

Synthesis of New Photocurable Oligoisoprenes and Kinetic Studies of their Radical Photopolymerization

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ABSTRACT: New photosensitive oligoisoprenes were synthesized by controlled degradation of high molecular weight cis-1,4-polyisoprene and successive chemical modification of the chain-ends. Oligomers with diacrylate extremities were synthesized, characterized, and used in photocrosslinking reactions in different conditions. The photoinitiated polymerization of the diacrylate oligoisoprenes was carried out using 2,2-dimethyl-2-hydroxyacetophenone (Darocur 1173) as initiator and the reaction was monitored by photocalorimetry-DSC and real time FTIR spectroscopy. The influence of oxygen, photoinitiator concentration, light intensity, diluting agent, and oligomers molecular weight on the reaction rate was investigated. It was found that the presence of oxygen does not influence the photopolymerization kinetics of the diacrylate oligoisoprenes. Maximum conversion was obtained for a photoinitiator concentration of 5% (w/w) and for a light intensity of 13.5 mW/cm². Decreasing the formulation viscosity by addition of a diluent (1,6-hexanediol diacrylate) raised the photopolymerization rate, by increasing the reactive species mobility. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polyisoprene; telechelic oligomers; antifouling coating; radical photopolymerization

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INTRODUCTION

The preparation of coatings based on natural renewable resources has become one of the more promising topics in material science. Liquid natural rubber (LNR) constitutes an important raw material for the coatings elaboration because of its interesting chemical and mechanical properties, such as resilience, strength, and fatigue resistance. The telechelic liquid natural rubber (TLNR) derived from the fragmentation of the natural rubber chains represents a powerful precursor of a very wide range of polymers. The chemical modification of such oligomers, derived from the degradation of cis-1,4-polyisoprene chains, has been the subject of research works in different groups, with the aim to control the nature of the chain extremities and the polydispersity of the chain lengths.^{1–8} Our group gained experience on the selective degradation of cis-1,4-polyisoprene chains using well-controlled oxidative chain cleavage to obtain carbonyltelechelic cis-1,4-polyisoprene oligomers.^{4,5} The subsequent chemical modifications of carbonyl end-groups and

carbon–carbon double bonds led to new functional cis-1,4-oligoisoprenes.^{6–8} In this study, a quaternary ammonium functionality was introduced with the aim to generate surfaces with antibacterial properties, as it is well known that the ammonium groups can adhere to the bacteria cell walls, diffuse through the membrane and promote the death of the microorganism.⁹

To obtain thin coatings, UV-curable systems appeared as an attractive alternative because these solvent-free resins can be cured within seconds at ambient temperature to yield highly resistant crosslinked polymers.^{9–12} 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 suitable reactive monomers and/or oligomers. In radical photopolymerization, free radicals are readily produced upon UV irradiation of aromatic carbonyl compounds, either by homolytic cleavage of C–C bonds, or by hydrogen abstraction from an H-donor molecule.¹⁰ Radical polymerization involves monomers or polymers containing vinyl unsaturations such as

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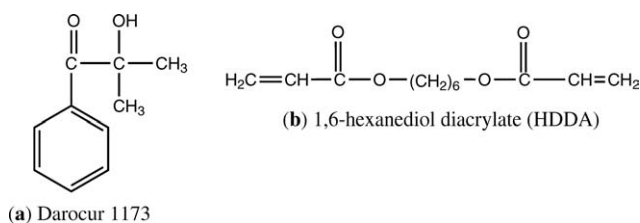


Figure 1. (a) Photoinitiator and (b) diluent.

acrylates, methacrylates, and unsaturated polyesters. However, acrylate containing polymers are mostly preferred due to the well-known reactivity of the acrylate double bond in radical polymerizations^{10,13,14} and many acrylate-functionalized telechelic and multifunctional monomers or polymers with ether, ester, carbonate, or silicone connecting units are now commercially available.^{10,15–20}

The objective of the present work was to elaborate crosslinked thin films by UV irradiation of new photocurable acrylic liquid natural rubber derived oligomers, via a radical polymerization mechanism. The effects of photoinitiator concentration, light intensity, molecular weight of photocurable oligomer, and diluting agent upon UV-curing were investigated in order to optimize the coating physical properties. The cationic polymerization of

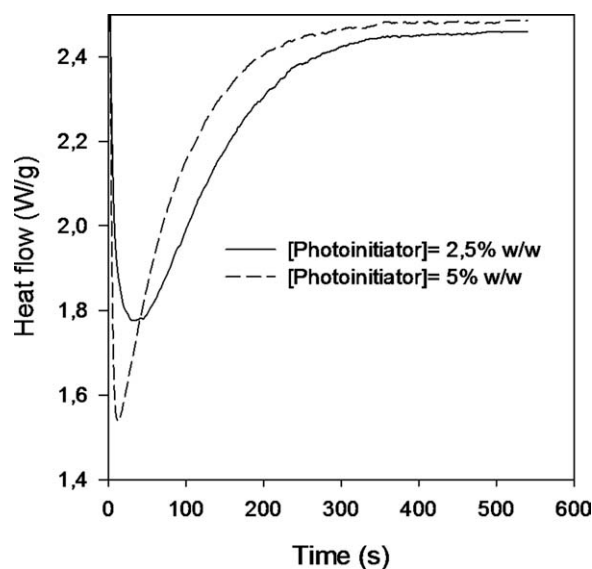


Figure 3. Example of photocalorimetry study: Heat flux versus time at various Darocur 1173 concentrations for a stoichiometric mixture at 25°C. Diacrylate oligomer molecular weight = 1750 g/mol, $I = 13.5$ mW/cm², and $T = 25^\circ\text{C}$.

analog oligomers will be presented in following papers as well as the results of the biological tests concerning the antibacterial/biocide activity of the materials.

EXPERIMENTAL

Materials

Cis-1,4-polyisoprene (Acros Organics, 98% cis, $M_w = 800,000$), metha-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 aluminium hydride (1M in ether, Aldrich) were used without previous purification. The triethylamine was distilled before use.

2,2-Dimethyl-2-hydroxyacetophenone [Darocur 1173, Aldrich, Figure 1(a)] was chosen as photoinitiator. 1,6-Hexanediol diacrylate [HDDA, Aldrich, 90%, Figure 1(b)] has been used as diluent.

