystallized from ethanol to give 30 g (0.134 mol.) of 4-hydroxychalcone (53.6% yield), mp = 156-157 °C.

^{1}H NMR ($CDCl_3$) :



6.85 ppm, doublet, 2H, H_f ,7.54 ppm, doublet, 1H, H_d, 7.66 ppm, 2H, H_a, 7.72 ppm, 1H, H_b, 7.76 ppm, triplet, 3H, H_e + H_c, 8.12 ppm, doublet, 2H, ^3J = 7.3 Hz, H_b.

^{13}C NMR ($CDCl_3$) :

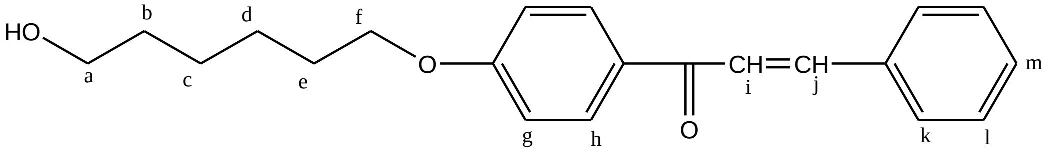


IR (KBr, ν (cm^{-1})): 3150 cm^{-1} : OH, 1646 cm^{-1} : C=O conjuguated ; 1607 cm^{-1} : non aromatic C=C.

b) *Synthesis of 4-(2-hydrohexyloxyy) chalcone* ***HHC***

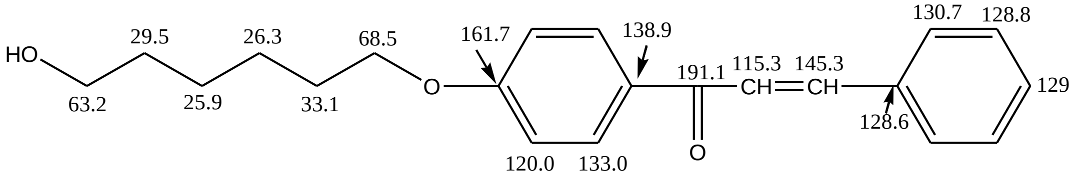
In a three necked flask equipped with a reflux condenser, a dropping funnel and a Dean stark are introduced 150 mL of ethanol, 29.1 g (0.130 mol.) of PHC and 5.24 g (0.131 mol.) of sodium hydroxyde previously dissolved in 5 mL of water. The mixture is stirred until a clear red solution is obtained then the water is eliminated from the reaction mixture by addition of 25 mL of toluene and azeotropic distillation (azeotropic point at 74.4°C). The solution is cooled at room temperature and then 26.75 g (0.196 mol.) of 6-chlorohexanol are added dropwise. The mixture is heated to reflux of ethanol and the reaction is monitored by TLC using chloroform/ethyl acetate (90/10: v/v) as eluent. The reaction is stopped after 72 h by addition of concentrated aqueous HCl solution until pH= 1. The product precipitate as a yellow powder which is washed with water until neutral pH and recrystallized from ethanol to give 21.64 g of HHC (yield: 51%), mp = 74-75 °C.

^{1}H NMR ($CDCl_3$) :



8.05 ppm, doublet, 2H, H_k, 7.80 ppm, doublet, 1H, H_j,7.60 ppm, doublet, 2H, H_h,7.55 ppm,multiplet, 1H, H_m,7.50 ppm, multiplet,2H, H_l, 7.40 ppm, doublet ,1H, ^3J = 15,7 Hz, H_i, 6.90 ppm, doublet, 2H, ^3J = 8.6 Hz, H_g, 4.05 ppm, triplet, 2H, ^3J = 6.3 Hz, H_a, 3.75 ppm, triplet, 2H, ^3J = 6.3 Hz, H_f, 1.85 ppm, multiplet, 2H, H_b, 1.60 ppm, multiplet,2H, H_e, 1.45 ppm, multiplet, 4H, H_c + H_d.

