

Synthesis and Crosslinking Kinetic Study of Epoxidized and Acrylated/Epoxidized Oligoisoprenes: Comparison Between Cationic and Radical Photopolymerization

Rachid Jellali,¹ Irène Campistron,¹ Albert Laguerre,¹ Laurence Lecamp,² Pamela Pasetto,¹ Claude Bunel,² Jean-Luc Mouget,³ Jean-François Pilard¹

¹UMR CNRS N° 6283, Méthodologie et Synthèse des Polymères, Département Méthodologie et Synthèse, Institut des Molécules et des Matériaux du Mans, Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

²Laboratoire Polymères, Biopolymères, Surfaces, Équipe MM, UMR 6270, INSA de ROUEN, Avenue de l'Université 76801 Saint-Étienne-du-Rouvray Cedex, France

³Laboratoire de Physiologie et de Biochimie Végétales, EA 2160, Mer, Molécules, Santé, Université du Maine Avenue O. Messiaen, 72085 Le Mans cedex, 9 France

Correspondence to: P. Pasetto (E-mail: pamelapasetto@univ-lemans.fr)

ABSTRACT: The photoinitiated polymerization of epoxidized hydroxytelechelic *cis*-1,4-polyisoprene and of a dual system (epoxidized/acrylated) telechelic *cis*-1,4-polyisoprene in the presence of 2,2-dimethyl-1,2-hydroxyacetophenone or/and hexafluoro-phosphate triarylsulfonium salt has been studied by real-time infrared spectroscopy. The synthesis of photosensitive oligoisoprenes was achieved by chemical modifications of hydroxytelechelic *cis*-1,4-polyisoprene obtained by controlled degradation of high molecular weight *cis*-1,4-polyisoprene. Then, the effect of light intensity, photoinitiator concentration, addition of reactive diluent and concentration of functional groups on the photopolymerization process was evaluated. Concerning the cationic process, the results showed that the kinetic profile improves when photoinitiator concentration and light intensity increase. The optimum concentration of triarylsulfonium salt used as photoinitiator was determined as 5% (w/w) and the optimum light intensity was 50 mW cm⁻². Reactive diluent (3-ethyl-3-hydroxymethyl oxetane) addition greatly improves the ultimate conversion and the polymerization rate. Subsequently, the photopolymerization kinetic of a dual epoxidized/acrylated system was studied. The results obtained using different photoinitiator mixtures and different intensity of irradiation showed that the crosslinking of acrylate functions at the chain-end prevents the progression of the cationic process at the oxirane groups along the chain. Thus, the mobility of the cationic reactive centers was restricted by the crosslinking at the high conversion of the acrylate double bonds. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: crosslinking; rubber; photopolymerization; coatings; biomaterials

Received 13 July 2012; accepted 8 August 2012; published online

DOI: 10.1002/app.38488

INTRODUCTION

The photoinitiated polymerization process is widely used for the rapid production of highly crosslinked polymer networks.^{1–3} The high cure speed, the reduced energy consumption and the very low organic solvent emission are the main advantages of this technology. In the process, radical or cationic species are generated by the interaction of the UV light with a suitable photoinitiator, which induces the curing reaction of reactive monomers and oligomers: in cationic photopolymerization strong Brønsted acids are generated by UV dissociation of onium salt (iodonium or sulfonium).¹ The cationic photoinduced process presents some advantages compared to the radi-

cal one,⁴ in particular lack of inhibition by oxygen, low shrinkage, good mechanical properties of the UV cured materials and good adhesion properties to various substrates. Moreover, the used monomers are generally less toxic and irritating. Different types of monomers and oligomers have been proposed and reported in the literature.^{1,5–16}

The synthesis of functional polymers from renewable resources has attracted considerable attention of polymer scientists throughout the world, because of their potential attributes as substitute petrochemical derivatives. Among these polymers, *cis*-1,4-polyisoprene from Natural Rubber (NR) has many special properties, including good resilience, good strength and fatigue

Additional Supporting Information may be found in the online version of this article.

© 2012 Wiley Periodicals, Inc.

resistance. Telechelic liquid natural rubber (TLNR) represents a versatile precursor of a very wide range of polymers. The selective cleavage of high molecular weight polymers to obtain TLNR and the chemical modification of such oligomers has been the center of the activity of different research groups.^{17–19} Our group focused its attention on selective degradation of *cis*-1,4-polyisoprene using well-controlled oxidative chain cleavage leading to new carbonyltelechelic *cis*-1,4-polyisoprene.^{20,21} Chemical modifications of carbonyl end-groups and carbon-carbon double bonds at various ratios led to new hydroxytelechelic *cis*-1,4-polyisoprenes.^{22–26}

In this work, the synthesis of various photosensitive oligoisoprenes is reported: epoxidized hydroxytelechelic *cis*-1,4-polyisoprene and epoxidized-acrylated telechelic *cis*-1,4-polyisoprene. Some of these oligomers include ammonium functions, with the aim to obtain coatings with antibacterial activity.^{27,28} The obtained macromonomers were subjected to UV curing; the effect of photoinitiator concentration and type, light intensity, epoxidation rate, presence of reactive diluent were investigated in cationic or hybrid cationic/radical UV-curing systems to generate flexible thin films.

EXPERIMENTAL

Materials

Cis-1,4-polyisoprene (Acros Organics, 98% *cis*, $M_w = 800,000$), *m*-chloroperbenzoic acid (mCPBA, Aldrich, 70%), periodic acid (Acros, 99%), sodium borohydride (Acros, 98%), acryloyl chloride (Aldrich, 96%), 1-iodooctane (Acros, 98%), sodium triacetoxyborohydride (Acros, 97%), diethanolamine (Aldrich, 99%), 3-diethylaminopropylamine (Aldrich, 99%), diethylamine (Acros, 99%), and lithium aluminum hydride (1M in ether, Aldrich) were used without previous purification. The triethylamine was distilled before use.

The 2,2-dimethyl-2-hydroxyacetophenone (Darocur 1173, Aldrich, Figure 1) and hexafluoro-phosphate triarylsulfonium salt (Degacur KI85, Aldrich, Figure 1) were chosen as photoinitiators. The 3-ethyl-3-hydroxymethyl oxetane (trimethylolpropane oxetane, TMPO, Aldrich, 90%, Figure 1) has been used as reactive diluent for cationic radiation curing.

Physico-Chemical Characterization

NMR Analysis. Molecular weights and structures of the different oligoisoprenes were determined by ¹H NMR spectroscopy. The ¹H NMR spectra are recorded on a Bruker 400 Fourier Transform spectrometer at 400.13 MHz, in CDCl₃ solutions using tetramethylsilane (TMS) as internal standard.

Irradiation. The samples were irradiated with a 350 W Oriel mercury vapor lamp that was introduced into the FTIR spectrophotometer by a flexible light guide. The UV radiation intensity was measured by a spectroradiometer (Intraspec II Oriel VLX/3W) at 365 nm.

