Research Article

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Visible light polymerization of epoxy monomers using an iodonium salt with camphorquinone/ethyl-4-dimethyl aminobenzoate

Walter F Schroeder,[a] Silvana V Asmussen,[a] Marco Sangermano[b] and Claudia I Vallo[a]*

Abstract

A visible light initiator system for the photoinduced cationic polymerization of epoxy monomers is reported. The system consists of camphorquinone (CQ) in combination with ethyl-4-dimethyl aminobenzoate (EDMAB) and a diaryliodonium salt (Ph$_2$ISbF$_6$.) The three-component system efficiently photoinitiates the polymerization of monomers containing an epoxycyclohexane group, 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (UVR) and 1,3-bis(3,4-epoxycyclohexyl-2-ethyl),1,1,3,3-tetramethyldisiloxane (SIB), under irradiation with blue light ($\lambda = 467$ nm). Very rapid photopolymerization resulted from irradiation of SIB containing Ph$_2$ISbF$_6$ in combination with CQ and better results were obtained in the presence of EDMAB. On the other hand, no polymerization was detected after irradiation of UVR photoactivated with Ph$_2$ISbF$_6$ and CQ. However, this monomer polymerized readily and to high conversion when EDMAB was present. Moreover, almost complete conversion of UVR occurs in the absence of external heating. The polymer resulting from UVR displayed higher values of compressive and flexural properties than the polymer prepared from SIB. This is explained in terms of a higher density of crosslinking points in UVR which is accompanied by a lower content of non-reacted monomer; this has a plasticizing effect on the hardened material.
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Keywords: cationic polymerization; visible light; epoxy; camphorquinone; iodonium salt

INTRODUCTION

Cationic photopolymerization has become an important method of crosslinking epoxy and vinyl ether monomers, and onium salts are well known as very effective photoinitiators.[1–5] The use of cationic photoinitiators, such as diaryliodonium and triarylsulfonium salts, provides a convenient method of generating powerful Brønsted acids *in situ*, which is the primary species that initiates polymerization, and obviates the difficulties of preparing and handling these materials.[1,2] The cationic photoinitiators can be dissolved into a multifunctional monomer, and then the polymerization can be triggered on demand by irradiating the mixture with light. Furthermore, this process has the added environmental benefits of totally eliminating the use of solvents and has inherently low energy input requirements. The high rate of crosslinking achieved on irradiation is ideal for high speed applications such as printing inks, coatings and adhesives. However, the major absorption bands of these initiators fall in the deep UV region (210–250 nm),[2,6] and the absence of overlap of these bands with the emission spectra of medium and low pressure mercury lamps and light-emitting diode (LED) curing units limits their application. Thus, photosensitizers are used in order to broaden the spectral sensitivity of onium salts to longer wavelengths.[6–10]

On irradiation with UV light (210–250 nm), diaryliodonium salts undergo fragmentation to yield a variety of reactive intermediates, including radicals, cations and radical cations.[1–5] The cationic species interact with a proton source, usually the monomer, impurity or solvent to generate strong Brønsted acids. Initiation of polymerization proceeds by protonation of the monomer and is followed by polymerization via a dark, i.e. non-photochemical, process. By using dyes as photosensitizers, it is possible to extend the spectral sensitivity of diaryliodonium salts into the visible region of the spectrum.[6–15] The mechanisms of photosensitization of onium salts have been summarized by Yagci and Reetz[2] and Crivello and Sangermano.[10] It is worth noting that the number of photosensitizers operating in the long wavelength UV and visible regions is limited. Crivello and Lam[8] reported attempts to use visible light absorbing dyes to sensitize the decomposition of iodonium salts. After screening nearly 75 different dyes, they reported that only five dyes possessed appreciable sensitizing