^{13}C NMR ($CDCl_3$) :



IR (KBr, ν (cm^{-1})) : 3255 cm^{-1} : OH, 1655 cm^{-1} : C=O conjuguated ; 1615 cm^{-1}: non aromatic C=C.

c) *Alkoxylation of epoxidized polyisoprenes (general procedures)*

Reactions were carried out with a molar ratio [CAN] / [epoxidized units] = 0.1. Thus, 0.96 g ($2.53*10^{-3}$ mol. of epoxidized units) of **E20** dissolved in 5 ml of dichloromethane is placed in a screw tube equiped with a magnetic stirrer. A solution of 6.78 g ($2.54*10^{-2}$ mol.) of 2-hydroxyhexyloxychalcone HHC and 0.139 g ($2.53*10^{-4}$ mol.) of CAN is then added. The tube is placed in an oil bath at 40°C for the selected time. Thereafter, the solution is concentrated, and the polymer is precipitated in methanol. It is finally purified by re-precipitation from dichloromethane (or chloroform) in methanol, then washed with methanol and dried under reduced pressure at 40°C for 48 to 72 h.

d) Photochemical studies

Photochemical studies were performed using a high pressure mercury lamp (Hanau, 250 W, with a luminous flux of 7 mW/cm^2 at 250 nm for samples placed at 5 cm from the UV lamp). A cooling system is placed between the UV lamp and the sample to avoid thermal effect of the irradiation process. Furthermore, the cooling system serves as a filter which cuts out most the light below 300 nm and thus prevents degradation of the polymer matrices from excitation of carbonyl and phenyl groups. Samples were prepared by casting a solution of the polymer in dichloromethane on a quartz cell. The thin film is dried under reduced pressure at 40 °C for 12 to 24 h and maintained in a desiccator under reduced pressure and in the dark until measurement. The photodimerization of the chalcone moiety was monitored in a discontinuous mode for the selected time by UV-Vis spectroscopy in the region between 200 and 500 nm at 25 °C. The progress of the reaction is monitored by the decrease in the intensity of the band corresponding to the C=C bond of the unsaturated carbonyl function which undergo a [2+2] cyclodimerization reaction under UV irradiation.

3. Results and discussion

3.1. Synthesis and characterization of the photosensitive polymers

In earlier papers [19,20], we found that alcoholysis of epoxidized units of epoxidized-1,4-polyisoprene catalyzed by CAN could be carried out using a molar ratio [alcohol]/[epoxidized units] varying from 10 to 2. The ring opening of the epoxidized units undergo formation of alkoxylated units (Fig.1), i.e. alkoxyalcohol units resulting from the nucleophilic attack of the alcohol onto the epoxidized units and allylether units. The latter are formed by reaction of the alcohol with secondary allylic alcohol units issued from the rearrangement of epoxidized units.

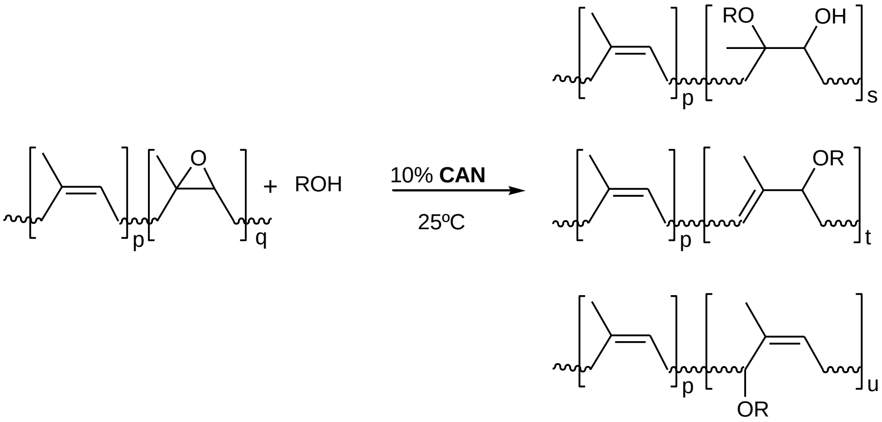


Figure 1: Alkoxylated units formed after alkoxylation of epoxidized 1,4-polyisoprene

The yield in alkoxylated units varied from 35 to 60% depending on the reaction conditions and alcohol structure. According to the results obtained, an increase in the yield of the reaction is obtained by increasing either the alcohol concentration or the temperature.

In the present study, the molar ratio r = [alcohol]/[epoxidized units], was kept to r = 5, and the reaction temperature fixed at 40°C in dichloromethane or in THF at 50°C (Fig. 2). Results of the alkoxylation reaction of **E20** and **E38** in dichloromethane solution (Table 1) show that the yield in alkoxylated units is relatively weak compared to the conversion percentage of the epoxidized units. The weak reactivity of the alcohols is due to the rearrangement of epoxidized units to allylic alcohol and ketone units.