Real Time Infrared Spectroscopy. The photocrosslinking reaction kinetics were monitored by Perkin Elmer FTIR 2000 spectrophotometer coupled with an irradiation unit. The sample was exposed simultaneously to the UV beam of a medium pressure mercury lamp (350 W Oriel) and to the IR beam of an FT-IR spectrophotometer.

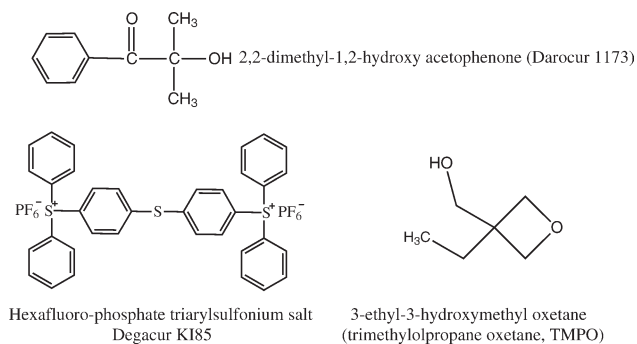


Figure 1. Chemical structures of reactants.

The $\delta_{\text{=CH}_2}$ of the acrylate functional groups at 1408 cm^{-1} , the $\nu_{\text{C-O}}$ of the epoxide function at 870 cm^{-1} and the $\delta_{\text{-CH}_3}$ of the *cis*-1,4-polyisoprene at 1380 cm^{-1} (reference band) were used to calculate the conversions. After baseline correction, conversion of the acrylate groups can be calculated after measurement of the absorbance at each time (t) of the reaction as follows:

$$C_{(c=c)t} = \frac{(A_{1408}/A_{1380})_0 - (A_{1408}/A_{1380})_t}{(A_{1408}/A_{1380})_0} \cdot 100$$

$$C_{(\text{epoxy})t} = \frac{(A_{870}/A_{1380})_0 - (A_{870}/A_{1380})_t}{(A_{870}/A_{1380})_0} \cdot 100$$

where $C_{(t)}$ is the conversion of these reactive functions at (t) time, A_0 is the initial absorbance and A_t is the absorbance of the functional groups at (t) time.

Thermogravimetric Analysis: TGA. Thermal stabilities were checked by thermogravimetric analysis (TGA-7 Perkin-Elmer). Experiments were carried out in nitrogen atmosphere (20 mL min^{-1}). A 50–600°C range was scanned at a heating rate of 10°C min^{-1} .

Synthesis

Preparation of Epoxidized Hydroxytelechelic *cis*-1,4-Polyisoprene (EHTPI). The controlled degradation of high molecular weight *cis*-1,4-polyisoprene was achieved by a method developed in our laboratory.^{20,21} In a first step, carbonyltelechelic *cis*1,4-polyisoprene (CTPI) was obtained by epoxidation with *m*-chloroperbenzoic acid, followed by oxirane units cleavage using periodic acid. To obtain 2000 g mol^{-1} molecular weight oligomers, *m*-chloroperbenzoic acid (3.62 g) dissolved in 100 mL of dichloromethane were added dropwise to a solution of *cis*-1,4-polyisoprene (20 g) in 500 mL of dichloromethane. The mixture was stirred at 0°C during 6 h. To the purified epoxidized *cis*-1,4-polyisoprene (epoxide ratio = 5%, 18 g) dissolved in 400 mL of tetrahydrofuran (THF), periodic acid (3.43 g) in 50 mL of THF was added dropwise. After stirring 6 h at 30°C, the tetrahydrofuran was removed under reduced pressure and the resulting product was dissolved in dichloromethane. Finally, this organic solution was washed with saturated aqueous solutions of NaHCO₃ and Na₂S₂O₃ and dried over MgSO₄. Filtration and elimination of solvent afforded the carbonyltelechelic *cis*1,4-polyisoprene (CTPI), with 95% yield.

The quantities of metachloroperbenzoic acid and periodic acid were determined using the following formulas [eqs. (1) and (2)]:

$$m_{mCPBA} = (m_{PI}) / 68.8 \cdot (\tau_e / 100) \cdot M_{mCPBA} \cdot (100 / 70) \quad (1)$$

$$m_{\text{periodic acid}} = (m_{EPI}) / 68.8 \cdot (\tau_e / 100) \cdot M_{\text{periodic acid}} \cdot 1.1 \quad (2)$$

(m_{PI}) is the weight of *cis*-1,4-polyisoprene; (68.8) is the molecular weight for isoprene unit in g mol^{-1} ; (τ_e) is the epoxide ratio; (M_{mCPBA}) is the molecular weight for *m*-CPBA in g mol^{-1} ; (m_{EPI}) is the weight of epoxidized *cis*-1,4-polyisoprene and ($M_{\text{periodic acid}}$) is the molecular weight for periodic acid in g mol^{-1} .

In a second step, the purified carbonyltelechelic *cis*-1,4-polyisoprene (CTPI) in THF (0.07 mol L^{-1}) was added dropwise to sodium borohydride ($4 \text{ mol equiv.}^{-1}$) dissolved in 30 mL of THF. After stirring for 6 h at 60°C , the excess of NaBH_4 was hydrolyzed with ice. The mixture was washed using a saturated solution of NaCl and dried over MgSO_4 . The solvent was evaporated under vacuum, leading to the expected hydroxytelechelic *cis*-1,4-polyisoprene (HTPI, yield was 93–98%). Subsequently, *m*-chloroperbenzoic acid ($X \text{ g}$, depending on the desired epoxide ratio) in 20 mL of dichloromethane was added dropwise to a solution of hydroxytelechelic *cis*-1,4-polyisoprene (HTPI) (20 g) in 500 mL of dichloromethane. After stirring 3 h at 0°C , the mixture was washed with saturated aqueous solutions of NaHCO_3 and dried under MgSO_4 . Solvent was evaporated under vacuum yielding 89% of epoxidized hydroxytelechelic *cis*-1,4-polyisoprene (EHTPI).

FTIR:—HTPI: $\nu_{C=C} = 1664 \text{ cm}^{-1}$; $\nu_{=CH} = 3035 \text{ cm}^{-1}$; $\nu_{OH} = 3350 \text{ cm}^{-1}$; $\delta_{C-H} = 834 \text{ cm}^{-1}$; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm^{-1} .

—EHTPI: $\nu_{C=C} = 1664 \text{ cm}^{-1}$; $\nu_{=CH} = 3035 \text{ cm}^{-1}$; $\nu_{OH} = 3350 \text{ cm}^{-1}$; $\delta_{C-H} = 834 \text{ cm}^{-1}$; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm^{-1} ; ν_{C-O} (epoxide) = 870 cm^{-1} ;

Characterization $^1\text{H NMR}$: Figure 1 in Supporting Information.

