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Synthesis of novel highly reactive silicone-epoxy monomers for cationic photopolymerizations

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Abstract

A series of novel cationically photopolymerizable silicone-epoxide monomers bearing substituted benzyl ether groups were prepared. Monomers with methoxy groups on the aromatic ring of the benzyl ether group were synthesized by sequential hydrosylation reactions of 1,1,3,3-tetramethyl disiloxane. Kinetic studies using real-time infrared spectroscopy of the cationic photopolymerizations of these novel monomers showed that those monomers with methoxy groups exhibited elevated rates of photopolymerization. The acceleration effect was explained on the basis of synergistic effects of two mechanisms, namely, the normal ring opening polymerization catalyzed by a Brönstead acid, and the cationic photopolymerization induced by the redox interaction between the free radicals formed in the backbone of the monomer and the onium salt used as photoinitiator. The methoxy groups on the aromatic ring of the benzyl ether enhance the stabilization of the carbocation formed in the structure of the monomer. Silicone-epoxy monomer with 2,5-dimethoxybenzyl ether group exhibited the higher photopolymerization rate. The latter compound can also be used as accelerator of the cationic photopolymerization of commercial silicone-epoxy monomer when used in low concentrations.

Keywords: Cationic photopolymerization; Ring-opening polymerisation: silicon-epoxy monomers; Real-time infrared spectroscopy

1. Introduction

The development of highly reactive systems is crucial for conveyorized in-line production of photocurable materials. The highly demanding automated processes that run at high speeds require the design of materials with improved reactivity and properties. Thus, the development of new photoinitiators, photosensitizers and monomers is one of the priorities in this field of photopolymerization. Accordingly, considerable efforts in our research group are in progress to try to address this necessity. In previous publications [1–3] we reported the synthesis of different types of cationic photopolymerizable monomers bearing substituted benzyl ether groups. These monomers exhibited higher rates of photopolymerization with respect to reference monomers that do not bear that group. This effect was attributed to the presence of the benzyl group that can stabilize either free radical or carbocation centers.

It was found that the diaryliodonium salt used as photoinitiator can interact with those monomers, promoting either the normal ring opening polymerization catalyzed by the photogenerated Brönstead acid as well as the oxidation of the free radicals formed in the backbone of the monomer, generating new carbocations that can participate in the cationic polymerization of the monomer. This interaction between the onium salts and free radicals has been studied previously by Ledwith [4,5], Neckers [6] and Crivello [7,8]. A mechanism has been proposed for the cationic photopolymerization of monomers with labile groups using diaryliodonium salts [9] (see Scheme 1). The photolysis of a diaryliodonium salt results in the generation of several reactive species, namely, aryl cations, aryl radicals and radical cations (Eq. (1)). These species react with the monomer or impurities in the reaction mixture to produce protonic acids (Eq. (2)). Protonic acids are the primary species that initiate the polymerization (Eqs. (3) and (4)). Usually, the radical products of the photolysis of a diaryliodonium salt do not participate in the cationic polymerization. However, when monomers bearing functional groups such as allyl, propargyl or benzyl ethers are present, these radicals can abstract the labile hydrogen atoms present in these groups to generate the corresponding carbon-centered resonance-stabilized free radicals (Eq. (5)). The subsequent

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redox interaction of these secondary radical species with the diaryliodonium salt results in the oxidation of the initially formed radical to the corresponding resonance stabilized cation with the reduction of the diaryliodonium salt to give a diaryliodine free radical (Eq. (6)). This radical is unstable and undergoes rapid decomposition to yield an aryliodide together with the regeneration of the aryl radical (Eq. (7)). Overall, Eqs. (1)–(7) consist of a photoinduced radical chain reaction in which during every cycle additional cationic species are produced. The cations generated by this chain reaction can initiate polymerization of the monomer. This brings as a consequence an apparent acceleration effect.

Based on our previous studies, we decided to synthesize several silicone-epoxy monomers bearing different methoxy-substituted benzyl ether groups. Although silicone-epoxy compounds are known by their high reactivity, undergoing facile and rapid cationic photopolymerization we thought that still there were room for improvement, by applying the aforementioned concept of redox interaction between the monomer and the photoinitiator.

Polymers derived from silicone-epoxy compounds have found applications in paper treatment, especially as controlled release additives. They are also used as coatings for wood and plastics. This article describes the synthesis of several novel epoxy-silicon monomers based on the principles outlined previously and discusses their behaviour in cationic photopolymerizations.

2. Experimental section

2.1. Materials and equipment

1,1,3,3-Tetramethyl disiloxane, allyl bromide, tetra-*n*-butylammonium bromide, 4-vinyl-1-cyclohexene 1,2-epoxide, benzyl alcohol, 4-methoxybenzyl alcohol, 2,5-dimethoxybenzyl alcohol, piperonyl alcohol, 3,4,5-trimethoxybenzyl alcohol, tris (triphenylphosphine) rhodium (I) chloride (Wilkinson catalyst), were all reagent-quality and were purchased from Aldrich Chemical Co. and used as received. The onium salt cationic photoinitiators, (4-*n*-decyloxyphenyl) diphenyl sulfonium hexafluoroantimonate (DPDPS), and (4-*n*-decyloxyphenyl) phenyliodonium (DPPI) hexafluoroantimonate were prepared as described by Crivello [10,11]. Synthesis of MSi1 was made according to the reported method [12]. ^{1}H and ^{13}C NMR spectra were obtained with a 200 MHz Varian Gemini 2000 spectrometer (Palo Alto, CA), at room temperature. Routine infrared spectra and photopolymerization kinetics were performed on a Magna Nicolet 550 Infrared spectrometer (Middleton, WI). Elemental analyses were determined on a Perkin–Elmer 2400 series Analyzer (Stamford, CN). Thermogravimetric analyses were carried out on a TGA U 500 from TA instruments (New Castle, DE).