The obtained polymers were characterized by ^{1}H NMR where the presence of the chalcone moiety is confirmed by the signals of aromatic protons in the region of the spectra between 6.5 ppm and 8.5 ppm (Fig. 3). The formation of alkoxylated units is confirmed by the presence of the signal at 3.55 and 4 ppm corresponding to the protons of alcohol and ether function respectively. Ketone and allylic alcohol units resulting from the rearrangement of the epoxidized units are identified by the presence of their functions at 2.3 ppm, 3.9 ppm and 4.0 ppm respectively [18].

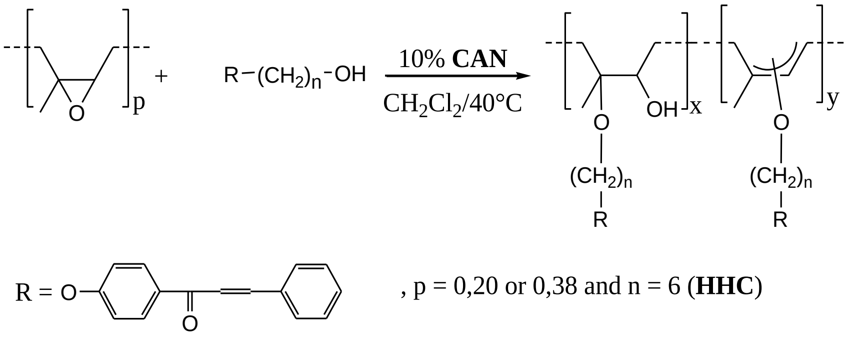


Figure 2: Photocrosslinkable polymers obtained from alkoxylation of epoxidized 1,4-polyisoprenes catalyzed by 10% CAN.

Table 1 : results of the alkoxylation reaction of **E20** and **E38** in dichloromethane solution at 40°C for 96 h, using 10% **CAN** and a molar ratio r = 5 .

Polymer	Alcool	τ (%)(£)	Yield (%)(¥)	Reference
E20	**HHC**	90	41	**E20HHC**
E38	**HHC**	85	40	**E38HHC**

£ : Percent of epoxidized units conversion.

¥ : Yield in alkoxylated units related to initial epoxidized units in the polymer.

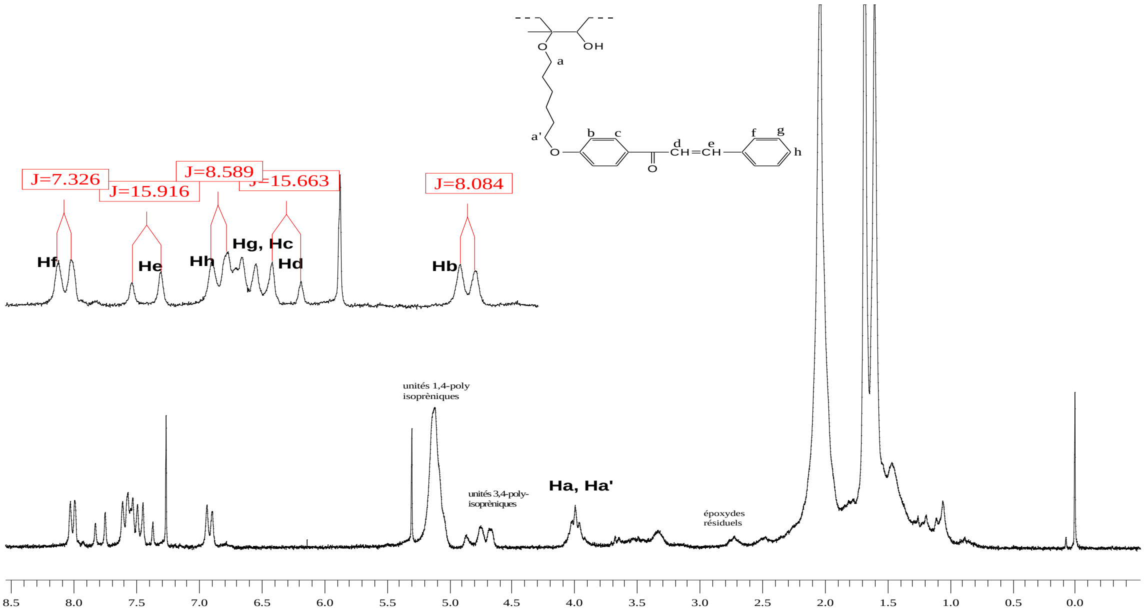


Figure 3 : ^{1}H NMR spectrum of E20HHC obtained in dichloromethane at 40°C for 96 h using 10% CAN and a molar ratio r = 5.