Instrumentation

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

Real Time Infrared Spectroscopy. Photocrosslinking reactions were followed by real time infrared spectroscopy (Perkin Elmer FTIR 2000 spectrometer) in attenuated total reflection (ATR). UV radiation from a 350-W Oriel mercury vapour lamp was introduced into the FTIR spectrometer sample chamber by a flexible light guide so that it did not interfere with the IR beam. The IR spectra were obtained from the spectrophotometer with

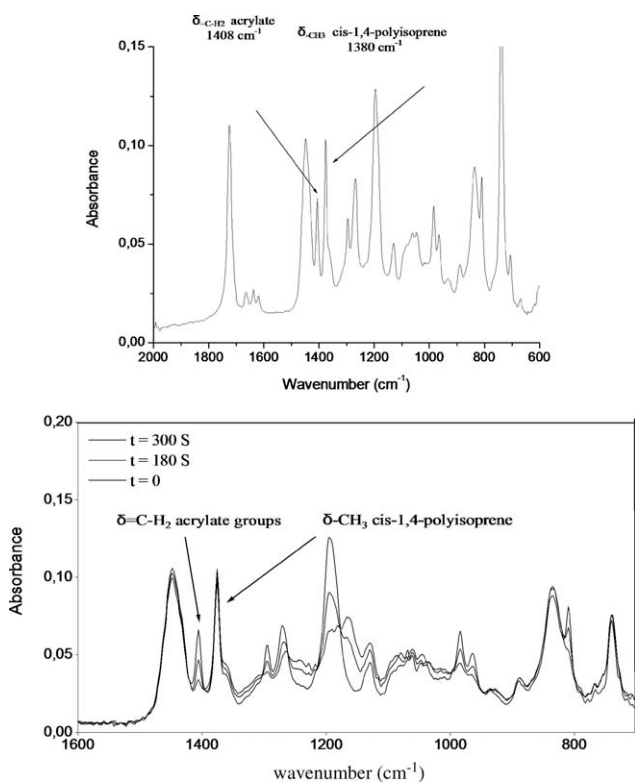
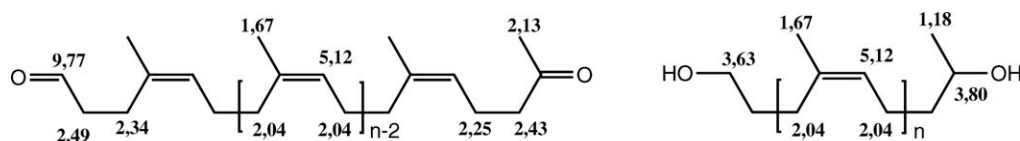


Figure 2. (a) Characteristic peaks in infrared spectroscopy of diacrylate oligoisoprene: $\delta_{\text{-CH}_3}$ of the cis-1,4-polyisoprene at 1380 cm^{-1} (reference band) and $\delta_{\text{-C-H}_2}$ of the acrylate functional groups at 1408 cm^{-1} . (b) Evolution of characteristic peaks [$\delta_{\text{-CH}_3}$ of the cis-1,4-polyisoprene at 1380 cm^{-1} (reference band) and $\delta_{\text{-C-H}_2}$ of the acrylate functional groups at 1408 cm^{-1}] with irradiation time.



Carbonyltelechelic cis-1,4-polyisoprene (CTPI)

Hydroxyltelechelic cis-1,4-polyisoprene (HTPI)

Figure 4. ¹H-NMR chemical shifts of CTPI and HTPI.

a resolution of 8 cm^{-1} . They were collected every 6 s to have a real time monitoring of the reaction. The absorbance of the peaks at 1408 cm^{-1} ($\delta_{\text{=CH}_2}$ of the acrylate functional groups) and at 1380 cm^{-1} (reference band, $\delta_{\text{>CH}_3}$ of the cis-1,4-polyisoprene, Figure 2) were used to calculate conversions with the following equation:

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

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

Photocalorimetry. The photopolymerization reactions were carried out in a differential scanning calorimeter (Perkin Elmer DSC 7). Heat flow versus time was recorded in isothermal mode (25°C) under nitrogen atmosphere (example in Figure 3). Conversion of the acrylate functional groups has been calculated after measurement of the specific polymerization enthalpy at each time of the reaction as follows²⁰:

$$C_{(t)} = \frac{\Delta H_{\text{exp}}}{\Delta H_{\text{th}}} \quad \text{with} \quad \Delta H_{\text{th}} = \frac{2\Delta H_a}{M}$$

$C_{(t)}$ is the conversion of the reactive functions at (t) time, ΔH_{exp} is the experimental polymerization enthalpy, ΔH_{th} is the theoretical polymerization enthalpy, ΔH_a is the polymerization enthalpy for acrylate function and M is the molecular weight of the diacrylate oligoisoprene.

Irradiation. The samples were irradiated with a 350 W Oriol mercury vapour lamp, which was introduced into the FTIR spectrometer or DSC photocalorimeter by a flexible light guide. The UV radiation intensity was measured by a spectroradiometer (Intraspec II Oriol VLX/3W) at 365 nm.

Viscosity. Viscosity values were calculated by Schott AVS-310 viscometer.

Size Exclusion Chromatography. Average molecular weights (M_n) of the different oligomers were measured using Size Exclusion Chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 mm Guard, $50 \times 7.5 \text{ mm}^2$) followed by two columns (Polymer Laboratories, 2 PL gel 5 mm MIXED-D columns, $2 \times 300 \times 7.5 \text{ mm}^3$), with a SpectraSYSTEM RI-150 and a SpectraSYSTEM UV2000 detectors. The elu-

ent used was THF at a flow rate of 1 mL/min at 35°C . Polystyrene standards (580–483,000 g/mol) were used to calibrate the SEC: polystyrene standardized molecular weights were corrected by the Benoit factor according to the known formula.²¹

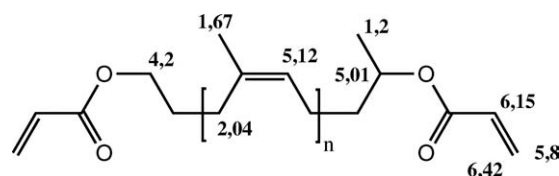
Syntheses

Preparation of Hydroxy Telechelic Cis-1,4-Polyisoprene (HTPI). The controlled degradation of high molecular weight cis-1,4-polyisoprene was achieved by a method developed in our laboratory.⁵ In a first step, cis-1,4-polyisoprene was epoxidized by reaction with meta-chloroperbenzoic acid and then cleavage of oxirane units was performed with periodic acid. The required quantities of meta-chloroperbenzoic acid and periodic acid were determined using the following eqs. (1) and (2):