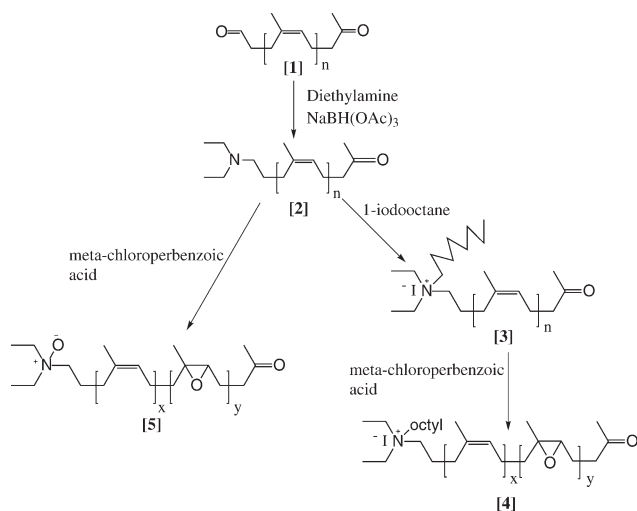


Figure 2. Synthesis of photocurable epoxidized cationomers [4] and [5] from carbonyl telechelic *cis*-1,4-polyisoprene.

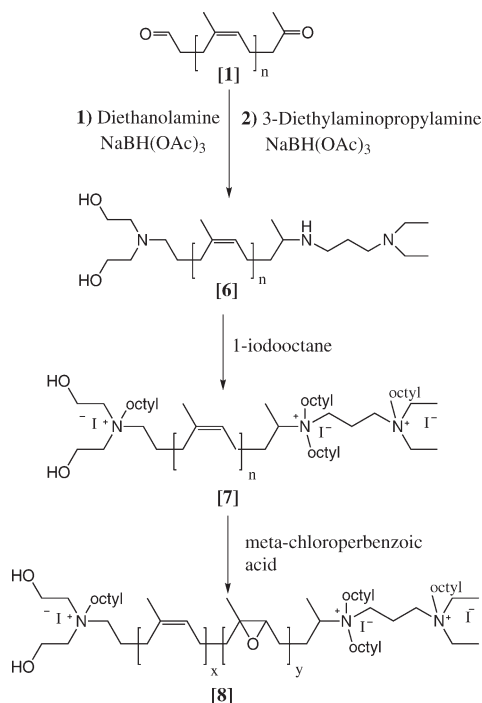


Figure 3. Synthesis of photocurable epoxidized cationomer [8] from carbonyl telechelic *cis*-1,4-polyisoprene.

Synthesis of Diacrylate Epoxidized *cis*-1,4-Polyisoprene. To a solution of epoxidized hydroxytelechelic *cis*-1,4-polyisoprene (EHTPI, 1 equivalent) in anhydrous dichloromethane ($C = 0.08 \text{ mol L}^{-1}$) and triethylamine (2.3 equivalents), acryloyl chloride (2.3 equivalents) was added dropwise at 0°C under nitrogen atmosphere. The solution was stirred at 0°C for 30 min, and then at room temperature for 24 h. The solution was washed with NaOH aqueous solution (1N), and the organic layer was dried over MgSO_4 . The solvent was evaporated under vacuum leading to the expected product (yield = 85%).

FTIR: $\nu_{C=C}$ (isoprene) = 1664 cm^{-1} ; $\nu_{=CH} = 3035 \text{ cm}^{-1}$; $\delta_{C-H} = 834 \text{ cm}^{-1}$; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm^{-1} ; $\nu_{C=O}$ (ester) = 1736 cm^{-1} ; $\nu_{C=C}$ (acrylate) = 1632 cm^{-1} ; $\delta_{=CH_2}$ (acrylate) = 1408 cm^{-1} ; ν_{C-O} (epoxide) = 870 cm^{-1} ; disappearance of ν_{OH} at 3350 cm^{-1} .

Characterization $^1\text{H NMR}$: Figure 2 Supporting Information.

Synthesis of Photocurable Epoxidized Cationomers. Compounds 2 and 6 (Figures 2 and 3) were prepared according to a methodology previously described by Kébir et al.^{22,23} Epoxidized cationomers (4 and 8) were synthesized in two steps starting from compound 2 and 6, respectively. For the first step, compounds 2 or 6 were dissolved in a solution of dichloromethane/acetonitrile: 3/1, and 1-iodooctane (5 equivalents/amine function). The mixture was stirred at 40°C for 24 h and then the solvent was removed under reduced pressure to give the cationomer 3 or 7 (yield = 100%).

In a second step, *m*-chloroperbenzoic acid ($X \text{ g}$, depending on the desired epoxide ratio) in 20 mL of dichloromethane was added dropwise to a solution of cationomer 3 or 7 in

dichloromethane. After stirring 3 h at 0°C, the mixture was washed with saturated aqueous solutions of NaHCO₃. The organic phase was concentrated, dried over MgSO₄, filtered and concentrated under vacuum leading to the epoxidized cationomer [4] and [8], respectively (yield for [4] = 89%, yield for [8] = 84%).

FTIR— α -carbonyl- ω -*N,N*-diethylaminotelechelic *cis*-1,4-oligoisoprene [2]: $\nu_{C=C}$ = 1664 cm⁻¹; ν_{CH} = 3035 cm⁻¹; δ_{C-H} = 834 cm⁻¹; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm⁻¹; decrease of $\nu_{C=O}$ at 1721 cm⁻¹.

— α -diethylpropylamino- ω -*N,N*-dihydroxyethylaminotelechelic *cis*-1,4-oligoisoprene [6]: $\nu_{C=C}$ = 1664 cm⁻¹; ν_{CH} = 3035 cm⁻¹; ν_{OH} = 3380 cm⁻¹; δ_{C-H} = 834 cm⁻¹; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm⁻¹; disappearance of $\nu_{C=O}$ at 1721 cm⁻¹.

—Cationomers 3 and 7: $\nu_{C=C}$ = 1664 cm⁻¹; ν_{CH} = 3035 cm⁻¹; δ_{C-H} = 834 cm⁻¹; ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm⁻¹.

—Epoxidized cationomers 4 and 8: ν_{CH_2,CH_3} *cis*-1,4-polyisoprene = 1448, 1376 cm⁻¹; ν_{C-O} (epoxid) = 870 cm⁻¹; decrease of $\nu_{C=C}$ = 1664 cm⁻¹; ν_{CH} = 3035 cm⁻¹; δ_{C-H} = 834 cm⁻¹.

Characterization ¹H NMR: Figure 3 Supporting Information.

RESULTS AND DISCUSSION

Functionalized Oligoisoprenes Synthesis

The epoxidized oligoisoprenes used in the photopolymerization reaction were obtained by chemical modifications of the carbonyltelechelic *cis*-1,4-polyisoprene oligomers, generated by the controlled degradation of high molecular weight *cis*-1,4-polyisoprene. In this procedure, first *cis*-1,4-polyisoprene was treated with different amounts of meta-chloroperbenzoic acid, leading to 2 and 5% epoxidized *cis*-1,4-polyisoprene (EPI). The cleavage of the so generated oxirane units was performed with periodic acid and led to the carbonyltelechelic *cis*-1,4-polyisoprene of two different molecular weights, depending on the epoxidation ratio. The successive steps were the reduction of the carbonyl end-groups to alcohol functions with sodium borohydride, epoxidation of isoprene double bonds using *m*-chloroperbenzoic acid and the addition of acryloyl chloride to give the epoxidized hydroxy telechelic *cis*-1,4-polyisoprene and the diacrylate epoxidized *cis*-1,4-polyisoprene of molecular weights 1750 and 4000 g mol⁻¹. ¹H NMR and FTIR analyses showed the partial epoxidation (epoxidation ratio = 20, 25, and 30%) of isoprene double bonds and the complete transformation of the alcohol functions in acrylate groups.