The yield in alkoxylated units were determined relatively to the epoxidized units in the starting polymer according to the equation (eq.1).

$$\% \cdot alkoxylated \cdot units = \frac{I_1}{I_1 + I_2} * 100 \qquad \text{(eq.1)}$$

Where:

I_1: area corresponding to the protons of alkoxylated units (obtained from the area of aromatic protons).
I_2: area of residual and rearranged epoxidized units obtained from the intensities of the signals of their characteristic protons.

Size exclusion chromatography characterization of the modified polymers (Table 2) revealed however a decrease in molecular weights of the polymers which can be attributed to degradation and crosslinking processes of the polymer chains during the reaction [19,20].

DSC analysis (Table 2) showed an increase of the glass transition temperature of the modified polymers, which is a consequence of the formation of the more hydrophilic alkoxylated units that can induce chains interaction by hydrogen bonding. The rigidity of chalcone moiety due to its aromatic groups is another factor that can increase the glass transition temperature [21].

Table 2: Molar masses, polydispersity indexes and glass transition temperatures of the modified polymers.

Polymer	yield (%)$^{(¥)}$	Mn (g/mol.)	Mw (g/mol.)	$I_p$$^{(¢)}$	Tg (°C)
E20	---	21000	30000	1.4	-49
E20HHC	41/(45)	13500	84300	6.2	-23
E38	---	28000	33200	1.2	-39
E38HHC	40/(47)	14500	77200	5.3	-9

¥ : yield in alkoxylated units and in brakets yield in alkoxylated units relative to the reacted epoxidized units, ¢ : polydispersity index.

However, no straightforward trend in the variation of Tg's with the degree of alcoholysis of the epoxidized units can be noticed. This is essentially due to the formation of secondary units such as allylic alcohol units and ketone units [18,19]. Thus, the overall effect on Tg's should be the sum of contributions of the different units resulting from the ring opening of epoxidized units.

3.2. Photochemical behaviour of the modified polymers

The synthesized polymers were subjected to photochemical irradiation using a high pressure mercury lamp. The photocrosslinking ability of the polymers was studied in the form of thin films at 25°C.

The photosensitive groups exhibited a maximum absorption of allowed π–π^* transition at 344nm (Fig.5). Table 3 shows the characteristic transitions in the UV-Vis. spectra of the irradiated polymers.

Table 3: positions of peaks maxima of the main absorbing groups

Polymer	Photosensitive alkoxy group	λ_{max} (nm)
E20HHC	**HHC**	344 (π–π*) C=C 278 (n–π*) C=O 245 and 285 (P_{iso})
E38HHC	**HHC**	344 (π–π*) C=C 278 (n–π*) C=O 245 and 285 (P_{iso})

Upon irradiation, chalcone moiety undergo cyclodimerization through a [$2\pi + 2\pi$] reaction (Fig. 4).

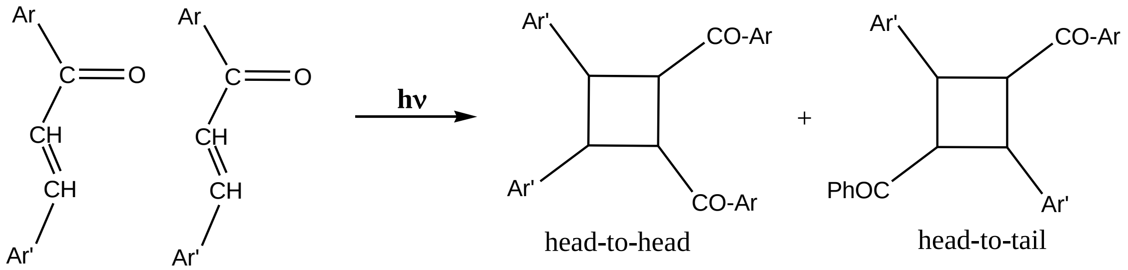


Figure 4: [2π+2π] cyclodimerization of chalcone group upon irradiation.