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

$$m_{\text{periodic acid}} = (m_{\text{EPI}})/68.8 \cdot (\tau_e/100) \cdot M_{\text{periodic acid}} \cdot 1,1 \quad (2)$$

where (m_{PI}) is the weight of cis-1,4-polyisoprene in grams, (68.8) is the molecular weight for isoprene unit in g/mol, (τ_e) is the epoxide percentage, (M_{mCPBA}) is the molecular weight of m-CPBA in g/mol, (m_{EPI}) is the weight of epoxidized cis-1,4-polyisoprene in grams and ($M_{\text{periodic acid}}$) is the molecular weight of periodic acid in g/mol. The calculated amount of meta-chloroperbenzoic acid was suspended in the required volume of dry dichloromethane to have a 0.1M solution, which was added dropwise to a solution of 20 g of cis-1,4-polyisoprene in 500 mL of dry dichloromethane (reaction time: 6 h, at 0°C). Yields for this reaction were around 95%. In a second step, a solution 0.4M of the corresponding amount of periodic acid in THF was added dropwise to a solution obtained dissolving 18 g of the purified epoxidized cis-1,4-polyisoprene (epoxide ratio 2 or 5%) in 400 mL of tetrahydrofuran (THF). After stirring for 6 h at 30°C , the tetrahydrofuran was evaporated and the product was dissolved in dichloromethane. This solution was washed with saturated aqueous solutions of NaHCO_3 and $\text{Na}_2\text{S}_2\text{O}_3$, dried over MgSO_4 , filtered and the organic solvent was eliminated to obtain the carbonyltelechelic cis-1,4-polyisoprene (CTPI). Yields for this reaction were in the range 90–96%. Two different theoretical molecular weights, 2000 g/

Figure 5. ¹H-NMR chemical shifts of diacrylate oligoisoprene.

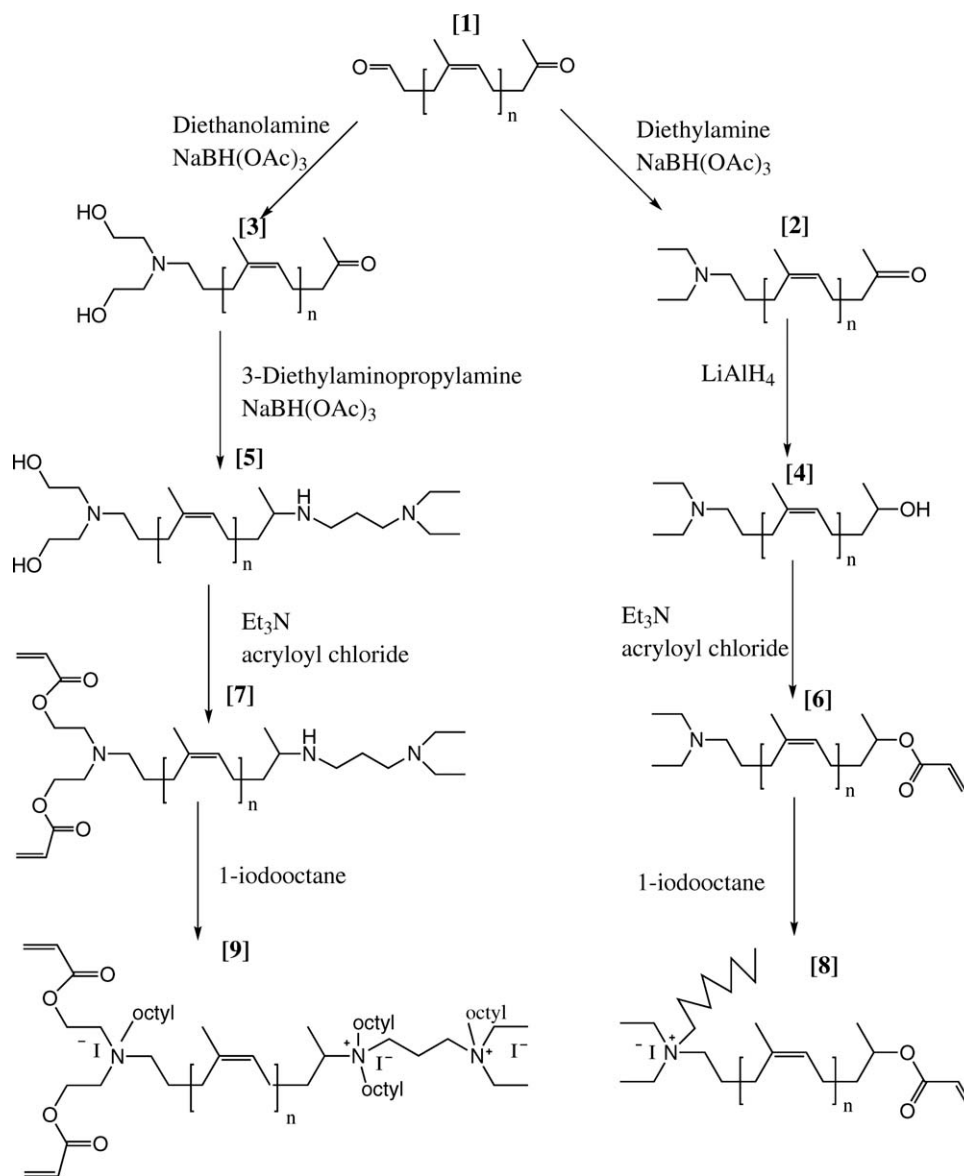


Figure 6. Synthesis of photocurable acrylic cationomers **8** and **9** from carbonyl telechelic cis-1,4-polyisoprene.

mol, and 5000 g/mol, were targeted using, respectively, 5% and 2% epoxidation. The values of the obtained molecular weights calculated from $^1\text{H-NMR}$ spectra were 1750 and 4000 g/mol; the values obtained from size exclusion chromatography were 2600 and 5700 g/mol in polystyrene equivalents (the real values corresponding to 1740 and 3820 g/mol using the Benoit equation).