2.1.1. Characterization of 1,3-bis[2-(3{7-oxabicyclo [4.1.0.] heptyl}) ethyl] tetramethyldisiloxane (MSi1)

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 0–0.20 (12H, m, Si–CH$_3$); 0.4 (4H, m, Si–*CH$_2$*–); 0.8–2.1 (18H, m, cyclohexyl *H*, superimposed with Si–CH$_2$–*CH$_2$*); 3.10 (4H, m, *H*-epoxide); IR (KBr) $\nu_{\max}$ (cm^{-1}): 1252, 1058, 884, 842, 794.

2.1.2. Preparation of benzyl allyl ether (I)

Into a 100 mL three-necked round bottom flask provided with a magnetic stirrer, argon inlet, and thermometer, were placed 7.70 g (0.071 mol) of benzyl alcohol, 2.8 g (0.07 mol) of powdered NaOH, 10.44 g (0.086 mol) of allyl bromide and 50 mL of freshly distilled toluene. This mixture was stirred for 15 min and then 2.56 g (0.0071 mol) of tetra-*n*-butylammonium bromide as phase transfer catalyst were added. The temperature was slowly raised to boiling point and held for 10 h. Then, the mixture was poured into 200 mL of distilled water. The phases were separated and the organic phase was washed three times with 50 mL of distilled water and dried over anhydrous sodium sulphate. After evaporation of solvent, the residue was vacuum distilled and there was obtained 5.63 g (53% theory) of a colorless liquid with a boiling point of 103–106 °C at 5 mmHg.

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 4.05 (2H, d, *CH$_2$*–CH=CH$_2$); 4.55 (2H, s, Ar–*CH$_2$*); 5.30 (2H, m, –CH=*CH$_2$*); 5.95 (1H, m, –*CH*=CH$_2$); 7.35 (5H, m, Ar–H); IR (KBr) $\nu_{\max}$ (cm^{-1}) 3075, 2995, 1641, 1614, 1512, 1243, 1162, 1039, 996, 910, 813, 765, 636, 523.

2.1.3. Preparation of 4-methoxybenzyl allyl ether (II)

The previous reaction was repeated using 10 g (0.072 mol) of 4-methoxybenzyl alcohol and 8.75 g (0.072 mol) allyl bromide. A colorless oil (9.14 g) was obtained on distillation with a boiling point 117–118 °C at 4.5 mmHg (yield: 72%).

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 3.80 (3H, s, OCH$_3$); 4.00 (2H, d, *CH$_2$*–CH=CH$_2$); 4.45 (2H, s, Ar–*CH$_2$*); 5.25 (2H, m, –CH=*CH$_2$*); 5.90 (1H, m, –*CH*=CH$_2$); 6.85 (2H, d, Ar–H); 7.25 (2H, d Ar–H); IR (KBr) $\nu_{\max}$ (cm^{-1}) 3075, 2995, 1641, 1614, 1512, 1243, 1162, 1039, 996, 910, 813, 765, 636, 523.

2.1.4. Preparation of 2,5-dimethoxybenzyl allyl ether (III)

The previous reaction was repeated using 7.0 g (0.041 mol) of 2,5-dimethoxybenzyl alcohol and 7.05 g (0.058 mol) of allyl bromide. A colorless oil was obtained on distillation with a boiling point 148–150 °C at 5 mmHg (yield 64% theory) 5.5 g.

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 3.80 (6H, s, O*CH$_3$*); 4.10 (2H, d, *CH$_2$*–CH=CH$_2$); 4.55 (2H, s, Ar–*CH$_2$*); 5.30 (2H, m, –CH=*CH$_2$*); 6.00 (1H, m, –*CH*=CH$_2$); 6.80–7.10 (3H, m, Ar–*H*); IR (KBr) $\nu_{\max}$ (cm^{-1}) 3075, 2995, 1641, 1614, 1512, 1243, 1162, 1039, 996, 910, 813, 765, 636, 523.

2.1.5. Preparation of 3,4-methylendioxybenzyl allyl ether (IV)

The previous reaction was repeated using 7.0 g (0.046 mol) of piperonyl alcohol and 6.67 g (0.055 mol) of allyl bromide. After evaporation of solvent, the residue was vacuum distilled and there was obtained 16.04 g (91.8% theory) of a colorless liquid **VIII** with a boiling point of 122–125 °C at 5 mmHg.

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 4.00 (2H, d, *CH$_2$*–CH=CH$_2$); 4.40 (2H, s, Ar–*CH$_2$*); 5.20 (2H, m, –CH=*CH$_2$*); 5.85 (1H, m, –*CH*=CH$_2$) superimposed on 5.95 (2H, s, O–*CH$_2$*–O); 6.80 (2H, m, Ar–*H*); 6.90 (1H, s, Ar–*H*); IR (KBr)

ν_{max} (cm^{-1}) 3075, 2995, 1641, 1614, 1512, 1243, 1162, 1039, 996, 910, 813, 765, 636, 523.

2.1.6. Preparation of 3,4,5-trimethoxybenzyl allyl ether (V)

The previous reaction was repeated using 10 g (0.050 mol) of 3,4,5-trimethoxybenzyl alcohol and 7.32 g (0.060 mol) of allyl bromide. A colorless oil (7.1 g) was obtained after purification by column chromatography using chloroform as eluent (yield 60%).

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 3.75 (3H, s, OCH$_3$); 3.80 (6H, s, OCH$_3$); 4.00 (2H, d, CH_2–CH=CH$_2$); 4.40 (2H, s, Ar–CH_2); 5.25 (2H, m, –CH=CH_2); 5.90 (1H, m, –CH=CH$_2$); 6.55 (2H, s, Ar–H); IR (KBr) ν_{max} (cm^{-1}) 3075, 2995, 1641, 1614, 1512, 1243, 1162, 1039, 996, 910, 813, 765, 636, 523.