* *Correspondence to: Claudia I Vallo, Institute of Materials Science and Technology (INTEMA), University of Mar del Plata, CONICET, Juan B Justo 4302, 7600 Mar del Plata, Argentina. E-mail: civallo@fi.mdp.edu.ar*

a *Institute of Materials Science and Technology (INTEMA), University of Mar del Plata, CONICET, Juan B Justo 4302, 7600 Mar del Plata, Argentina*

b *Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, C. so Duca degli Abruzzi 24, I-10129, Torino, Italy*
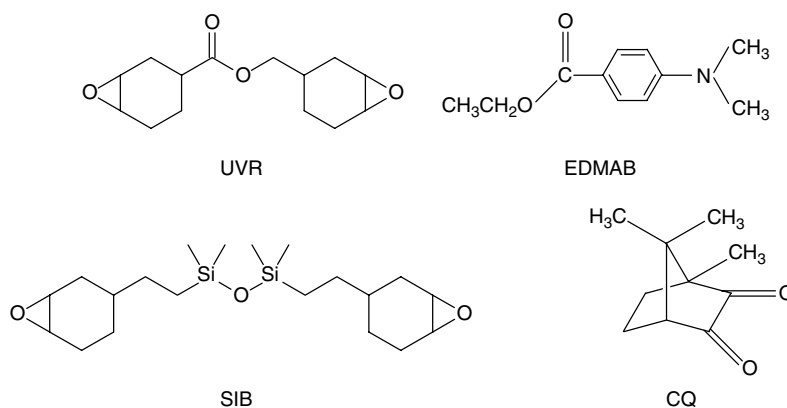
Scheme 1. Molecular structure of UVR, SIB, CQ and EDMAB.

ability. In more recent reports Yagci's group described the use of a dithienothiophene derivative,[16] acylgermanes[17] and substituted vinyl halides[18] as a long wavelength photosensitizer for onium salts. Similarly, Fouassier's group developed a three-component photoinitiating system based on acridinedione/silane/iodonium salt to extend the sensitivity of the iodonium salt into the visible spectrum.[19,20] The use of camphorquinone (CQ) as a visible light photosensitizer in the iodonium-initiated cationic polymerization of epoxy and vinyl ethers has been reported in recent studies. Crivello and Sangermano studied polymerization photoinitiated by a diaryliodonium salt in combination with CQ of monomers that can serve as hydrogen donors.[10] In addition, Crivello developed an efficient three-component visible light sensitive photoinitiator system, based on CQ/benzyl alcohol/diaryliodonium salt, for the cationic ring-opening photopolymerization of epoxide monomers.[11] Oxman et al.[12] studied the free radical/cationic hybrid photopolymerizations of acrylates and epoxides using CQ as sensitizer in a three-component photoinitiator system.

It is well known that CQ, in combination with electron donating co-initiators such as ethyl-4-dimethyl aminobenzoate (EDMAB), acts as an efficient visible light photoinitiator for free radical polymerization of methacrylate monomers.[21,22] Thus, the combination of the CQ/EDMAB pair and iodonium salt as potential initiating systems for cationic polymerization of epoxy monomers was explored in this study. The function of the aromatic amine in the cationic polymerization is dictated by its basicity and nucleophilicity toward the propagating cationic centre. If the amine has low basicity and the carbocation is less electrophilic, then the amine functions mainly as co-initiator. Otherwise, it will function as a terminator.[9,12]

The efficiency of the CQ/EDMAB pair in combination with an iodonium salt as visible light photoinitiator of epoxy monomers was assessed by monitoring the conversion of epoxy groups and the temperature evolution as a function of irradiation time. Particular attention was devoted to the thickness effect when curing with long wavelength light. The characterization of the polymerized materials was carried out by measuring some selected flexural and compressive properties.

EXPERIMENTAL
Materials and general procedures
The epoxy monomers used in this study were 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate (UVR) (UVR-6110, Dow Chemical Co., Midland Michigan, USA) and 1,3-bis(3,4-epoxycyclohexyl-2-ethyl),1,1,3,3-tetramethyldisiloxane

(SIB) (SIB 1092.0, Gelest Inc., Philadelphia, USA). The iodonium salt was p-(octyloxyphenyl) phenyliodonium hexafluoroantimonate (Ph_2ISbF_6) (OMAN071, Gelest Inc., Philadelphia, USA). CQ and EDMAB were from Sigma Aldrich, Buenos Aires, Argentina.. All materials were used as received. The structures of these chemicals are shown in Scheme 1. The monomers were activated for visible light polymerization by the addition of 2 wt% Ph_2ISbF_6, 1 wt% CQ and 1 wt% EDMAB.