In a third step, the purified CTPI was dissolved in THF ([CTPI] = 0.07 mol/L) and it was added dropwise to a solution of four equivalents of sodium borohydride dissolved in the appropriate volume of THF to have a 0.3 mol/L solution. After stirring for 6 h at 60°C , the excess of NaBH_4 was hydrolyzed. The reaction mixture was transferred in a separating funnel and washed with a saturated solution of NaCl ; the organic phase was concentrated, dried over MgSO_4 , filtered and concentrated again. Average yields for this reaction were 93–98%.

FTIR: - **CTPI**: $\nu_{\text{C}=\text{C}} = 1664 \text{ cm}^{-1}$; $\nu_{\text{C}=\text{H}} = 3035 \text{ cm}^{-1}$; $\nu_{\text{C}=\text{O}} = 1721 \text{ cm}^{-1}$; $\delta_{\text{C}-\text{H}} = 834 \text{ cm}^{-1}$; $\nu_{\text{CH}_2, \text{CH}_3}$ cis-1,4-polyisoprene = 1448, 1376 cm^{-1} .

FTIR: - **HTPI**: $\nu_{\text{C}=\text{C}} = 1664 \text{ cm}^{-1}$; $\nu_{\text{C}=\text{H}} = 3035 \text{ cm}^{-1}$; $\nu_{\text{OH}} = 3350 \text{ cm}^{-1}$; $\delta_{\text{C}-\text{H}} = 834 \text{ cm}^{-1}$; $\nu_{\text{CH}_2, \text{CH}_3}$ cis-1,4-polyisoprene = 1448, 1376 cm^{-1} ; disappearance of $\nu_{\text{C}=\text{O}}$ at 1721 cm^{-1} .

^1H NMR chemical shifts of CTPI and HTPI are shown in Figure 4.

Synthesis of Diacrylate Cis-1,4-polyisoprene. Acryloyl chloride (2.3 equivalents) was added dropwise to a solution containing 1 equivalent of hydroxytelechelic cis-1,4-polyisoprene (HTPI), dissolved in anhydrous dichloromethane (0.08 mol/L), and triethylamine (2.3 equivalents), at 0°C , under nitrogen atmosphere. After maintaining the solution at 0°C for 30 min, the mixture was allowed to stir at room temperature for 24 h. The solution

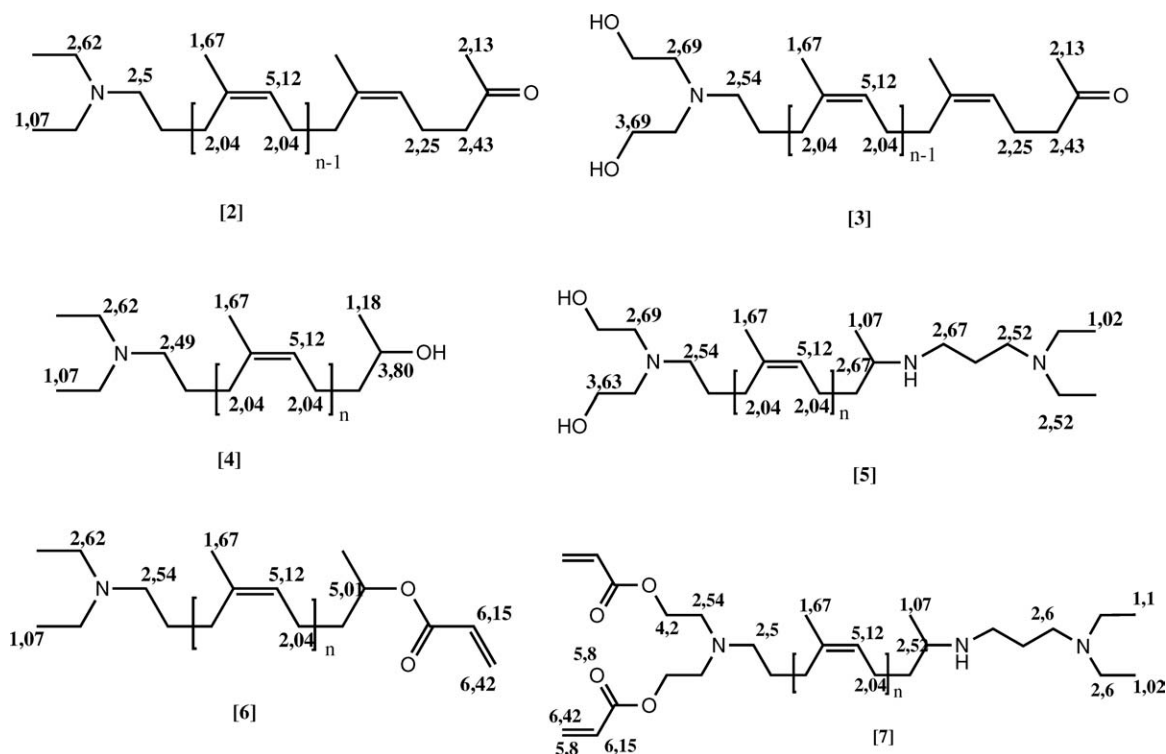


Figure 7. ¹H-NMR chemical shifts of functionalized oligomers 2, 3, 4, 5, 6, and 7.

was then transferred in a separating funnel and washed with a NaOH aqueous solution (1N); after phase separation, the organic phase was dried over MgSO₄ and filtered. After solvent evaporation, the liquid oligomer was obtained with 92% yield.

FTIR: $\nu_{C=C}$ (isoprene) = 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; $\nu_{C=O}$ (ester) = 1736 cm⁻¹; $\nu_{C=C}$ (acrylate) = 1632 cm⁻¹; δ_{C-H_2} (acrylate) = 1408 cm⁻¹; disappearance of ν_{OH} at 3350 cm⁻¹. ¹H NMR chemical shifts are shown in Figure 5.