To obtain oligomers with amino chain-ends, the direct reductive amination of carbonyl compounds was performed. This is a one step reaction that transforms selectively the aldehyde groups in amino groups.^{22,23,26} Thus, carbonyl telechelic *cis*-1,4-polyisoprene was modified without any protection of the ketone moiety using prefunctionalized amines. The reductive amination reaction was monitored by ¹H NMR; the spectra showed a complete disappearance of the aldehydic proton signal at 9.77 ppm, whereas the methylketone moiety seemed unchanged. Product 8 was obtained by a second reductive amination using 3-diethylaminopropylamine (Figure 3). After replacement of the carbonyl

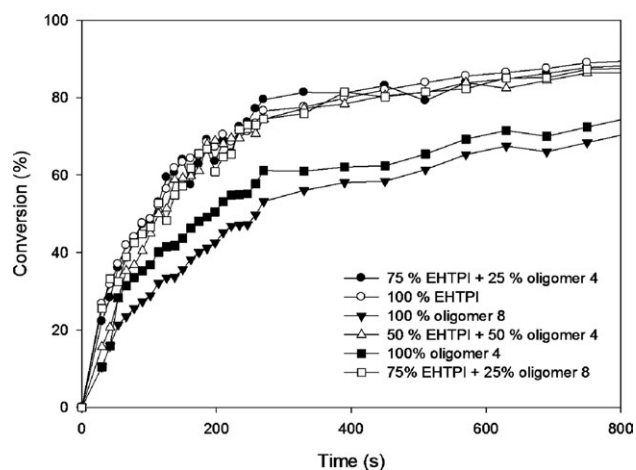


Figure 4. Conversion of epoxide functions versus irradiation time of EHTPI, oligomer 4, oligomer 8 and mixture of EHTPI/cationomers (4 and 8). [PI] = 5% (w/w); I = 50 mW cm⁻².

with the amino group, the ¹H NMR spectrum showed the shift of the α -methyl group protons in the methyl ketone from 2.13 to 1.07 ppm and the appearance of a new peak at 2.67 ppm that belongs to the hydrogen in α of the NH group.

The synthesis of epoxidized cationic oligoisoprenes from products 2 and 6 was realized according to two strategies. The first strategy consists in epoxidation of isoprene double bond followed by the quaternization of the tertiary amine. ¹H NMR analyses of the product obtained by oligomer 2 epoxidation showed the displacement of the signals relative to protons in α and β position of the nitrogen atom towards higher values compared to the spectrum of oligomer 2 (3.1 and 3.25 versus 2.5 and 2.62) (Figure 4 Supporting Information). This result indicates the tertiary amine quaternization, which may be due to the amine protonation with the *m*-chloroperbenzoic acid (product A, Figure 4 Supporting Information). Nevertheless, basic washings with potassium tert-butyrate and sodium hydroxide solutions did not allow the regeneration of the tertiary amine. Previous studies^{29,30} showed that the tertiary amine is easily oxidizable by the mCPBA. The most likely hypothesis is the oxidation of the amines to *N*-oxyde (product B, Figure 4 Supporting Information). Similar results were obtained via the epoxidation of oligomer 6.

The second strategy consists in quaternization of tertiary amine followed by isoprene double bonded epoxidation. Oligomers (2 and 6) were quaternized using iodoctane. In the ¹H NMR spectra of compounds 3 and 7, the amine functions quaternization was confirmed by the displacement of the signals relative to protons in α and β position of the nitrogen atom towards higher values. For example, CH₃—; CH₂—N; N—CH₂ groups shift respectively from 1.07; 2.60; 2.5 ppm, to 1.38; 3.55; 3.30 ppm after quaternization of oligomer 2. Finally, cationomer 3 and 7 were partially epoxidized using *m*-chloroperbenzoic acid to give epoxidized cationomer 4 and 8 with different epoxidation ratios of 20, 25, and 30%. The partial epoxidation was confirmed by the appearance of the signals relative to oxirane proton at 2.69 ppm. As the quaternary ammonium is the group responsible for the antibacterial activity of the coatings, two

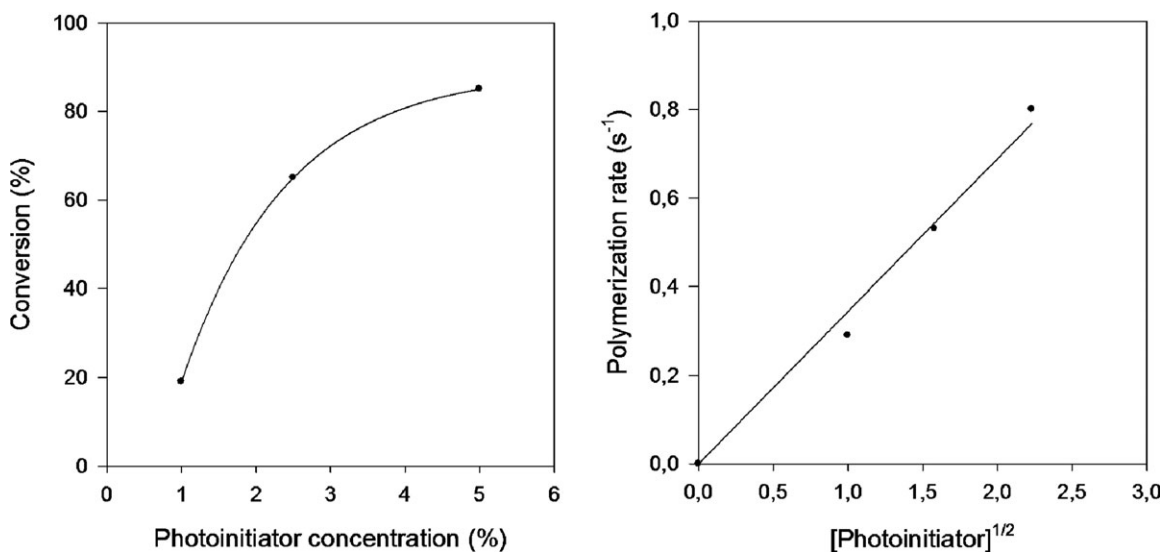


Figure 5. Ultimate conversion versus photoinitiator concentration and photopolymerization rate versus $[I_0]^{1/2}$ of EHTPI exposed to UV light intensity: $I = 50 \text{ mW cm}^{-2}$.

different structures were designed for the cationic polymerizable units: compounds **4** and **8** (Figures 2 and 3), which differ in the number of ammonium groups per monomer and in the distance of these groups from the oxirane groups.