The radiation source was an LED unit (Valo, Ultradent, USA) with a wavelength range 410–530 nm and irradiance equal to 600 mW cm^{-2}. The intensity of the LED was measured with the chemical actinometer potassium ferroxialate, which is recommended for the 253–577 nm wavelength range.

Conversion of epoxy groups
Fourier transform infrared (FTIR) spectra were acquired with a Nicolet 6700 Thermo Scientific. Mid-infrared (MIR) spectra were acquired over the range 700–1200 cm^{-1} from 32 co-added scans at 2 cm^{-1} resolution. The monomer containing the photoinitiator system was coated onto a polyethylene film and covered with another polyethylene film. The assembly was sandwiched between two NaCl plates and was tightly attached to the sample holder using small clamps. The thickness of the films was about 100 μm. The specimens were irradiated at regular time intervals and spectra were collected immediately after each exposure interval. The conversion of epoxy groups was calculated from the decay of the absorption band located at 745 cm^{-1} using as internal reference the peaks centred at 1731 cm^{-1} and 1252 cm^{-1} in UVR and SIB, respectively. The extent of reaction in thick specimens was also assessed. The polymerization was carried out on samples 2 mm thick and 10 mm in diameter. The monomers were sandwiched between two glass plates separated by a 2-mm rectangular rubber spacer containing a 10-mm circular hole. The moulds were previously treated with a releasing agent in order to avoid adhesion between the epoxy and the glass after polymerization. The specimens were irradiated at regular time intervals and spectra were collected immediately after each exposure. The conversion at the surface of the samples was evaluated from the decay of the band at 745 cm^{-1} by attenuated total reflectance using a Nicolet 6700 Thermo Scientific equipped with a diamond crystal (4 cm^{-1}, 64 scans).

Temperature evolution during photopolymerization
The temperature during polymerization was monitored with fine K-type thermocouples (Omega Engineering Inc., USA) embedded

in the monomer specimens in the upper half of the sample where the temperature is more uniform. This was verified after the experiment by visual examination of the sample with a magnifying lens. The thermocouples were connected to a data acquisition system that registered temperature every 2 s. Three replicates were conducted for each experiment. The irradiance at the base of the sample was 300 mW cm^{-2}. The studies were carried out on samples 2 mm thick and 10 mm in diameter identical to those used in measurements of conversion.

Photolysis of CQ dissolved in UVR and SIB monomers

The photodecomposition of CQ was followed using the changes in absorbance at the wavelength of its maximum absorption. The absorption spectra of CQ were measured with a UV–visible spectrophotometer (1601 PC, Shimadzu) at room temperature (*ca* 20 °C) in the UVR and SIB monomers. Bleaching experiments were carried out on samples 2.0 ± 0.2 mm thick sandwiched between 1-mm thick glass microscope slides separated by a rubber gasket. The geometry of the sample specimens was identical to that used in measurements of conversion or temperature evolution (2 mm thick and 10 mm in diameter). The concentration of CQ in the monomers was 1 wt%. The extinction coefficient of CQ in the epoxy monomers was 42 (±1) L mol^{-1} cm^{-1}. Oxygen was not removed from the resin before irradiation. An identical cell containing the corresponding epoxy monomer was used as reference.