2.1.7. One-pot synthesis of 1-[2-(3{7-oxabicyclo[4.1.0.] heptyl})ethyl], 3-[(benzyloxy)propyl]tetramethyldisiloxane (MSi2)

A mixture of 20 g (0.15 mol) of distilled 1,1,3,3-tetramethyl disiloxane, 22.23 g (0.15 mol) of benzyl allyl ether (I) and 50 mL of dry toluene was charged into a 250 mL three neck round-bottom flask fitted with a reflux condenser and thermometer. Then, 15 mg of Wilkinson catalyst were added and the reaction mixture was heated at 55 °C for 4 h. After this time, it was observed that the vinyl peaks at 5.5 ppm had disappeared during formation of compound **VI**. No attempts were made to isolate this product.

Next, 18.62 g (0.15 mol) of 3-vinyl-7-oxabicyclo [4.1.0] heptane was slowly added to the reaction mixture and the temperature was raised to 96–100 °C for 12 h and then cooled to room temperature. The reaction mixture was passed through a chromatography column using silica gel as support and hexane: ethyl acetate 95:5 as eluent. After removal of the solvent, 49 g (80% theory) of a clear oil were obtained.

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 0 (12 H, m, Si–CH_3); 0.50 (4H, m, Si–CH_2); 0.8–2.2 (9H, m, cyclohexyl H, superimposed with O–CH$_2$–CH_2–CH$_2$); 3.10 (2H, m, H-epoxide); 3.45 (2H, t, O–CH_2–CH$_2$–CH$_2$); 4.50 (2H, s, Ar–CH_2–O–); 7.25 (5H, m, Ar–H); IR (KBr) ν_{max} (cm^{-1}): 1625, 1255, 1058, 841, 796.

2.1.8. Characterization of 1-[2-(3{7-oxabicyclo [4.1.0.] heptyl})ethyl], 3-[(4-methoxybenzyloxy)propyl]tetramethyldisiloxane (MSi3)

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 0 (12 H, m, Si–CH_3); 0.45 (4H, m, Si–CH_2); 0.8–2.20 (9H, m, cyclohexyl H, superimposed with O–CH$_2$–CH_2–CH$_2$); 3.10 (2H, m, H-epoxide); 3.40 (2H, t, O–CH_2–CH$_2$–CH$_2$); 3.80 (3H, s, OCH_3); 4.40 (2H, s, Ar–CH_2–O–); 6.85 (2H, d, Ar–H); 7.25 (2H, d, Ar–H); IR (KBr) ν_{max} (cm^{-1}): 1603, 1258, 1040, 842, 796.

2.1.9. Characterization of 1-[2-(3{7-oxabicyclo[4.1.0.]heptyl}) ethyl], 3-[(2,5-dimethoxybenzyloxy)propyl]tetramethyldisiloxane (MSi4)

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 0 (12 H, m, Si–CH_3); 0.45 (4H, m, Si–CH_2); 0.8–2.20 (9H, m, cyclohexyl H, superimposed with O–CH$_2$–CH_2–CH$_2$); 3.10 (2H, m, H-epoxide); 3.40 (2H, t, O–CH_2–CH$_2$–CH$_2$); 3.75 (6H, s, OCH_3); 4.45 (2H, s, Ar–CH_2–O–); 6.75–7.00 (3H, m, Ar–H); IR (KBr) ν_{max} (cm^{-1}): 1685, 1593, 1256,1218, 1179, 1158.06, 1050, 842, 798.

2.1.10. Characterization of 1-[2-(3{7-oxabicyclo[4.1.0.]heptyl})ethyl], 3-[(3,4-methylenedioxybenzyloxy)propyl]tetramethyldisiloxane (MSi5)

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 0–0.10 (12 H, m, Si–CH_3); 0.45 (4H, m, Si–CH_2); 0.8–2.20 (9H, m, cyclohexyl H, superimposed with O–CH$_2$–CH_2–CH$_2$); 3.10 (2H, m, H-epoxide); 3.40 (2H, t, O–CH_2–CH$_2$–CH$_2$); 4.40 (2H, s, Ar–CH_2–O–); 5.9 (2H, s, O–CH_2–O); 6.70 (2H, s, Ar–H); 6.85 (1H, s, Ar–H); IR (KBr) ν_{max} (cm^{-1}): 1685, 1593, 1256,1218, 1179, 1158.06, 1050, 842, 798.

2.1.11. Synthesis of 1-[2-(3{7-oxabicyclo[4.1.0.]heptyl})ethyl], 3-[(3,4,5-trimethoxybenzyloxy)propyl]tetramethyldisiloxane (MSi6)

^{1}H NMR (CDCl$_3$, 200 MHz) δ ppm: 0 (12 H, m, Si–CH_3); 0.50 (4H, m, Si–CH_2); 0.8–2.20 (9H, m, cyclohexyl H, superimposed with O–CH$_2$–CH_2–CH$_2$); 3.10 (2H, m, H-epoxide); 3.40 (2H, t, O–CH_2–CH$_2$–CH$_2$); 3.80 (3H, s, OCH_3); 3.85 (6H, s, OCH_3); 4.40 (2H, s, Ar–CH_2–O–); 6.55 (2H, s, Ar–H); IR (KBr) ν_{max} (cm^{-1}): 1602, 1255, 1130, 1062, 841, 796.

2.2. Studies of the rates of photoinitiated ring-opening cationic epoxide polymerization by fourier transform real-time infrared spectroscopy (FT-RTIR)

The kinetics of the cationic photopolymerizations of the monomers synthesized during this investigation were monitored with FT-RTIR. A Nicolet Magna 550 Fourier transform infrared spectrometer equipped with a DTGS detector was fitted with a UVEXS model SCU 110 mercury lamp in which the light was carried through a flexible wand to the sample compartment. The end of the wand was placed at a predetermined distance and directed at an incident angle of 45° onto the sample window. The intensity of the UV irradiation was measured with a UV Process Supply Inc. Control cure radiometer. All kinetics experiments in this investigation were conducted at 25 °C with various light intensities.