Synthesis of Photocurable Acrylic Cationomers. Compounds 4 and 5 (Figure 6) were prepared according to a methodology described by Kébir et al.^{6,22} starting from the carbonyltelechelic cis-1,4-polyisoprene (CTPI). Acrylate cationomer **8** and diacrylate cationomer **9** were synthesized with an identical procedure in two steps starting from compounds 4 and 5, respectively. In the first step, acryloyl chloride (1.3 equivalents for 4 or 2.6 equivalents for 5) was dropwise added to a solution of 4 or 5 in anhydrous dichloromethane (concentration of oligomer = 0.08 mol/L), in presence of triethylamine (1.3 equivalents for 4 or 2.6 equivalents for 5), at 0°C, under nitrogen atmosphere. After keeping the solution at 0°C for 30 min, the mixture was left stirring at room temperature for 24 h. The solution was then transferred in a separating funnel and washed with a NaOH 1 mol/L aqueous solution. After phase separation, the organic phase was dried over MgSO₄, the suspension was filtered, and solvent eliminated by rotavapor. Yields of liquid oligomers were around 85% for both compounds 6 and 7.

In a second step, compounds 6 or 7 (Figure 6) were dissolved in a solution of dichloromethane:acetonitrile = 3 : 1, and 1-iodooctane (5 equivalents/amine function) was added. The solution was stirred at 40°C for 24 h and then the solvent and excess of unreacted 1-iodooctane were removed under reduced pressure to give the oligomers **8** or **9**. The reaction was complete.

FTIR - α -carbonyl- ω -*N,N*- diethylaminotelechelic cis-1,4-oligoisoprene (**compound 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.

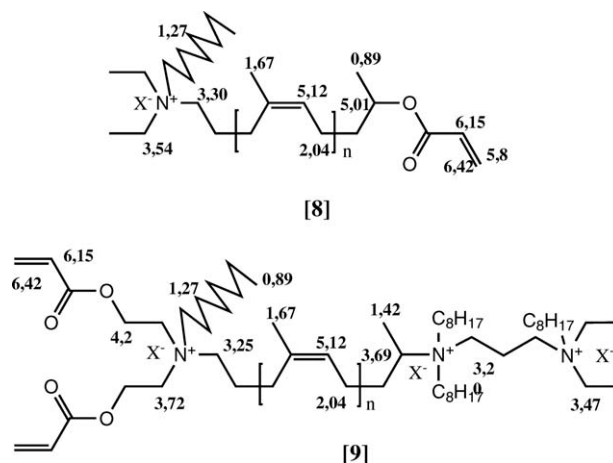


Figure 8. ¹H-NMR chemical shifts of products 8 and 9.

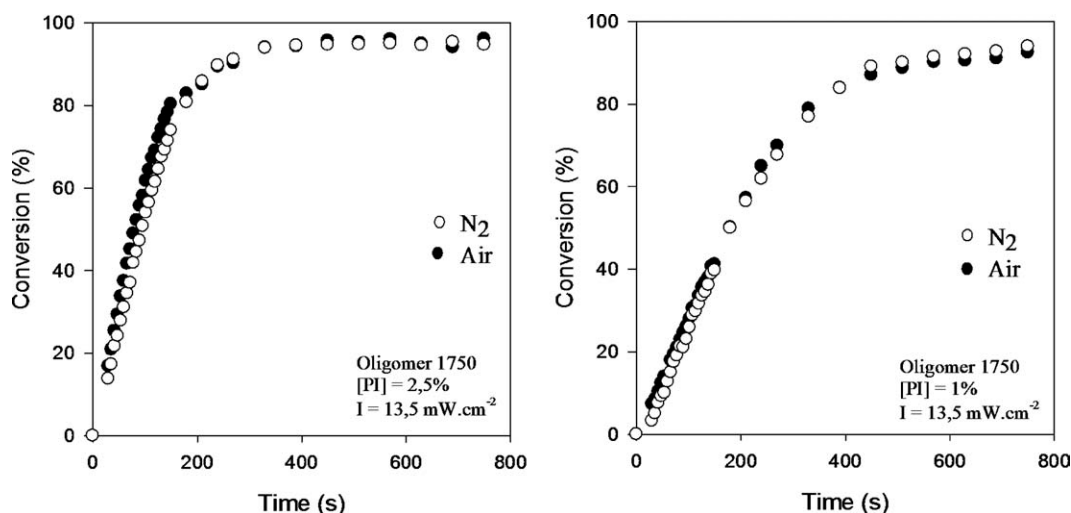


Figure 9. Conversion of acrylate functions against irradiation time of diacrylate oligoisoprenes exposed to UV light under air or nitrogen atmosphere. (Left) photoinitiator concentration 2.5%; (right) photoinitiator concentration 1%. Conversions have been obtained by DSC measures.

FTIR - α -carbonyl- ω -*N,N*- dihydroxyethylaminotelechelic cis-1,4-oligoisoprene (**compound 3**): $\nu_{C=C} = 1664 \text{ cm}^{-1}$; $\nu_{CH} = 3035 \text{ cm}^{-1}$; $\nu_{OH} = 3380 \text{ cm}^{-1}$; $\delta_{C-H} = 834 \text{ cm}^{-1}$; $\nu_{C=O(\text{ester})} = 1736 \text{ cm}^{-1}$; ν_{CH_2,CH_3} cis-1,4-polyisoprene = 1448, 1376 cm^{-1} ; decrease of $\nu_{C=O}$ at 1721 cm^{-1} .

FTIR - α -hydroxy- ω -*N,N*- diethylaminotelechelic cis-1,4-oligoisoprene (**compound 4**): $\nu_{C=C} = 1664 \text{ cm}^{-1}$; $\nu_{CH} = 3035 \text{ cm}^{-1}$; $\nu_{OH} = 3370 \text{ cm}^{-1}$; $\delta_{C-H} = 834 \text{ cm}^{-1}$; ν_{CH_2,CH_3} cis-1,4-polyisoprene = 1448, 1376 cm^{-1} ; disappearance of $\nu_{C=O}$ at 1721 cm^{-1} .

FTIR - α -Diethylpropylamino- ω -*N,N*- dihydroxyethylaminotelechelic cis-1,4-oligoisoprene (**compound 5**): $\nu_{C=C} = 1664 \text{ cm}^{-1}$; $\nu_{CH} = 3035 \text{ cm}^{-1}$; $\nu_{OH} = 3380 \text{ cm}^{-1}$; $\delta_{C-H} = 834 \text{ cm}^{-1}$; ν_{CH_2,CH_3} cis-1,4-polyisoprene = 1448, 1376 cm^{-1} ; disappearance of $\nu_{C=O}$ at 1721 cm^{-1} .