Photopolymerization Study

Preliminary studies were performed to obtain antibacterial polymer films by cationic polymerization. The epoxidized hydroxytelechelic *cis*-1,4-polyisoprenes (EHTPI) (Figure 1 Supporting Information) were used in combination with oligomers **4** or **8**. It was verified (for the desired cationomer concentration 25 and 50% in weight) that the results found for the reaction of EHTPI alone are the same then those obtained in presence of oligomers **4** or **8** (Photopolymerization Kinetics of Mixtures of EHTPI and Cationomers section). Therefore in the following sections only the results referred to the reaction of the epoxidized hydroxytelechelic *cis*-1,4-polyisoprene are reported.

Photopolymerization Kinetics of Mixtures of EHTPI and Cationomers. UV-curing experiments of EHTPI, cationomer **4**, cationomer **8** and EHTPI/cationomers mixtures have been carried out with formulations containing 5% of photoinitiator (hexafluoro-phosphate triarylsulfonium salt). The plot of the conversion versus the irradiation time is showed in Figure 4. The result was compared with the conversion of epoxide functions in the case of the EHTPI reacting alone in the same conditions. The same results were obtained with different mixtures containing 25 and 50% of cationomer and EHTPI alone. However, concerning the formulations based on 100% of cationomers, we observed a decrease of conversion and photopolymerization rate. This result is probably due to the brown coloration of cationomers after quaternization using iodoctane which may restrict the UV irradiation diffusion in the coating.

Influence of the Photoinitiator Concentration. Photopolymerization of the epoxidized hydroxytelechelic *cis*-1,4-polyisoprene (molecular weight = 2000 g mol^{-1} , epoxidation ratio

= 30%) in the presence of increasing concentrations of hexafluoro-phosphate triarylsulfonium salt was first studied. Samples were cured with 50 mW cm^{-2} light intensity at 25°C . Ultimate conversion versus photoinitiator concentration and photopolymerization rate versus $[I_0]^{1/2}$ are represented in Figure 5.

After 15 min of UV irradiation, a high initial rate and ultimate conversion in epoxide functions (85%) are obtained for high initial concentration of the initiator (5%). When a lower initial initiator concentration (1 or 2.5%) was used, the rate of polymerization was slightly lower and the maximal ultimate conversion was only 60%. This weak conversion in epoxide functions is probably due to the weak concentration in reactive centers. Samples analysis after 24 h showed an increase of the ultimate conversion. Contrary to the radical process, the initiator species remains active and the reaction continues after irradiation interruption.³¹ However, the conversion does not exceed 85% for the different photoinitiator concentrations. The high glass transition temperature (T_g) of the polymer formed is likely to be the main reason for the incomplete conversion. Indeed, for temperatures close to the T_g , the mobility is reduced, limiting the diffusion of the reactive centers.

The rate of polymerization increases with photoinitiator concentration and it is directly related to the number of initiating species generated [eq. (3)].

$$R_p = k_p[M]_0 \left(\frac{\varphi \varepsilon I_0 [PI]_0}{k_t} \right)^{1/2} \quad (3)$$

φ is the quantum yield, ε is the photoinitiator molar extinction coefficient, I_0 is the light intensity of the UV radiation, $[PI]_0$ is the photoinitiator concentration, k_p and k_t are respectively the propagation and termination rate constants and $[M]_0$ is the initial monomer concentration. The concentration of photoinitiator is one of the key factors that affected the generation of the initiating species.

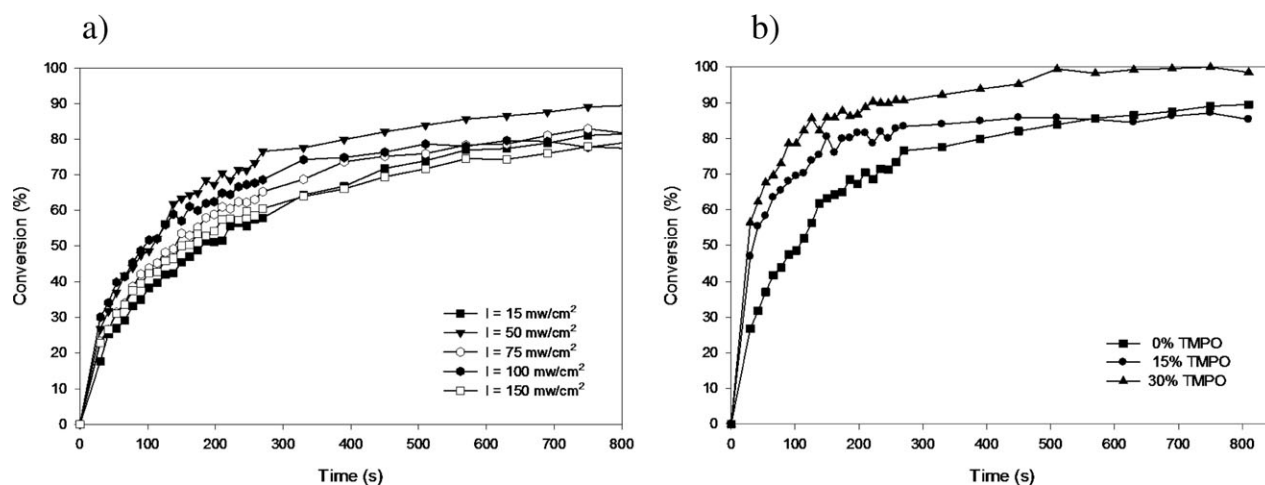


Figure 6. (a) Conversion in epoxide functions versus irradiation time of EHTPI for different light intensity; [PI] = 5% (w/w). (b) Conversion in epoxide functions versus irradiation time of mixtures of EHTPI and TMPO exposed to UV. [PI] = 5% (w/w); $I = 50 \text{ mW cm}^{-2}$.

Influence of the Light Intensity. The photopolymerization of a mixture of EHTPI (molecular weight = 2000 g mol^{-1} , epoxidation ratio = 30%) and photoinitiator (5% w/w) was studied at 25°C for light intensity ranging from 15 to 150 mW cm^{-2} . Figure 6(a) shows the evolution of the conversion of epoxide functions versus time. According to the kinetic profile of the reaction of photopolymerization, the rate of polymerization increases with the light intensity¹ [eq. (3)], therefore systems cannot be in volumic equilibrium because volume shrinkage rate is slower than chemical reaction rate. This difference generates a temporary excess of free volume which increases the mobility of the residual epoxide functions and reactive species.³² Intensity of irradiation did not have a significant influence on the ultimate conversion; 24 h after irradiation, the conversion in epoxide functions was stabilized around 80–90%.

Addition of Reactive Diluent: The 3-Ethyl-3-Hydroxymethyl Oxetane (Trimethylolpropane Oxetane, TMPO). The reactive diluents allow the decreasing of the viscosity of mixtures and they improve the thermo-mechanical properties of the coatings. The diminution of the mixture viscosity promotes the photopolymerization increasing the chains mobility. Besides, the addition of reactive diluents has a direct influence on the rate of polymerization while increasing the concentration of reactive functions.

In the case of a cationic photopolymerization, several works^{33–35} showed that the presence of moisture or hydroxyl functions has a beneficial effect on the reaction of photopolymerization. Penczek and Kubisa^{36,37} have shown that in the presence of alcohols, the polymerization rate of epoxidized monomers can be improved. They have proposed an « activated monomer mechanism ».