Samples for kinetics analysis were prepared as follows. A homogeneous solution of the desired monomer with the designated photoinitiator was prepared (all concentrations are given as molar percentages with respect to the monomer, unless otherwise noted). The solutions were spread as thin films between two layers of 12 micron-thick, corona-treated oriented polypropylene films and then fixed to the metallic sample holder by means of magnetic strips. The course of the photopolymerization was followed by simultaneously monitoring both the decrease in the infrared absorption band at 830 cm^{-1} due to the epoxy group of the epoxidized oils and the increase of the band at 1160 cm^{-1} due to the polyether formed. Each kinetic run was carried out a minimum of five times.

The resulting data were averaged and the conversion versus irradiation time curves is presented. The kinetic parameter, $R_p/[M_0]$, for selected kinetic runs was determined from the initial slopes of the irradiation time-conversion curves according to Eq. (8).

$$\frac{R_p}{[M_0]} = \frac{([\text{conversion}]_{t2} - [\text{conversion}]_{t1})}{(t_2 - t_1)} \quad (8)$$

where R_p and $[M_0]$ are, respectively, the rate of polymerization and the initial monomer concentration and the conversions are as determined from the curves at irradiation times t_1 and t_2.

Data were collected at a rate of one spectrum per second. Data processing was performed with the OMNIC Series software (Scheme 1).

3. Results and discussion

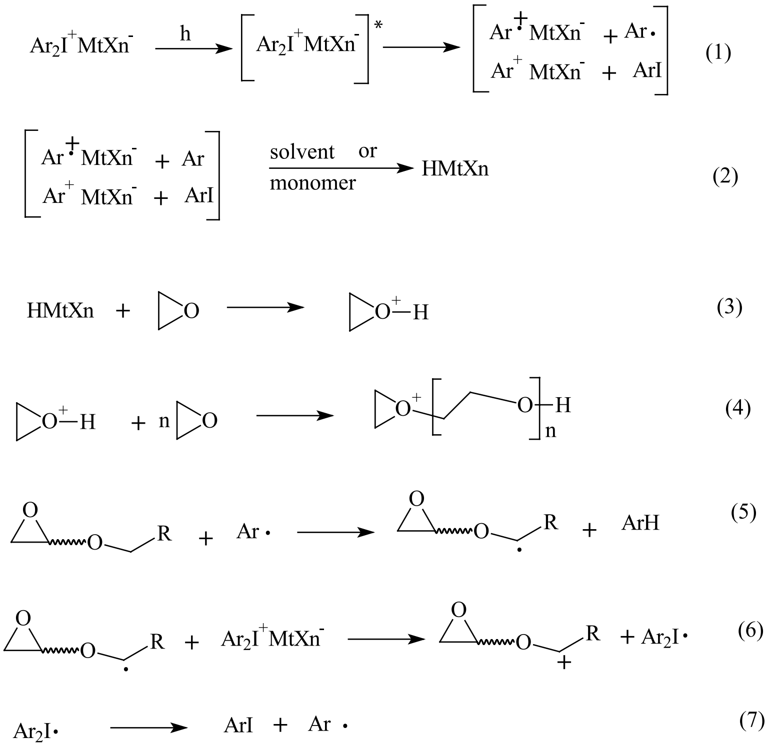
The proposed monomers were synthesized by means of the well-known hydrosylation reaction [13]. The synthetic methodology is depicted in Scheme 2. In a first step, the benzyl alcohols were etherified by means of the Williamson reaction using allyl bromide and sodium hydroxide under phase transfer-catalyzed conditions to give the corresponding benzyl allyl ether **I**. Crivello [14] reported that 1,1,3,3-tetramethyldisiloxane can be regioselectively hydrosilylated with 4-vinyl-1-cyclohexene 1,2-epoxide. We took advantage of this fact in order to functionalize the silicone backbone with the benzyl ether. Using the aforementioned reaction, we obtained compound **VI**. Combining compounds **I** and **VI** in stoichiometric ratios, at 95–100 °C in toluene under anhydrous conditions, the desired monomers (MSi2 in Scheme 2) were prepared in moderate yields. Table 1 shows the structures of the prepared silicone-epoxy monomers and in Fig. 1 is shown the proton NMR spectrum of monomer MSi4.

3.1. Cationic photopolymerization studies

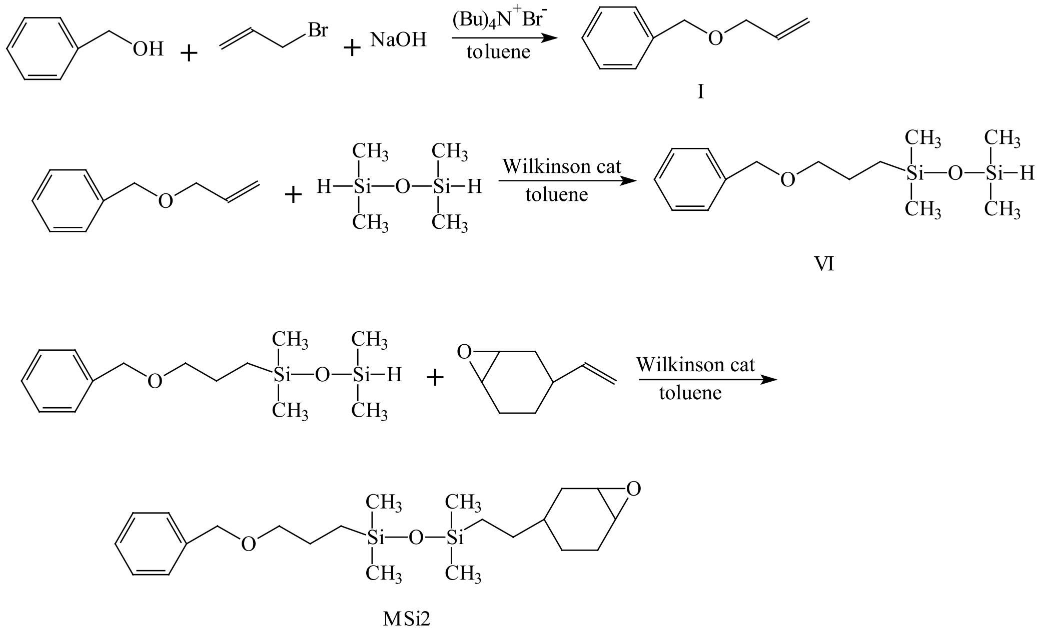
The reactivity of the prepared silicon-epoxy monomers was investigated by means of FT-RTIR. This technique involves monitoring the change in the intensity of characteristic bands of epoxide groups (790–915 cm^{-1}) that undergo photopolymerization, as a function of time. The resulting data were averaged and the conversion vs. time curves are presented.