FTIR - Acrylate and diacrylate aminotelechelic cis-1,4-oligoisoprene (**compound 6 and 7**): $\nu_{C=C}$ (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} ; $\nu_{C=O(\text{ester})} = 1736 \text{ cm}^{-1}$; $\nu_{C=C}$ (acrylate) = 1632 cm^{-1} ; δ_{C-H_2} (acrylate) = 1408 cm^{-1} ; disappearance of ν_{OH} at 3380 cm^{-1} .

FTIR - Acrylic cationomers (**compounds 8 and 9**): $\nu_{C=C}$ (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} .

^1H NMR chemical shifts of compounds 2, 3, 4, 5, 6, and 7 are shown in Figure 7; ^1H NMR chemical shifts of compounds 8 and 9 are shown in Figure 8.

RESULTS AND DISCUSSION

Diacrylate Oligoisoprenes Synthesis

The different diacrylate oligoisoprenes (Figure 5) used in the photoreticulation 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-poly-

isoprene 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 lead to the carbonyltelechelic cis-1,4-polyisoprene of two different molecular weights, depending on the chosen percentage of epoxidation. The successive steps were: (1) the reduction of the carbonyl end-groups to alcohol functions with sodium borohydride and (2) the addition of acryloyl chloride to give the diacrylate oligoisoprenes of molecular weight 1750 or 4000 g/mol. ^1H -NMR and FTIR analyses showed the complete transformation of the alcohol functions in acrylate groups.

To obtain oligomers with secondary amine chain ends, the direct reductive amination of carbonyl compounds was performed. This is a one-step reaction in which only the formyl

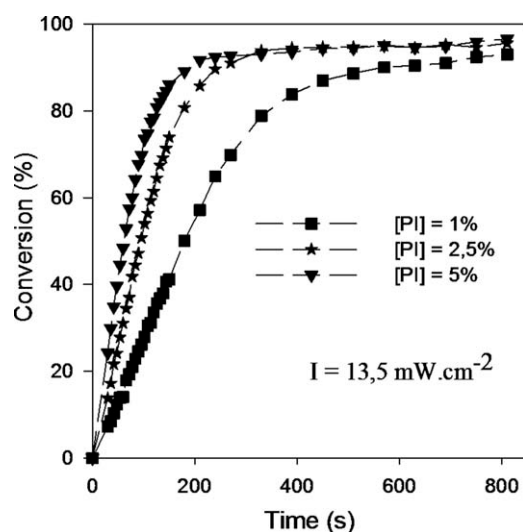


Figure 10. Conversion of acrylate functions versus irradiation time of diacrylate oligoisoprenes exposed to UV light for different photoinitiator concentrations [PI].

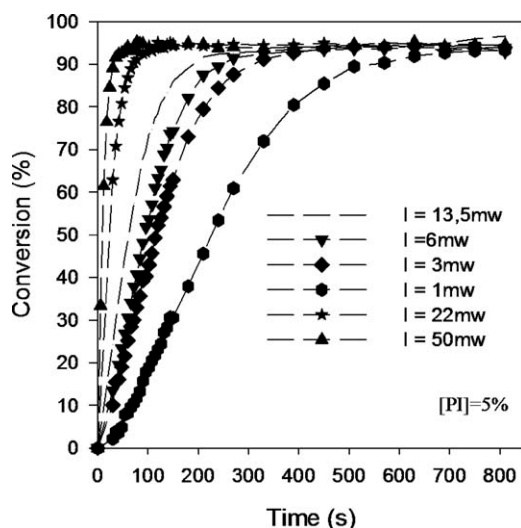


Figure 11. Conversion of acrylate functions versus irradiation time of diacrylate oligoisoprenes exposed to increasing light intensities of UV light.

groups react to give amino groups.^{6,23} Thus, carbonyl telechelic *cis*-1,4-polyisoprene was modified selectively without any protection of the ketone moiety using pre-functionalized amines. Further modification of these functionalities led to mono or diacrylic oligoisoprenes in two or three steps. The reductive amination reaction was monitored by ¹H NMR; the spectra showed a complete disappearance of the aldehydic proton signal at δ 9.77, whereas the methylketone moiety seemed unchanged. Product 5 was obtained by a second reductive amination from product 3 using 3-diethylaminopropylamine. After replacement of the carbonyl with the amino group, the ¹H NMR spectrum showed the shift of the α -methyl group protons in the methyl ketone from δ 2.13 to 1.07 and the appearance of a new peak at δ 2.67 that belongs to the hydrogen bonded to the ex-carbonyl carbon.

The synthesis of cationic oligoisoprenes functionalized with acrylate moieties was performed by esterification of products 4 and 5 with acryloyl chloride. The chemical structures of the photocurable oligomers (products 6 and 7) were confirmed by ¹H NMR and FTIR. The IR analysis of acrylate oligoisoprenes shows the disappearance of peaks assigned to the -OH functions at 3350 cm⁻¹ and appearance of the characteristic peaks of ester and acrylate functions [$\nu_{\text{C=O(ester)}} = 1736 \text{ cm}^{-1}$; $\nu_{\text{C=C(acrylate)}} = 1632 \text{ cm}^{-1}$; $\delta_{\text{C-H}_2(\text{acrylate})} = 1408 \text{ cm}^{-1}$]. Finally, the nitrogen atoms in the photocurable oligomers (6 and 7) were quaternized using haloalkanes. We opted for an iodoalkane because of its higher reactivity with respect to the other haloalkanes (chloroalkanes, bromoalkanes).^{23,24} As the quaternary ammonium is the group responsible for the antibacterial activity of the coatings, two different structures were designed for the cationic polymerizable units: compounds 8 and 9 (Figure 6), which differ in the number of ammonium groups per monomer and in the distance of these groups from the acrylate double bonds and therefore from the coating surface. Several formulations were prepared mixing different percentages of the unfunctionalized acrylate oligomers to com-

pounds 8 or 9. The crosslinked surfaces obtained from the photopolymerization of these formulations have been the object of biological tests performed with algae, bacteria and fungi to assess the antibacterial/ bactericide activity.²⁶

In the ¹H NMR spectra of compounds 8 and 9, 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. CH₃-; CH₂-N; N-CH₂ groups shift, respectively, from 1.07; 2.60; 2.49 ppm, to 1.38; 3.55; 3.30 ppm after quaternization.