Mechanical characterization

Flexural and compression tests were carried out on an Instron testing machine (model 4467) at a crosshead displacement rate of 2 mm min^{-1}. All test specimens were photopolymerized in ambient atmosphere at room temperature (20 ± 2 °C). Flexural and compressive specimens were irradiated for 20 and 40 s respectively on each side. Prior to mechanical testing, the specimens were stored at 20 ± 2 °C for about 24 h. A set of test specimens was also post-cured at 150 °C for 2 h. The flexural modulus E and the flexural strength σ_f were measured in three-point bending using sample dimensions recommended by the ISO 4049:2000(E): (25 ± 2) × (2 ± 0.1) × (2 ± 0.1) mm. Results were computed using the standard formulae

$$E = \frac{L^3 \ P}{4 \, b \, d^3 \, y} \quad (1)$$

$$\sigma_f = \frac{3 \ P}{2 \, b \, d^2} \quad (2)$$

Crosslinked epoxy resins are brittle in nature. Like other brittle materials, they are weak in tension but quite strong in compression and capable of yielding under uniaxial compression. Therefore, the yield strength was determined in compression. Samples for compression testing were made by injecting the monomers into quartz cylindrical disposable moulds of 6 mm internal diameter. The moulds were previously treated with a releasing agent in order to avoid adhesion between the epoxy and the glass after polymerization.

Cylindrical specimens having a length to diameter ratio of 1.5 were deformed between metal plates lubricated with molybdenum disulfide. The deformation was calculated directly from the crosshead speed. True stress–deformation curves were obtained by dividing the load by the cross-sectional area. The compressive yield strength σ_y was determined at the maximum load. A minimum of four specimens were prepared for the measurement of flexural and compressive properties.

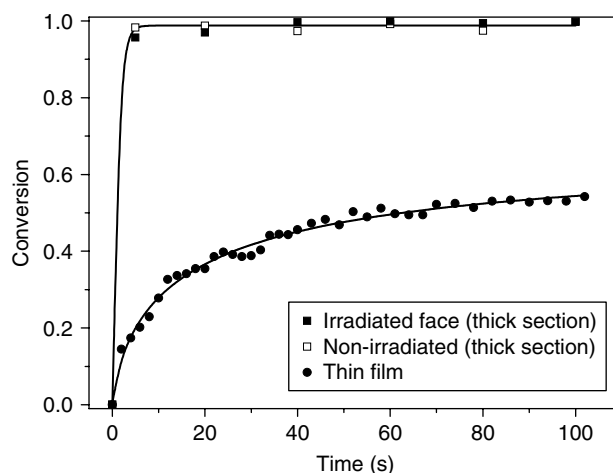**Figure 1.** Monomer conversion *versus* irradiation time for thin films and 2-mm-thick specimens of UVR containing 2 wt% Ph$_2$ISbF$_6$ in combination with 1 wt% CQ and 1 wt% EDMAB.

RESULTS AND DISCUSSION

Conversion of epoxy groups *versus* irradiation time

The progress of the polymerization was monitored by following the decrease in absorbance of the characteristic IR band of the epoxide groups centred at 745 cm^{-1}. The conversion curves *versus* time of UVR and SIB monomers containing different photoinitiator systems are presented in Figs 1–3. Figure 1 shows the visible light photopolymerization of UVR containing 2 wt% Ph$_2$ISbF$_6$ with 1 wt% CQ and 1 wt% EDMAB. No polymerization was detected after 60 s of irradiation in the absence of EDMAB. However, this monomer polymerized readily and to high conversion when EDMAB was present. A marked effect of sample thickness on the extent of reaction is shown in Fig. 1. The conversion in thin films was approximately 48% after 100 s irradiation while in samples 2 mm thick the conversion was 98% after 5 s irradiation at both irradiated and non-irradiated faces. This is attributed to different temperatures reached during polymerization in samples of different thicknesses. The polymerization reaction is highly exothermic, which results in an increase in the sample temperature during the process and this effect becomes more important as the sample thickness increases.[23] A higher sample temperature induces an increase in the mobility of the reaction environment (i.e. monomer, propagating species and polymer) and consequently increases the reaction rate. Therefore, the greater conversion of epoxy groups in 2-mm-thick samples is attributed to thermal effects. The temperature evolution during polymerization of UVR and SIB monomers will be examined in more detail later.