Fig. 2 shows the comparison of the kinetic curves of the photopolymerization of the silicone-epoxy monomers when they are subjected to UV irradiation, using DPPI as the photoinitiator at 0.5 mol%. In this investigation, monomer MSi1 served as a model monomer to provide baseline reactivity with which to measure any enhancement effects on the rate due to the proposed free radical enhancement mechanism. The absence of labile benzylic hydrogens makes MSi1 ideal for this purpose. Besides, this monomer is widely used in certain applications of radiation curing technologies.

It was found that most of the monomers exhibited high reactivity even when rather low UV light intensity was used. All monomers with the benzyl ether group displayed higher photopolymerization rates than MSi1. It can be seen clearly that higher photopolymerization rates are achieved going from the monomer with unsubstituted benzyl ether to



Scheme 1. Mechanism of the photoinitiated ring-opening polymerization of epoxides (R = allyl, propargyl or benzyl); MtXn^- = non-nucleophilic anions such as SbF_6^-, PF_6^-, BF_4^-.



Scheme 2. Synthetic method for the preparation of silicone-epoxide monomers. Chemical structure of crosslinked silicone-epoxy polymers.

monomers with two and three methoxy groups. This can be due to a better stabilization of the benzyl carbocation formed by the interaction of the free radical interaction between the monomer and the photoinitiator. As methoxy groups are strong electron-donor groups, an increase in number, results in increasing electronic density in the aromatic ring and this brings as a consequence a better stabilization of the secondary carbocation formed in the backbone of the monomer.

The silicone-epoxy monomer with the dimethoxy-substituted benzyl ether group, MSi4, surpassed the activity of model monomer, showing the highest reactivity of the synthesized monomers. This result can be explained again on the basis of electronic effects induced by the position of the substituents in the aromatic ring of the benzyl ether group in the silicone epoxy compound. It has been recognized in the literature [15,16] that aromatic excited states are likely to exhibit reactivity different from that of corresponding ground states. Zimmerman [17] et al. studied the substituent effects in the photosolvolysis of benzyl acetates. They found that in the photoreaction, the methoxy group in the *meta* position was strongly rate enhancing. This is in contrast with the ground state behaviour. In the ground state the expected increased π-electron density was found at the *ortho* and *para* positions relative to an electron-donating substituent, while in the first excited state, selective electron transmission to the *ortho* and *meta* position was noticed. The increased electron density at these sites helps to stabilize the positive charge of the benzyl cation intermediate. Thus, in the case of the MSi4 the stronger activation in the *meta* and *ortho* positions of the aromatic ring results in a better stabilization of benzyl cation.

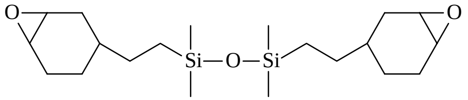
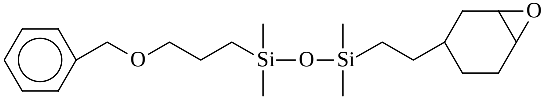
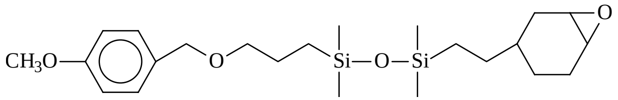
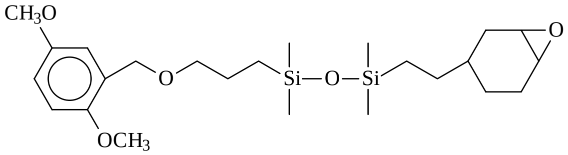
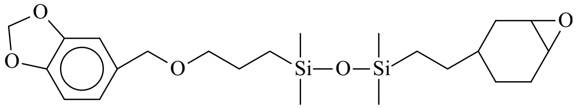
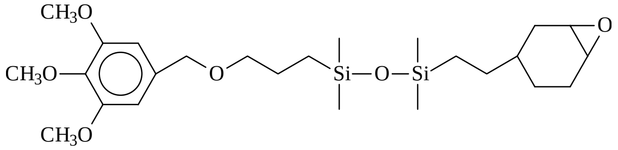
Shown in Fig. 3 is the effect of the concentration of photoinitiator DPPI on the photopolymerization rate of the silicone-epoxy monomer MSi6. It can be observed that even when the photoinitiator is used at 0.1 mol% the photopolymerizable system is rather reactive. As expected, there was a remarkable increase in the photopolymerization rate and an appreciable augment in the conversion when the concentration of the photoinitiator is raised to 1 mol%. The increase in the concentration of photoinitiator brings as a consequence an increase of reactive species and the polymerization proceeds to higher levels. The exothermic nature of the ring opening polymerizations leads the polymerization to higher conversions.

Fig. 4 shows a study in which the light intensity was varied when monomer MSi6 was photopolymerized with 0.5 mol% of DPPI. It was found that the reactivity of the system is high even when the UV light intensity is as low as 2 mW/cm^2. When light intensity is augmented to 5 and 8.5 mW/cm^2, both photopolymerization rates and conversion are improved, and read 60–71%, respectively.