Photopolymerization: Kinetic Studies

Preliminary studies were performed in order to obtain homogeneous polymer films by radical polymerization. At the beginning, only the diacrylate oligomers (Figure 5) were used as model to investigate the influence of certain parameters on the photopolymerization; subsequently they were used in combination with oligomers 8 or 9 to impart antibacterial properties to the surface. It was verified that the results found for the reaction of diacrylate oligomers alone are the same in presence of oligomers 8 or 9, therefore in the following sections only the studies referred to the reaction of the diacrylate oligomers are reported.

Oxygen Inhibition. Free-radical photopolymerization is known to be inhibited by molecular oxygen, which can quench the excited triplet state of the photoinitiator molecules and scavenge the initiator and polymer radicals. This problem has limited the application of free-radical photopolymerization in the synthesis of thin films and coatings. Different approaches have been used to overcome the free-radical sensitivity to oxygen: it is possible to work under inert atmosphere but the required equipment is expensive; waxes, or shielding films can be used to prevent oxygen from entering the system; high concentrations of free-radical initiator or high intensity irradiation sources can be employed to produce a larger number of radicals, which consume the oxygen rapidly and allow the growth of the polymer chains,²⁷ and finally it is possible to add other chemical additives, such as amines, to capture the oxygen.²⁷⁻³¹

In this study, as first thing we wanted to estimate the influence of the oxygen presence on the photocrosslinking kinetics of diacrylate oligoisoprenes, so the first photopolymerizations have been carried out in presence and absence of oxygen and they were monitored respectively by real time FTIR and photocalorimetry-DSC. Various mixtures of diacrylate oligoisoprenes (molecular weight = 1750 g/mol) were used in the presence of 1% and 2.5% (w/w) of Darocur 1173 at 25°C. The light intensity was constant and equal to 13.5 mW/cm². The evolution of the

Table I. Viscosity and Molecular Weight of Diacrylate Hexanediol (HDDA) and Diacrylate Oligoisoprenes

	Oligomer 4000	Oligomer 2000	Hexanediol diacrylate
Viscosity (Pa s)	9,6	3,6	5×10^{-3} à 8×10^{-3}
Molecular weight (g/mol)	4000	1750	230

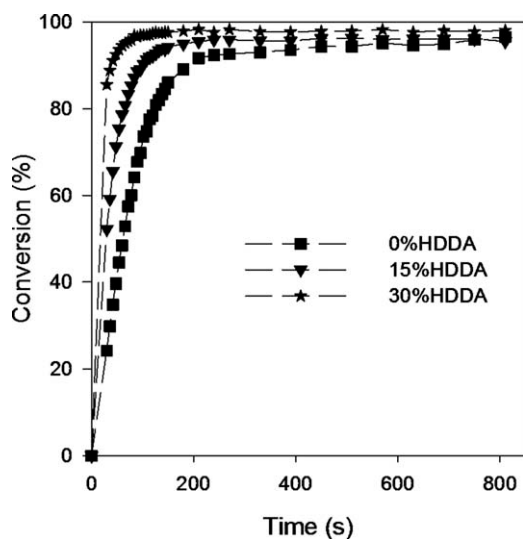


Figure 12. Influence of diluting agent percentage (HDDA). [PI] = 5% (w/w); $I = 13.5 \text{ mW/cm}^2$.

conversion of the acrylate functions under air or nitrogen atmosphere is shown in Figure 9. We could observe that there was no significant difference between photopolymerization in the presence and absence of oxygen. The conversion in acrylate functions was nearly quantitative in the two conditions and the polymerization rates were almost identical. The reaction rate increased only with the photoinitiator percentage, as we see comparing graphs on the left and on the right in Figure 9, and this behavior is due to the higher concentration of active centres produced increasing the photoinitiator amount. Decker et al.³² showed that the inhibition time depends on the concentration of photoinitiator and on the intensity of the irradiation.³³ In our case (especially when we used 5% weight initiator) probably the presence of an important quantity of free radicals from the initiator allowed the fast reduction of the initial concentration of oxygen and left free radicals to react with the monomer. It has been demonstrated³² that there is a steady state concentration of dissolved oxygen in the polymerization medium for which the rate of propagation is bigger than the rate of oxygen consumption so that the propagation can proceed. In our case this steady state concentration must be reached very early: in fact it was found³⁴ that polymerizations that start from oligomers and polymers differ from polymerizations that start from small monomers because they are more viscous so the oxygen diffusion is critically limited. Our oligomer pre-polymerization mixtures are extremely viscous therefore we think we may be in this oxygen limited diffusion case. Concerning the effect of the light intensity in reducing oxygen influence, the experiments to compare nitrogen and air atmosphere have been carried out at 13.5 mW/cm^2 , which is a relatively high intensity. If we look at Figure 11, we can notice for the lowest intensities a different trend of the curves at the very beginning of the reaction, for 1, 3, and 6 mW/cm^2 , as if there was an induction period that disappears as the intensity is raised and is not observed for 13.5 mW/cm^2 .

As it was found that the presence of the oxygen did not disrupt the progress of the photocrosslinking reaction, in the continuation of the work kinetics have been followed by real time FTIR.

Influence of Photoinitiator Concentration. The influence of photoinitiator concentration on the photocrosslinking of diacrylate oligoisoprenes (molecular weight = 1750 g/mol) was studied at 25°C . Darocur 1173 was chosen as photoinitiator because it met the usual criteria of absorbing in the UV region where the oligomers do not absorb and where the UV lamps emits and also because, in comparison to other commonly used solid photoinitiators, it could be easily dispersed in the viscous polymerization mixture.

The photoinitiator concentration varied in the range 1–5% (w/w) and light intensity was kept constant (13.5 mW/cm^2). An almost complete conversion of the acrylate functions was reached for all the photoinitiator concentrations employed (Figure 10). This almost quantitative conversion is due to the high reactivity of the acrylate functions and to the choice of a reaction temperature (25°C) extensively superior to the glass transition temperature of the materials ($T_g = -45^\circ\text{C}$): in these conditions the chains mobility is maintained, allowing the diffusion of the active centres.

As expected, the higher initial rate was obtained for 5% (w/w) Darocur 1173 (Figure 10). According to eq. (3), the polymerization rate (R_p) increases with photoinitiator concentration²¹:

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

where φ is the quantum yield, ε is the photoinitiator molar extinction coefficient, I_0 is the light intensity of the UV radiation, $[\text{PI}]_0$ 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.