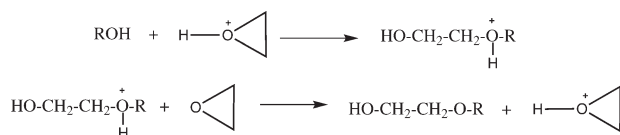


Figure 7. Activation mechanism of epoxidized monomer in presence of alcohol.

According to this mechanism, a rapid exchange of proton occurs when the oxonium propagating end reacts with an added alcohol (Figure 7). Then, there is a subsequent proton transfer from the growing chain to the monomer that thereafter can start new chains. As the terminal group is a hydroxyl group, the process continues until all monomer is consumed.

For this work, the reactive diluent used was the 3-ethyl-3-hydroxymethyl oxetane (trimethylolpropane oxetane, TMPO). In addition to its low viscosity, this product possesses the hydroxyl function that can accelerate the photopolymerization process. Table I presents the molecular weight and viscosity of EHTPI for different epoxidation ratios, and of 3-ethyl-3-hydroxymethyl oxetane (TMPO). Different formulations containing the PIHTE4-30% (molecular weight = 2000 g mol^{-1} , epoxidation ratio = 30%), 5% w/w of photoinitiator and the increasing quantities of diluent have been prepared. The samples were irradiated with a light intensity of 50 mW cm^{-2} . The kinetic study was performed following the conversion of epoxide functions. The plots of conversions versus irradiation times [Figure 6(b)] confirms the improvement effect of the reactive diluent on the polymerization rate and ultimate conversion. The increase of the chains mobility and the promoted transfer of the reactive centers between reactive functions allow reaching an ultimate conversion in epoxide functions close to 100%.

To check the complete polymerization of the oxetane, a thermogravimetric analysis of the oxetane monomer (TMPO) and

Table I. Viscosity and Molecular Weight of EHTPI and TMPO

	EHTPI4-20%	EHTPI-25%	EHTPI-30%	TMPO
Molecular weight (g mol^{-1})	4000	4000	4000	116
Epoxidation ratio (%)	20	25	30	-
Viscosity (Pa S^{-1})	17.3	22	23.9	0.025

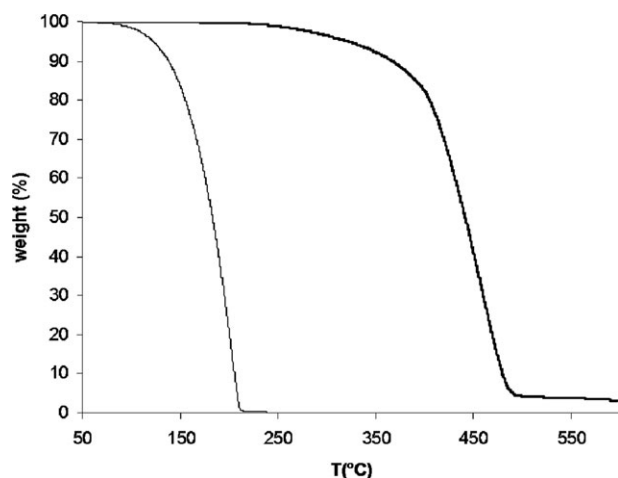


Figure 8. Thermogravimetric analysis of TMPO and mixture (TMPO + EHTPI) after UV irradiation.

of the mixture (EHTPI + TMPO) after irradiation is performed. The result (Figure 8) shows no mass loss corresponding to the TMPO during the degradation of the coating synthesized by irradiation of the formulation (TMPO + EHTPI).

Effect of the Epoxidation Ratio: Concentration of Reactive Functions. Generally, the photopolymerization process is directly related to the concentration of monomer¹ and the increase in the concentration of the reactive functions accelerates considerably the reaction rate. To study the effect of different epoxidation ratios, formulations containing EHTPI (molecular weight = 2000 g mol⁻¹) and 5% w/w of degacur KI 85 have been irradiated under UV light ($I = 50 \text{ mW cm}^{-2}$). Ultimate conversion and rate of photopolymerization versus epoxidation ratio are represented in Figure 9. We observed a small variation of ultimate conversion and polymerization rate for the different epoxidation ratios. Normally, photopolymerization rate is proportional to concentration of reactive functional groups $[M]_0$ [eq. (3)]. Therefore, it must increase with epoxidation

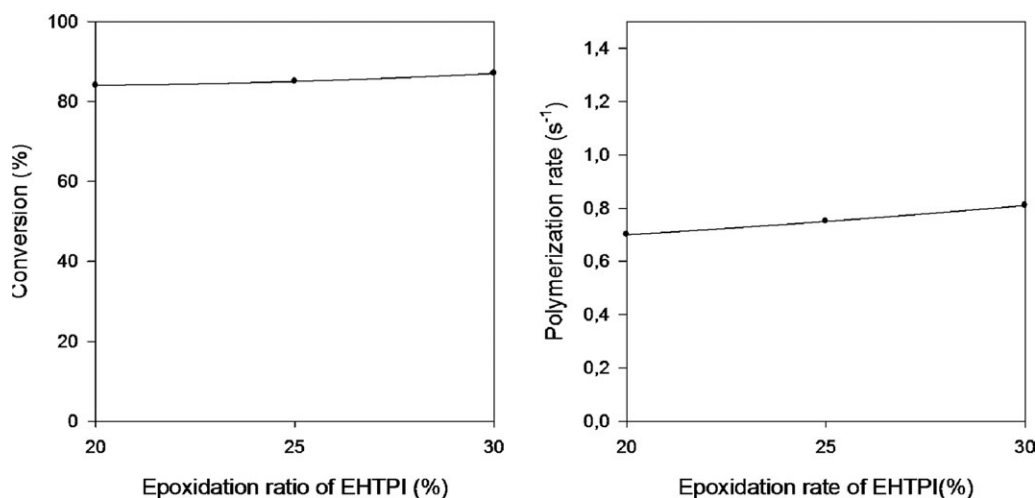


Figure 9. Ultimate conversion and photopolymerization rate versus epoxidation ratio of EHTPI exposed to UV light intensity: $I = 50 \text{ mW cm}^{-2}$; $[PI] = 5\%$.

ratios. However, in the present study, this effect is compensated by the reduced mobility due to the high viscosity (Table I) and increasing of the crosslinking density.

Photopolymerization of the Diacrylate Epoxidized Telechelic *cis*-1,4-Polyisoprene (dETPI)

For this part of the work, the kinetic study of polymerization consisted in following the evolution of conversion of the two reactive functions: acrylate and epoxide.