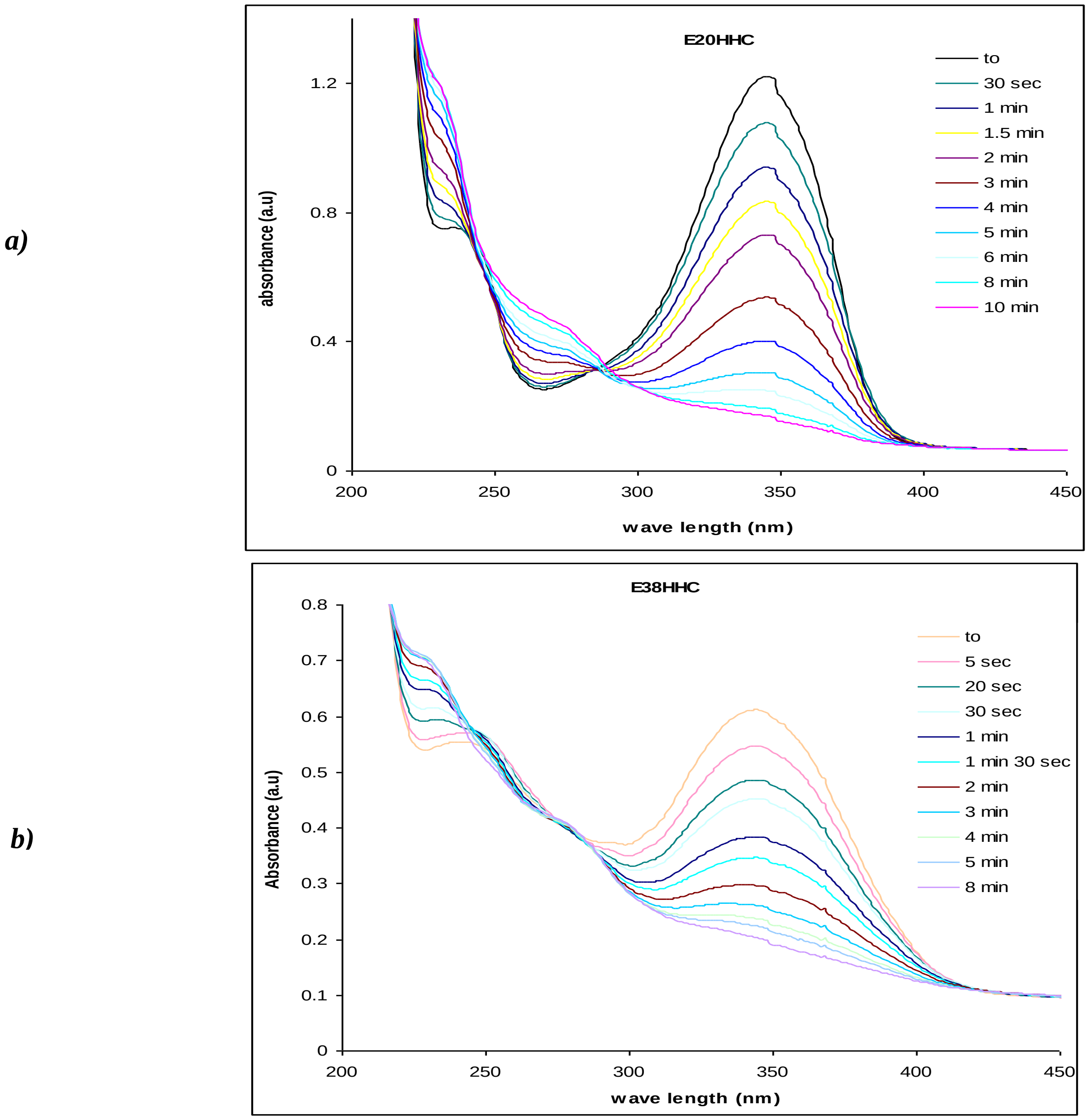


Figure 5 : UV-Vis spectra of the irradiated polymers vs. Time, a) **E20HHC**, b) **E38HHC**.