Next, a study of the effect of the structure of the onium salt on the photopolymerization of MSi3 was carried out. The results are shown in Fig. 5. In both cases the concentration of the photoinitiator was 0.5 mol% with respect to the monomer used. It can be seen that the diaryliodonium salt displayed a better initiating behaviour. This effect was attributed to the difference in reduction potentials of these onium salts. The iodonium salt DPPI with a reduction potential of -0.2 V is more easily reduced than the triaryl sulfonium salt DPDPS with a reduction potential of -1.01 to -1.46 V [18–20]. The reduction potentials of the onium salts are related with the results obtained in Fig. 4 in the sense that the diariliodonium salt can be reduced more easily by the secondary carbon-centered free radical formed in the structure of monomer, generating new reaction sites for cationic polymerization.

The results of the FT-RTIR study of the photosensitization of the polymerization of MSi2 are shown in Fig. 6. The results showed in Fig. 2 demonstrated that MSi2 was not as reactive as the other monomers with methoxy groups in their structure. Thus, we decided to test if by using photosensitizers the photocuring efficiency of this monomer could be improved.

Table 1

Notation	Structure	Yield[a] (%)	Elemental analysis	
			Calcd. %C%H	Found %C%H
MSi1		85	62.77 10.01	62.18, 10.27
MSi2		48.6	64.97 9.42	63.89, 9.22
MSi3		61.2	63.25 9.23	63.01 9.48
MSi4		56.3	61.76 9.07	61.28 9.57
MSi5		68.8	61.29 8.50	60.88 8.23
MSi6		42.4	60.44 8.93	59.98 8.42

[a] Overall yield of two stages, except for MSi1 that is in one stage.

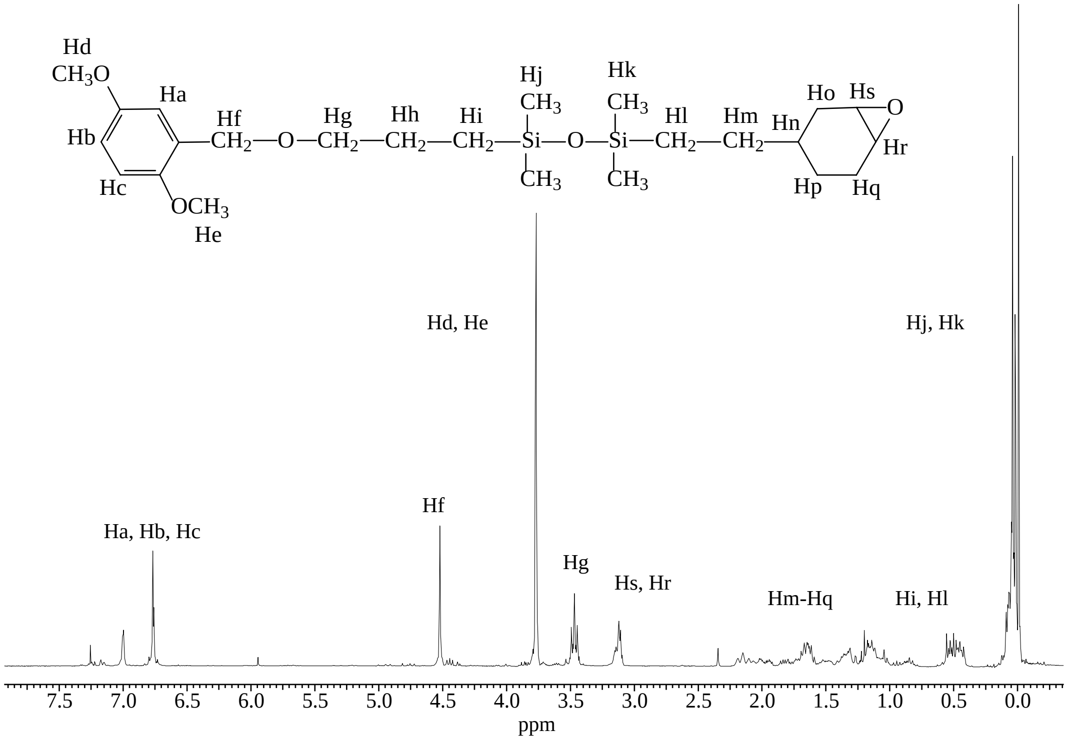


Fig. 1. ^{1}H NMR spectrum of MSi4 in $CDCl_3$.

We tried three different photosensitizers, anthracene, perylene and 2-ethyl anthraquinone. The kinetics curves corresponding to the different photosensitized systems shows that perylene was the best photosensitizer for the decomposition of the diaryliodonium salt under the conditions of irradiation, while anthracene and 2-ethylantraquinone presented similar activities. Both perylene and anthracene are known as electron-transfer photosensitizers while 2-ethyl antraquinone can act by energy transfer mechanism. There is also the possibility that the diradical produced from the triplet state of 2-ethyl anthraquinone can react with the labile hydrogen atom of the monomer, generating monomer-bound free radicals that can react in the same the way as it was explained in Scheme 1. However, the results obtained lead to the conclusion that the electron-transfer mechanism was more efficient in sensitizing our curing system.

It was of some interest to determine whether the highly reactive monomer MSi4 could be employed to accelerate the photopolymerization of MSi1. Accordingly, a study shown in Fig. 7 in which the photopolymerization of MSi1 was used alone and with varying amounts of MSi4 ranging from 5 to 20 mol%. As it can be seen in Fig. 7 the photopolymerization rate of MSi1 can be greatly increased with only 5 mol% of MSi4. When the concentration of MSi4 is augmented to 10 and 20% the slopes of the kinetic curves are practically the same than the curve employing 5 mol%, meaning that the photopolymerization rate is very similar in the three cases; although, it seems that increasing concentration of MSi4 results in a faster start of the photopolymerization. Thus, we can deduce that only 5 mol% of MSi4 is enough in order to obtain an effective acceleration effect on the photopolymerization rate of MSi1.