Figures 2 and 3 show the visible light photopolymerization of SIB monomer containing 2 wt% Ph$_2$ISbF$_6$ and 1 wt% CQ carried out in the absence or presence of EDMAB, respectively. As Fig. 2 shows, very effective photopolymerization of SIB can be conducted using Ph$_2$ISbF$_6$ in combination with CQ and better results are obtained in the presence of EDMAB (Fig. 3). The conversion after 10 s irradiation of thin films was approximately 65% or 70% in the absence or presence of EDMAB, respectively. Similarly, the extent of reaction in 2-mm-thick samples containing 2 wt% Ph$_2$ISbF$_6$ with 1 wt% CQ was 80% and increased to 91% when 1 wt% of EDMAB was added. Results presented in Figs 1–3 reveal that the three-component system efficiently photoinitiates the polymerization of UVR and SIB monomers under irradiation with visible light. Moreover, almost
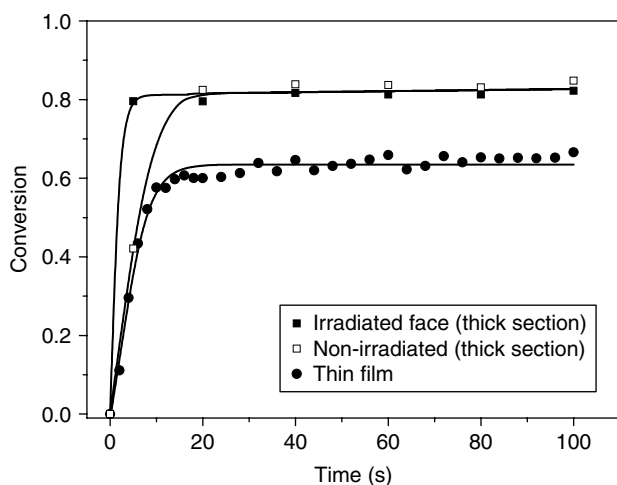
Figure 2. Monomer conversion *versus* irradiation time for thin films and 2-mm-thick specimens of SIB containing 2 wt% Ph$_2$ISbF$_6$ in combination with 1 wt% CQ.
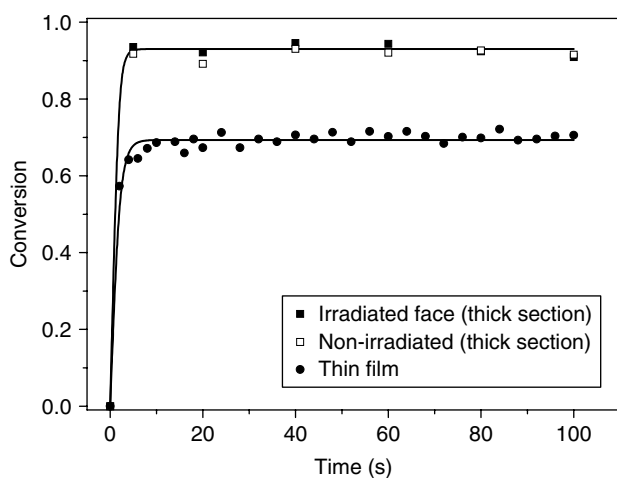

Figure 3. Monomer conversion *versus* irradiation time for thin films and 2-mm-thick specimens of SIB containing 2 wt% Ph$_2$ISbF$_6$ in combination with 1 wt% CQ and 1 wt% EDMAB.

complete conversion of UVR occurs in the absence of external heating.