Cationic Initiator System Alone. In a first time, we used a cationic photoinitiator alone. Indeed, the photolysis of a triarylsulfonium salt initiator leads to the formation of cationic, radical and radical-cationic species (Figure 5 Supporting Information). The radicals generated during this photolysis can initiate radical photopolymerization. Figure 10 shows the evolution of the conversion in acrylate and epoxide functions for different concentrations of cationic photoinitiator (hexafluoro-phosphate triarylsulfonium salt: degacur KI85). We noticed that the conversions of the acrylate functions remained always weak (around 15%) and did not evolve when the photoinitiator concentration increased. This was probably due to the low concentration in free radicals generated by the cationic photoinitiator, part of which will be inhibited by oxygen presence (Figure 6 Supporting Information).³⁹ Therefore we concluded that the evolution of the conversion of the epoxide functions presents the same profile (Figure 10) than that of a cationic photopolymerization alone and no radical photopolymerization is occurring at the same time. However, a light decrease of the ultimate conversion is observed: it is possible that the crosslinking of a part of the acrylate functions in the chain-ends decreases the mobility of the reactive centers making the access to the epoxide functions more difficult.

Dual Initiator System. It was demonstrated that the cationic initiation system was not efficient to completely polymerize the acrylate functions. Coatings with dEHTPI and different mixtures of the free-radical initiator (darocur 1173) and of the cationic initiator (degacur KI 85) were then studied for different light intensities. The ultimate conversions of the acrylate double

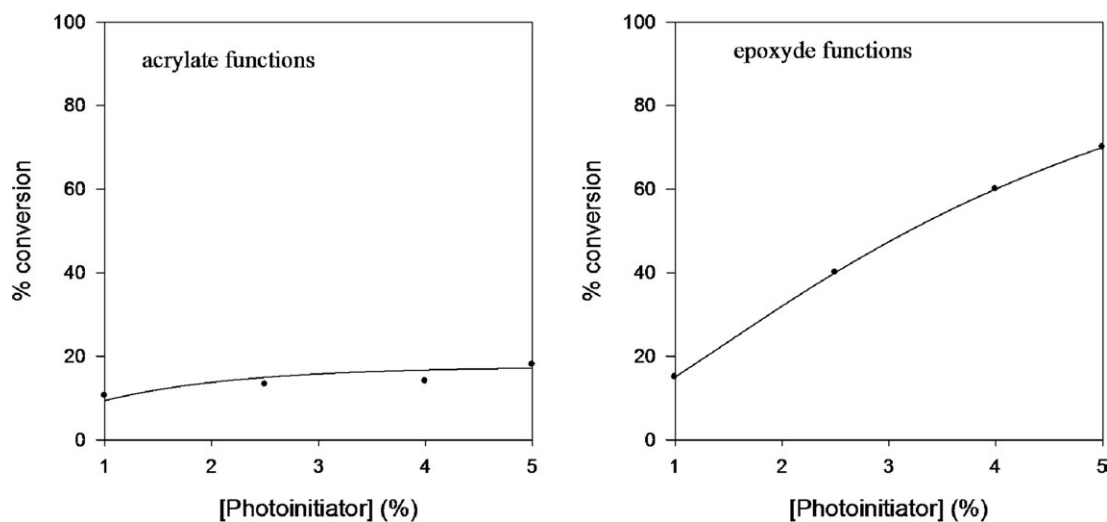


Figure 10. Ultimate conversion of acrylate and epoxide functions versus photoinitiator concentration of EHTPI exposed to UV light ($I = 50 \text{ mW cm}^{-2}$).

bonds and of the epoxide functions measured by infrared real time spectroscopy are represented in Figure 11 and Table II. An induction period for the cationic photopolymerization of epoxide functions was observed. This phenomenon increases with increasing concentration of radical photoinitiator. The results obtained for different mixtures of photoinitiator and different light intensities showed that the conversion of epoxide functions decreases when the acrylate functions conversion increases. Besides, the postpolymerization phenomenon observed in the case of the cationic process alone, did not occur. 24 h after the irradiation end, the conversion of epoxide functions had not evolved. Normally, the cationic active center is known to be long lived after the initiation light is shuttered,³¹ thus only the photodecomposition of the initiator requires initiation light, and the propagation or chain-growth steps are independent of the light. Ideally, polymerization will continue until no monomer can access the active center.

When cationic photopolymerization process starts, the conversion of acrylate function is well advanced (range 20–50%). Thus, the mobility of the cationic reactive centers is restricted due to vitrification resulting from the high conversion of the acrylate double bonds and crosslinking. In the same way, the conversion in acrylate functions never reached 100%, some of these groups being inaccessible because of the crosslinking between epoxide functions.

CONCLUSION

In the present work, an epoxidized hydroxytelechelic *cis*-1,4-polyisoprene and a dual system (epoxidized/acrylated) telechelic *cis*-1,4-polyisoprene were obtained by controlled degradation of high molecular weight *cis*-1,4-polyisoprene. Synthesis of these photosensitive oligoisoprenes was achieved by simple chemical reactions giving access to products with well defined structure and molecular weight.

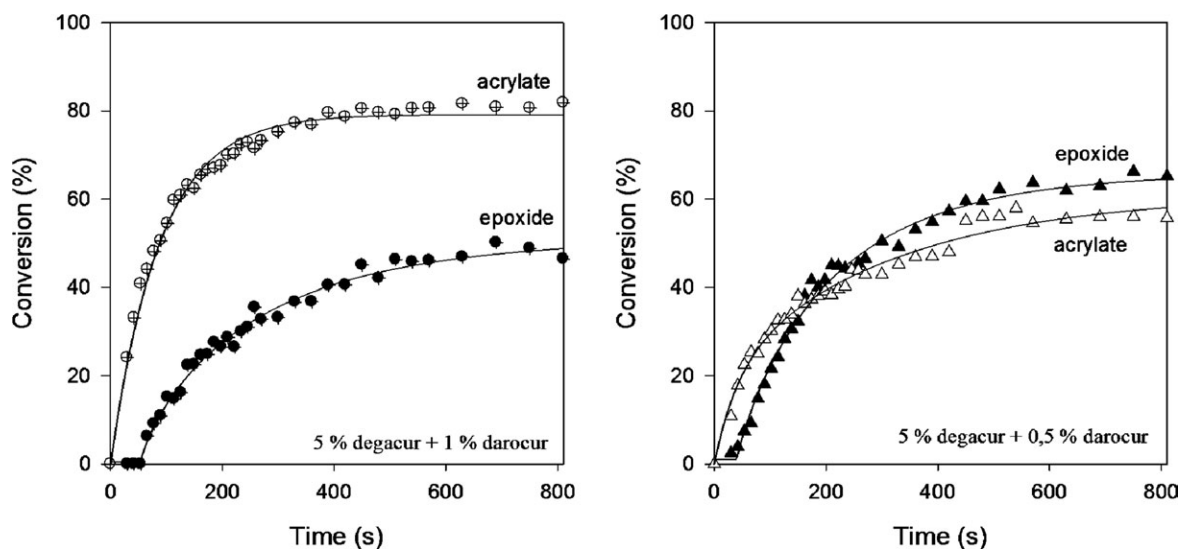


Figure 11. Conversion profile of acrylate and epoxide functions for different mixtures of photoinitiator. Samples were cured with $I = 50 \text{ mW cm}^{-2}$.