3.2. Thermal analysis of the photocrosslinked films

A study to determine the thermal stability of the polymers derived from the prepared monomers was carried out. The synthesized silicone-epoxy monomers were photocured as thin films on glass slides. The liquid monomer solution with 0.5 mol% of DPPI was spread on the slide and irradiated with UV light. After 2 min of irradiation a thin film was obtained. The film was washed with chloroform and dried under vacuum. It was observed that all of the monomers were insoluble in most organic solvents. The crosslinking of the sample can be attributed to the fact that there are two reactive sites where polymerization can proceed (see Fig. 9). Thereafter, thermogravimetric analysis was performed on these films at a heating

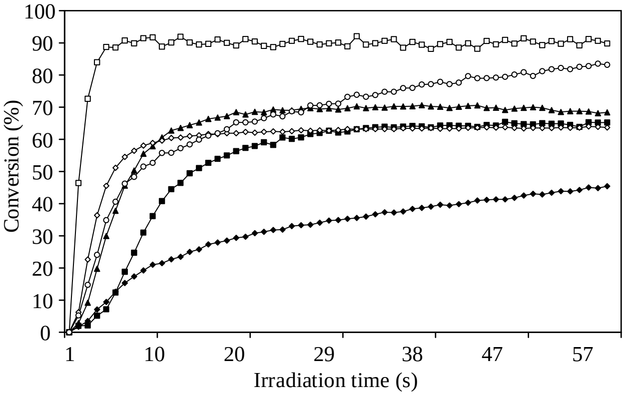


Fig. 2. FT-RTIR comparative study of the cationic photopolymerization of different silicone-epoxy monomers MSi1 (♦); MSi2 (■); MSi3 (▲); MSi4 (□); MSi5 (○); MSi6 (◇), (photoinitiator, 0.5% DPPI; light intensity 5 mW/cm^2).

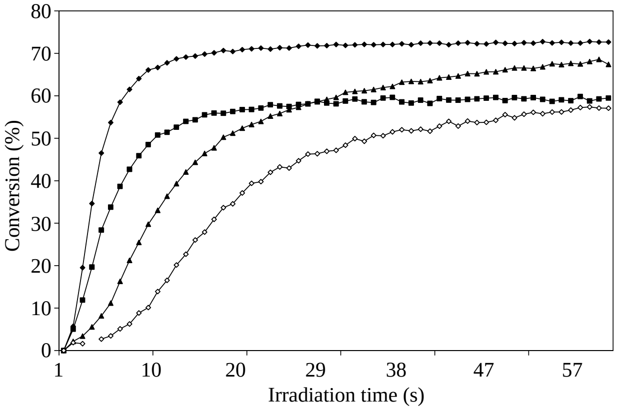


Fig. 3. Comparison of the effect of the concentration of photoinitiator DPPI on the photopolymerization rate of MSi6 at 5 mW/cm^2, 1% (♦); 0.5% (■); 0.25% (▲); 0.1% (◇).

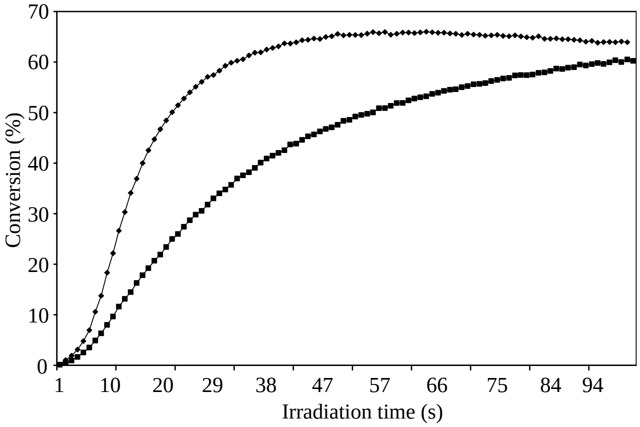


Fig. 4. FT-RTIR study of the photoinitiated cationic ring-opening polymerization of MSi3 with 0.5 mol% of photoinitiator at 5 mW/cm^2 of UV light DPPI (♦); DPDPS (■).

rate of 20 °C/min in nitrogen atmosphere. After reaching 600 °C, oxygen was introduced in the chamber. The obtained curves are depicted in Fig. 8. It was found that in the case of MSi1 the maximum weight loss was at 452 °C with a sharp loss in the weight of the sample. The monomers MSi2, MSi3

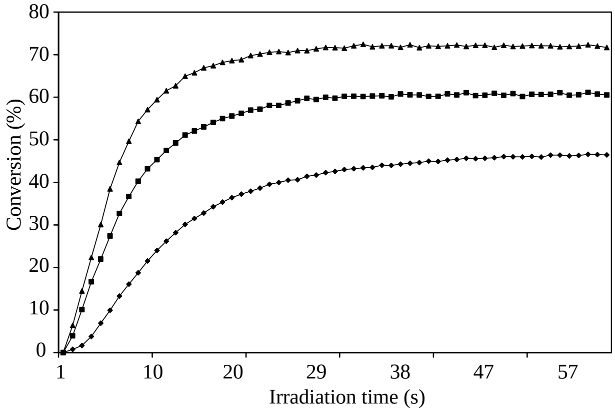


Fig. 5. Comparison of the effect of the UV light intensity on the photopolymerization rate of MSi6 with 0.5 mol% of DPPI, 8.5 mW/cm^2 (▲); 5 mW/cm^2 (■); 2 mW/cm^2 (♦).