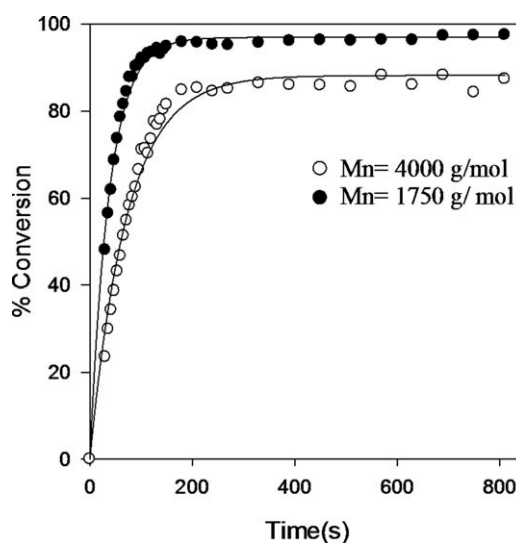


Figure 13. Influence of oligoisoprene molecular weight. [PI] = 5% (w/w); $I = 13.5 \text{ mW/cm}^2$.

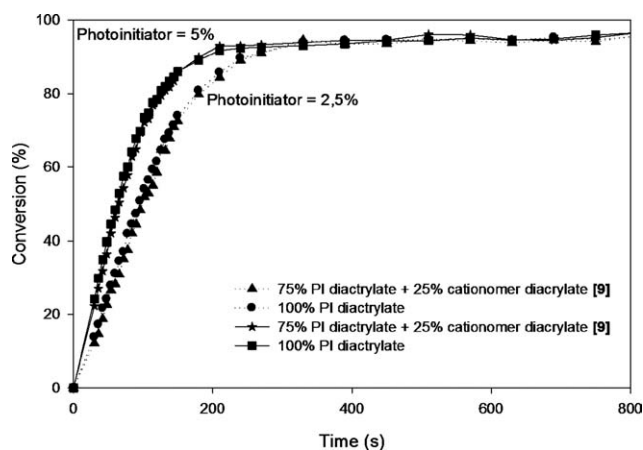


Figure 14. Conversion of acrylate functions versus irradiation time of diacrylate oligoisoprenes and mixture of diacrylate PI/diacrylate cationomer exposed to UV light (13.5 mW/cm^2) for different photoinitiator concentrations [PI].

Influence of Light Intensity. The influence of light intensity in the photopolymerization of diacrylate oligoisoprenes (molecular weight = 1750 g/mol) was studied with a photoinitiator concentration of 5% (w/w), at 25°C . The light intensity varied in the range $1\text{--}50 \text{ mW/cm}^2$. The plot of the conversion versus the irradiation time (Figure 11) showed that the polymerization rate increases with light intensity as expected [eq. (3)]. This plot was used later to estimate the polymerization time in function of the light intensity.

Photopolymerization in Presence of a Diluent. Diluting agents are added to the polymerization mixture to decrease its viscosity and to adjust the resulting thermo-mechanical properties of the coatings. A low viscosity favours the polymerization process because it increases the chains mobility. Photopolymerization of diacrylate oligoisoprenes (molecular weight = 1750 g/mol) was carried out in absence and in presence of two different percentages of diacrylate hexanediol (HDDA) as diluent. HDDA was chosen because its viscosity is very low in comparison to the oligoisoprenes one (viscosity values are reported in Table I). It was found that the diluent has a beneficial effect on the photopolymerization rate, which increases with HDDA percentage (Figure 12). This effect is mainly due to an increased mobility of the free radicals and chain ends in conditions of reduced viscosity of the medium and by the increased concentration of reactive functional groups [as photopolymerization rate is proportional to $[M]_0$, as shown by eq. (3)]. Nevertheless, we must also consider that, by adding HDDA molecules, we add supplementary acrylate groups to the polymerizable groups at the oligomers chain ends, so that we increase the total number of double bonds. Consequently, another contribution is given to increase the total concentration of reactive functional groups and to explain the increment in the polymerization rate. Therefore when discussing the effect of the addition of a diluting agent to a polymerization mixture, several factors have to be taken into account to draw conclusions above the polymerization kinetics. As described by Harikrishna et al.,³⁵

diluent viscosity and number of functionalities are the main parameters to look at when choosing the most appropriate diluent for the curing system.

Influence of Diacrylate Oligoisoprene Molecular Weight. The influence of diacrylate oligoisoprene chain length in the photocrosslinking reaction was studied using two oligomers with 1750 and 4000 g/mol molecular weight [photoinitiator concentration 5% (w/w), at 25°C , light intensity 13.5 mW/cm^2]. We observed that both conversion and photopolymerization rate decreased when oligomers molecular weight increased (Figure 13). The oligoisoprenes with the higher molecular weight have also the higher relative viscosity (Table I), and, as underlined before, a high mixture viscosity decreases the chains mobility and limits the diffusion of active centres, leading to a lower final conversion and photopolymerization rate.

Photopolymerization Kinetics of Mixtures of Diacrylate Oligomers and Cationomers. Once performed the kinetic study of the polymerization of the diacrylate oligoisoprenes, they were mixed with different percentages of ammonium oligomers. In Figure 14, the conversion of acrylate functions versus time is showed in the case of a mixture of 25% in weight of cationomer **9** and 75% in weight of acrylate oligomer. Two different percentages of photoinitiator were used and the result was compared with the conversion of acrylate functions in the case of the diacrylate oligomer reacting alone in the same conditions. No significant difference was observed. The same results were obtained with different percentages of cationomer **9** and diacrylate oligomers, therefore we concluded that there is not a significant difference concerning the kinetic behavior of diacrylate oligomers an mixtures of them and cationomers.

CONCLUSIONS

The controlled degradation of high molecular weight *cis*-1,4-polyisoprene (natural rubber) to give carbonyl telechelic oligomers is described, as well as the successive chemical modification of their chain ends to generate a variety of functional telechelic oligoisoprenes. The introduction of acrylate functional groups at the oligomer chains ends allowed their use as macromonomers in a radical photopolymerization process, leading to crosslinked surfaces with singular properties.

Kinetic studies of the photoinitiated polymerization of diacrylate oligoisoprenes were carried out; the reactions were monitored by real time FTIR and photocalorimetry-DSC. The effect of different parameters, such as oligomer viscosity and molecular weight, percentage of diluting agent, light intensity, on the polymerization rate and final conversion were investigated and conditions to obtain thin polymer coatings have been optimized.

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