Figure 5 shows the UV-Vis. spectra recorded after several periods of irradiation of the synthesized photosensitive polymers. A successive decrease in absorption maxima of the C=C double bound at 344 nm indicates the consumption of the C=C double bounds in the [2+2] cycloaddition reaction which is followed by the appearance of new absorption bands at 278 nm and 247 nm corresponding to the non conjugated C=O group. The presence of isobestic point is a further proof for the continuity of the same photochemical process (i.e. photodimerization reaction of carbonyl conjugated double bonds). Indeed, at an isobestic point, the absorbance of the evolved species remains constant. Hence the analytical concentrations and the molar extinction coefficients of the species are equal suggesting that no side reaction takes place during the photochemical process.

As the composition of the polymer changed, one could expect a shift in the position of the maxima from E20 to E38 due to the variation in the polarity of the medium. However, this is not observed, and the maximum absorption positions are close to each other irrespective to the percentage of epoxidized units in the starting polymer. Hence, it is reasonable to suggest that, the photosensitive group do not develop specific interactions with the rest of the polymer backbone that can modify the energies of the molecular orbitals involved in the transitions state upon irradiation (i.e.: π–π* transition of the carbonyl conjugated double bond of the photosensitive group).

The extent of photocrodimerization process was studied assuming a first order kinetic that can be represented by the equation (eq.3) [22, 23] .

$$\%conversion = \frac{A_o - A_t}{A_o - A_\infty} * 100 \qquad \text{(eq.3)}$$

Where A_o, A_t and A_∞ are the absorbance intensities at t = 0, t and infinity respectively.

The graphs obtained (Fig.6), show no significant difference in the photochemical reactivity of the chalcone group irrespective to the polymer composition (i.e.: the percentage of epoxidized units in the starting polymers). This result confirms the [2+2] character of the photochemical process of the reaction which is, generally, governed by topochemical factors [24-27] and the photoreactive sites created during the film casting [28, 29] rather than the sterical effects of the polymer backbone. Moreover, the irradiation process occurs at a temperature higher than the Tg's of the synthesized polymers and no effect of the segmental mobility of the polymer chains could be expected.

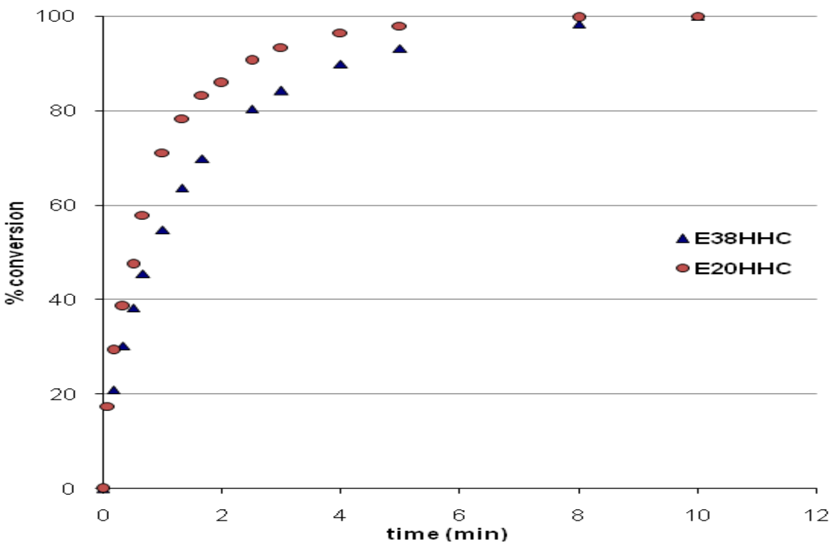


Figure 6: rate of consumption of the C=C double bonds of the photosensitive polymers upon UV. irradiation *vs.* time

Conclusion

In this study, we prepared photocrosslinkable elastomers by addition of chalcone type photosensitive alcohol to epoxidized 1,4-polyisoprenes (E20 and E38). The reaction were carried in mild conditions in the presence of cerium ammonium nitrate CAN as catalyst and the yield in alkoxylated units averages 40% for 90% conversion of epoxidized units. The polymer compositions were determined by ^{1}H NMR spectroscopy and the molecular weights by size exclusion chromatography. Thin films obtained by casting technique were irradiated by UV light to undergo photocrosslinking reaction. The efficiency of the photocrosslinking process was monitored by UV-Vis analysis of the irradiated samples. The results obtained showed that upon UV irradiation, the photosensitive alkoxy groups undergo [2+2] cyclodimerization reaction which is responsible for the photocrosslinking process of the polymer network. The efficiency of the photochemical process were found to be independent of the polymer composition in photosensitive group and confirmed the [2+2] character of the reaction.

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