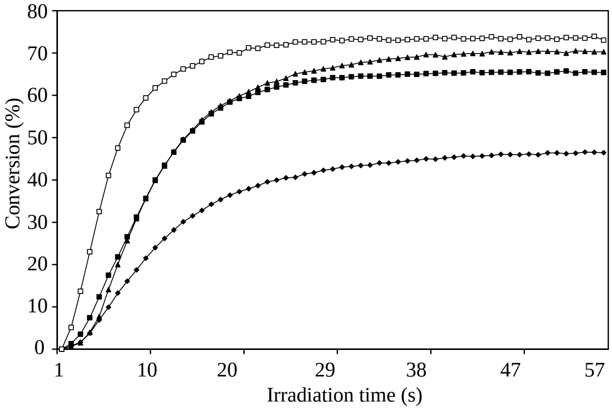


Fig. 6. FT-RTIR comparative study of the cationic photopolymerization of MSi2 using different types of photosensitizers blank with no photosensibilizer (♦); Anthracene (■); 2-ethyl anthraquinone (▲) perylene (□), photoinitiator, 0.5% DPPI; light intensity 2 mW/cm^2.

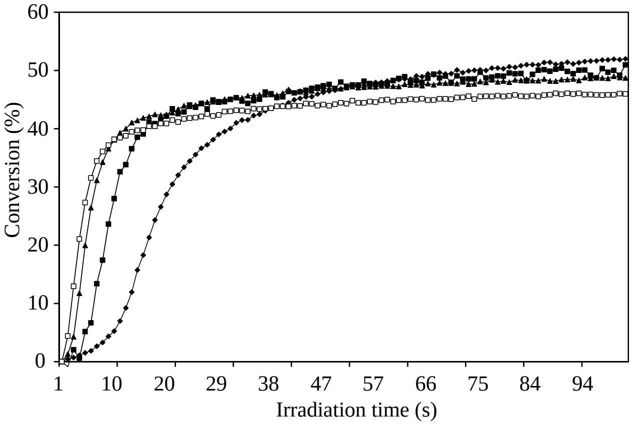


Fig. 7. Comparison of the effect of different concentration of MSi4 as accelerator on the ring opening polymerizationof MSi1. 0 mol% MSi4 (♦); 5 mol% MSi4 (■); 10 mol% MSi4 (▲); 20 mol% MSi4 (□). Photoinitiator, 0.5% DPPI; light intensity 2 mW/cm^2.

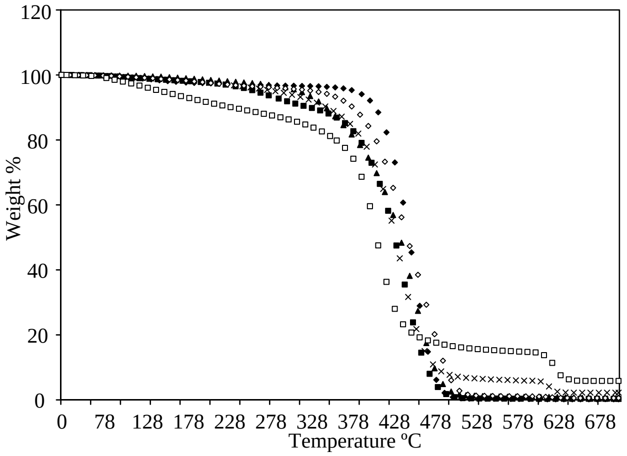


Fig. 8. TGA comparative study of the thermal stability of the polymers derived from the silicone-epoxy monomers. The analyses were run at a heating rate 20 °C/min under nitrogen blanketing; after 600 °C, oxygen is introduced to the sample chamber. MSi1 (♦); MSi2 (■); MSi3(▲); MSi4 (×); MSi5 (◇); MSi6 (□),

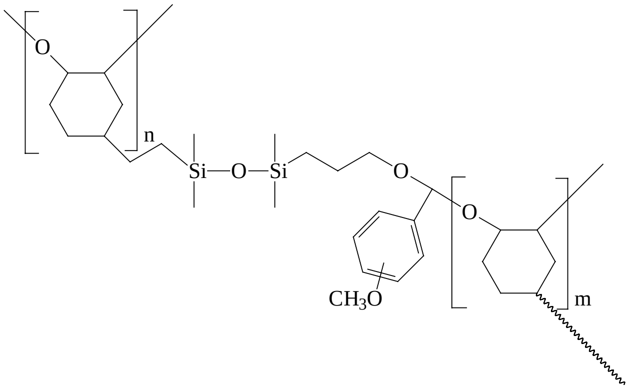


Fig. 9. Chemical structure of crosslinked silicone-epoxy polymers.

and MSi5 showed similar behaviour to MSi1 with a maximum weight loss at 438, 451 and 465 °C, respectively. In the case of the more reactive monomers MSi4 and MSi6 the mass/temperature curves, clearly show a two-step mass loss effect that is more pronounced for the latter. It is likely that in these two cases the degradation of the polymer involves the release of the methoxy groups in the first step followed by further crosslinking of the sample. In both cases the second step reaches its maximum weight loss at 610 °C. Here, we can assume that the polymers derived from synthesized monomers displayed similar stability than those obtained with commercial silicone-epoxy monomer MSi1 with the exception of MSi6.

4. Conclusions

The prepared silicone-epoxy monomers with the benzyl ether displayed very high reactivity in comparison with a similar commercial monomer without the benzyl ether group. The monomers were tested by means of real-time infrared spectroscopy and it was found that high photopolymerization rates could be achieved using low concentration of photoinitiators and low UV light intensity. As a direct result of the dual mechanisms mentioned in the introduction of the paper, these monomers undergo polymerization at high rates. It was also found that monomers with electron-donor substituent such as methoxy groups, in the benzyl ether moiety displayed excellent reactivity. This is due to a better stabilization of the benzyl cation formed. The monomer MSi4 exhibited the highest photopolymerization rate and when it was used in low concentrations it acted as an accelerator for the photopolymerization rate of MSi1.

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