It is worth mentioning that the presence of light absorbing photoinitiators in a photocuring resin inevitably results in attenuation of the light intensity along the radiation path and often limits the cure depth in a sample to be polymerized.[24-27] This effect occurs when the light fails to reach the deeper layers of a sample because the absorbing species near the irradiated surface absorb most of it. As a result of light attenuation in 2-mm-thick specimens of methacrylate monomer photoactivated with 1 wt% CQ/EDMAB, the value of conversion at the irradiated surface was about 18% higher than that at the non-irradiated surface.[27] On the other hand, the values of conversion of UVR and SIB at the irradiated and non-irradiated surfaces in 2-mm-thick specimens were similar (Figs 1–3). Differently from free radical photopolymerization, the only part of a photoinitiated cationic polymerization that is dependent on light is the photolysis of the photoinitiator.[28,29] Once the active species are formed, the polymerization itself proceeds by a normal cationic process. Thus, the similar values of conversion at the irradiated and non-irradiated

surfaces in 2-mm-thick specimens are the result of the well-known 'dark cure' or 'post-polymerization' effect.[28,29] This contrasts with most free radical photopolymerizations, which cease after the irradiation is extinguished because of rapid termination.

The possible initiating mechanism in systems containing a diaryliodonium salt in combination with CQ has been proposed by previous researchers[9,10] and will be briefly described here. Irradiation of the CQ with visible light results in the formation of its singlet state, which is rapidly converted to its triplet state by intersystem crossing (Scheme 2). The excited CQ molecule is initially reduced by a hydrogen donor (in our case the amine) to the ketyl radical which in turn is oxidized back to CQ by the iodonium salt. The resulting strong Brønsted acid derived from this process initiates the cationic ring-opening polymerization. In the case of the CQ/EDMAB pair, the mechanism is analogous to that proposed by Bi and Neckers for the visible light cationic polymerization of cyclohexene oxide in the presence of a diaryliodonium salt.[9] These authors developed a system based on a xanthene dye in combination with an aromatic amine to sensitize the diaryliodonium salt. Although the initiating mechanism is apparently complex, it is assumed to involve the generation of α-amino radicals by the abstraction of a hydrogen atom from the amine by the photoexcited dye (Scheme 3). The diaryliodonium salt oxidizes the α-amino radicals to the respective cations, which initiate the polymerization. Subsequently, these free radicals induce the chain decomposition of the diaryliodonium salt, producing a dramatic rate enhancement in the polymerization.

As mentioned previously, Crivello developed a photoinitiator system based on CQ in combination with a benzyl alcohol to generate free radicals by the absorption of visible light.[11] Subsequently, the radicals participate in the free radical chain induced decomposition of a diaryliodonium salt. Crivello reported a very effective photopolymerization of the SIB monomer using the three-component photoinitiator. In contrast, no photopolymerization was detected when benzyl alcohol was omitted. Similarly, the UVR monomer was very sensitive to the amount of benzyl alcohol present. No observable polymerization took place even after visible light irradiation for 5 min when only CQ and diaryliodonium salt were present. However, appreciable polymerization of the monomer took place when 5 wt% benzyl alcohol was added. The absence of polymerization of SIB monomer containing iodonium salt and CQ reported by Crivello[11] can be attributed to a lower irradiance of the light source compared with that used in this study. At high light intensities the polymerizations generally proceed to high conversion, whereas at low irradiation intensity the conversions are reduced. This is due to the presence of termination reactions that are more important when fewer reactive species are generated at low light intensities.

In the case of polymerization of thin films, the conversion of UVR containing the three-component photoinitiator (Fig. 1) increased monotonically with time reaching 48% after 100 s irradiation while the SIB monomer with the same photoinitiator system reached 70% conversion after 10 s irradiation (Fig. 3). No change in temperature was recorded during irradiation of the thin films and therefore, in the absence of thermal effects, the different degrees of reaction reached by UVR and SIB are explained in terms of the reactivity of each monomer. Crivello and colleagues reported a detailed investigation of the reactivity of a wide variety of epoxy monomers.[30,31] Based on the results of those studies, the authors concluded that epoxide ring strain is one of the most important factors in determining their reactivity. Monomers containing the highly strained epoxycyclohexane and epoxycyclopentane rings