Table II. Conversion of Acrylate and Epoxide Functions of dEHTPI with Different Photoinitiator Mixtures Irradiated with Different Light Intensity

Sample	I (mW cm ⁻²)	[degacur/ darocur] % w/w	% conversion acrylate	% conversion epoxide
1	50	5/1	75	40
2	50	5/0.5	50	60
3	50	5/2	90	10
4	25	5/0.5	60	30
5	10	5/0.5	80	15
6	5	5/0.5	85	7

Real-time infrared spectroscopy was used to monitor the cationic photopolymerization and the kinetic of hybrid systems (acrylated/epoxidized). For the cationic process, the ultimate conversion and the polymerization rate were influenced by the photoinitiator concentration, the light intensity and the reactive diluent concentrations. Addition of a reactive diluent allowed reaching a maximal ultimate conversion and enhanced considerably the polymerization rate. Besides, a postpolymerization phenomenon was observed, which improves the ultimate conversion of 20–30% after the irradiation end. Concerning the photopolymerization of dual epoxidized/acrylated system, the development of the acrylate network affects the epoxide conversion. The experimental results with various initiator mixtures showed that the epoxide conversion decreases when the acrylate conversion increases.

REFERENCES

- Decker, C. *Prog. Polym. Sci.* **1996**, *21*, 593.
- Decker, C.; Nguyen, T. V. T.; Xuan, H. L. *Eur. Polym. J.* **1996**, *32*, 559.
- Sangermano, M.; Bongiovanni, R.; Malucelli, G.; Priola, A.; Thomasb, R. R.; Medskerb, R. E.; Kim, Y.; Kausch, C. M. *Polymer* **2004**, *45*, 2133.
- Takimoto, Y. In *Radiation Curing in Polymer Science and Technology: Polymerization Mechanisms*; Fouassier, J. P., Ed.; Elsevier: London, **1993**; Vol. 3, p 269.
- Crivello, J. V. *Nucl. Inst. Meth. Phys. Res. B* **1999**, *151*, 8.
- Ortiz, R. A.; Lopez, D. P.; Cisneros, M. L. G.; Valverde, J. C. R.; Crivello, J. V. *Polymer* **2005**, *46*, 1535.
- Crivello, J. V.; Lee, J. L. In *Radiation Curing of Polymeric Materials*; Hoyle, C. E., Kinstle, J. F., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, **1990**; Vol. 417, p 398.
- Crivello, J. V.; Lee, J. L. *J. Polym. Sci.* **1990**, *28*, 479.
- Decker, C.; Thi, V. T. N.; Thi, H. P. *Polym. Int.* **2001**, *50*, 986.
- Crivello, J. V.; Jo, K. D. *J. Polym. Sci. Polym. Chem.* **1993**, *31*, 1483.
- Crivello, J. V.; Lohden, G. *J. Polym. Sci. Polym. Chem.* **1996**, *34*, 2051.
- Crivello, J. V.; Jo, K. D. *J. Polym. Sci. Polym. Chem.* **1993**, *31*, 2143.
- Decker, C.; Morel, F. *Polym. Mater. Sci. Eng.* **1997**, *76*, 70.
- Decker, C.; Bianchi, C.; Decker, D.; Morel, F. *Prog. Org. Coat.* **2001**, *42*, 253.
- Pappas, S. P. *UV-Curing Science and Technology*; Plenum Press: New York, **1992**.
- Crivello, J. V.; Ortiz, R. A. *J. Polym. Sci. Polym. Chem.* **2001**, *39*, 3578.
- Orozco, J. C.; Cantow, H. J. *Polym. Bull.* **1984**, *12*, 203.
- Mauler, R. S.; Guaragna, F. M.; Gobbi, D. L.; Samios, D. *Eur. Polym. J.* **1997**, *33*, 399.
- Nor, H. M.; Ebdon, J. R. *Prog. Polym. Sci.* **1998**, *23*, 143.
- Brosse, J. C.; Campistron, I.; Derouet, D.; El Hamdaoui, A.; Houdayer, S.; Reyx, D. *J. Appl. Polym. Sci.* **2000**, *78*, 1461.
- Gillier-Ritoit, S.; Reyx, D.; Campistron, I.; Laguerre, A.; Singh, R. P. *J. Appl. Polym. Sci.* **2003**, *87*, 42.
- Kébir, N.; Morandi, G.; Campistron, I.; Laguerre, A.; Pilard, J. F. *Polymer* **2005**, *46*, 6844.
- Morandi, G.; Kebir, N.; Campistron, I.; Gohier, F.; Laguerre, A.; Pilard, J. F. *Tetrahedron Lett.* **2007**, *48*, 7726.
- Kébir, N.; Campistron, I.; Laguerre, A.; Pilard, J. F.; Bunel, C.; Couvercelle, J. P. *Polymer* **2005**, *46*, 6869.
- Kébir, N.; Campistron, I.; Laguerre, A.; Pilard, J. F.; Bunel, C.; Couvercelle, J. P. *e-Polymers* **2006**, *48*, 1.
- Jellali, R.; Campistron, I.; Laguerre, A.; Pasetto, P.; Lecamp, L.; Bunel, C.; Mouget, J. L.; Pilard, J. F. *J. Appl. Polym. Sci.*, 2012, DOI: 10.1002/app.37691.
- Jellali, R.; Campistron, I.; Laguerre, A.; Gohier, F.; Hellio, C.; Pilard, J. F.; Mouget, J. L. *Biofouling, Elaboration de revêtements antifouling par photoréticulation d'oligoisoprènes fonctionnalisés: étude de leurs activités antibactériennes, antifongiques et antialgues*. PhD dissertation, 2008, Université du Maine.
- Bunel, C.; Campistron, I.; Hellio, C.; Jellali, R.; Laguerre, A.; Mouget, J. L.; Pilard, J. F. Patent No. WO 2,010,043,800, **2010**.
- O'Neil, I. A.; Cleator, E.; Tapolczay, D. J. *Tetrahedron Lett.* **2001**, *42*, 8247.
- Sammelson, R. E.; Kurl, M. J. *Tetrahedron Lett.* **2001**, *42*, 3419.
- Decker, C.; Nguyen, T. V. T.; Xuan, H. L. *Eur. Polym. J.* **1996**, *32*, 1319.
- Lecamp, L.; Youssef, B.; Bunel, C.; Lebaudy, P. *Polymer* **1997**, *38*, 6089.
- Chen, J.; Soucek, M. D. *J. Appl. Polym. Sci.* **2003**, *90*, 2485.
- Hartwig, A.; Schneider, B.; Lühring, A. *Polymer* **2002**, *43*, 4243.
- Hartwig, A.; Koschek, K.; Lühring, A.; Schorsch, O. *Polymer* **2003**, *44*, 2853.
- Penczek, S.; Kubisa, P.; Szymanski, R. *Makromol. Chem. Macromol. Symp.* **1986**, *3*, 203.
- Kubisa, P. *Makromol. Chem. Macromol. Symp.* **1988**, *13/14*, 203.
- Yagci, Y.; Schnabel, W. *Angew. Makromol. Chem.* **1999**, *270*, 38.
- Lee, T. Y.; Guymon, C. A.; Sonny Jonsson, E.; Hoyle, C. E. *Polymer* **2004**, *45*, 6155.