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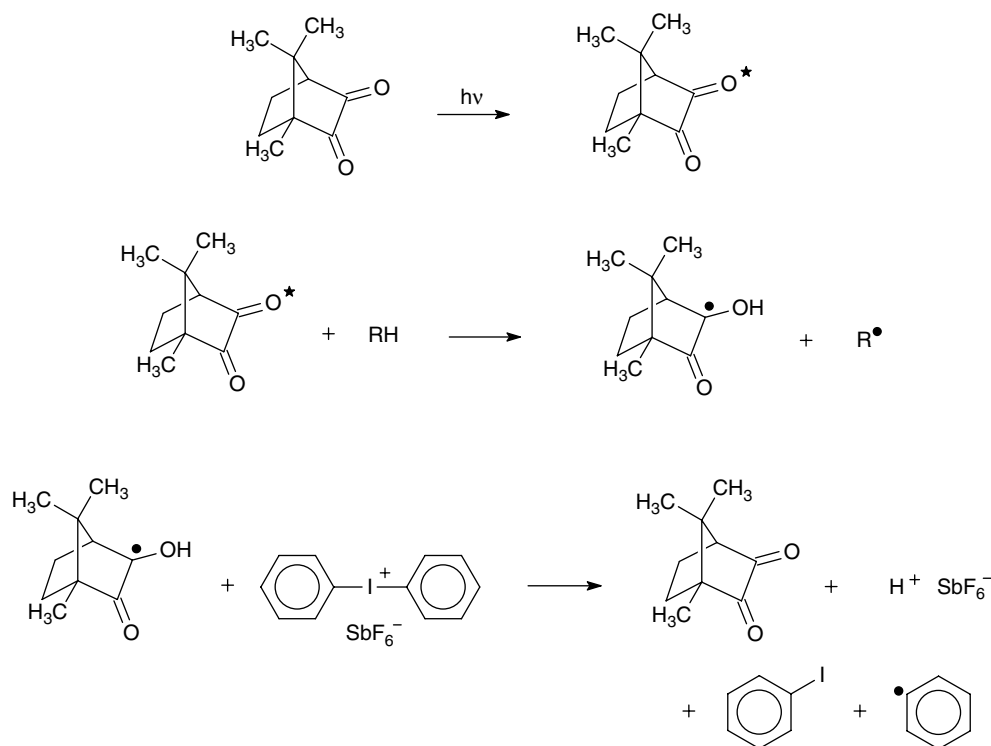
Scheme 2. Proposed photosensitization of Ph₂ISbF₆ by CQ which accounts for the regeneration of CQ during irradiation with visible light.
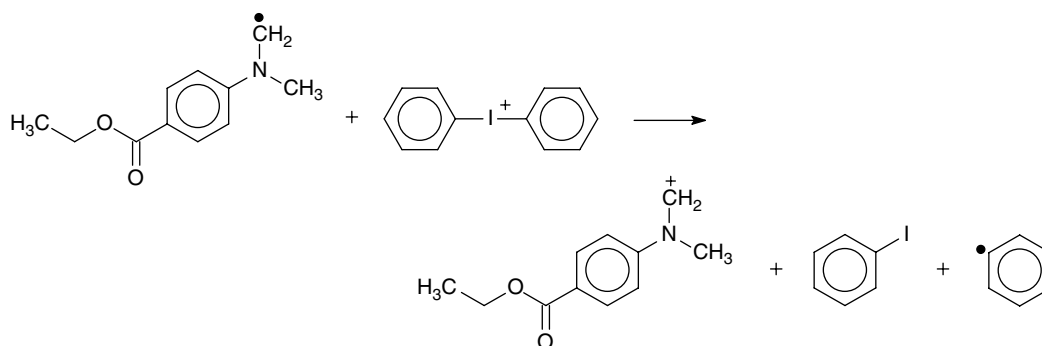
Scheme 3. Proposed photosensitization of Ph₂ISbF₆ by CQ in the presence of EDMAB.

were found to be the most reactive and considerably more reactive than open-chain epoxy compounds. On the other hand, Crivello and Varlemann[30] found that epoxide monomers containing ester carbonyl groups undergo polymerization at substantially lower rates than monomers that do not contain those groups. Further studies showed that this effect is due to the higher nucleophilic and basic character of the ester carbonyl, which leads to a different mechanism of propagation in these compounds. The ester carbonyl group can directly interact with the protonated epoxide group in either an intermolecular or intramolecular fashion to produce a comparatively low reactivity dialkoxycarbenium ion. Alternatively, the carbonyl group may reduce the activity of epoxide monomers through hydrogen bonding with the protonated epoxide group produced during the initiation process. Conversely, Jang and Crivello[31] concluded that silicone epoxide monomers such as SIB that incorporate both epoxycyclohexane groups and siloxane linkages are among the most reactive epoxide monomers. They proposed that the outstanding reactivity of this monomer could be attributed to two major factors. First, the ring

strain inherent in the epoxycyclohexane ring system is probably the largest contributing factor. Second, there are no basic groups in the structure of SIB that can compete with the epoxide oxygen for either the initiating photogenerated acid or the positively charged growing chain ends. In addition, siloxane (Si–O–Si) bonds are not ether-like and are not readily protonated.

Temperature evolution during photopolymerization

Differently from polymerizations carried out in thin films, the conversion reached in 2-mm-thick samples of UVR (Fig. 1) was higher than that of SIB with the same photoinitiator system (Fig. 3). In order to explain the opposite trends in conversion of UVR and SIB observed in thin films and 2-mm-thick specimens the temperature evolution during irradiation was examined. No significant change in temperature was recorded during irradiation of thin films. Conversely, Fig. 4 shows that the heat liberated by the exothermic reaction results in a sharp temperature rise during the initially fast polymerization. At this stage, the rate of heat transfer by conduction and convection is much lower than the rate
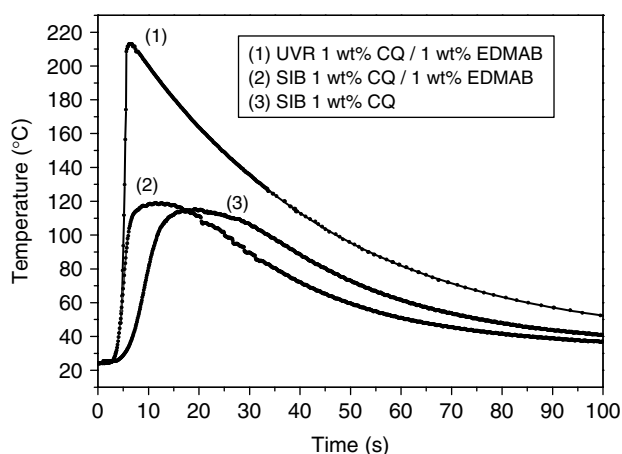
Figure 4. Temperature evolution during photopolymerization of UVR and SIB containing different photoinitiator systems.

of heat production; therefore, a considerable part of the energy liberated is accumulated in the system. Finally, as the conversion of epoxy groups approaches a plateau due to vitrification of the resin, the rate of heat production becomes negligible compared with the rate of heat transfer, and so the temperature decreases. The reactivity of the two epoxy monomers can be assessed by the sharpness of the exothermic portion of the curves and the peak temperature reached during polymerization. When 1 wt% CQ was added to the UVR monomer containing 2 wt% Ph_2ISbF_6 and irradiated with visible light no appreciable polymerization took place. In contrast, in the presence of 1 wt% EDMAB the temperature of UVR increased to 213 $^\circ$C. The temperature evolution during irradiation of SIB containing Ph_2ISbF_6 in combination with CQ (Fig. 4) reveals a very effective photopolymerization of this monomer with visible light (peak temperature 115 $^\circ$C). The presence of EDMAB produced a moderate increase in polymerization rate (peak temperature 120 $^\circ$C).

As Fig. 4 shows, the peak temperature during polymerization of UVR was 213 $^\circ$C whereas that of SIB containing CQ or CQ/EDMAB was 115 $^\circ$C or 120 $^\circ$C, respectively. This difference is attributed to a different content of epoxy groups per mass unit in UVR and SIB. The molar masses of UVR and SIB are 252 and 383 g mol^{-1} respectively. This is equivalent to 7.94 and 5 mol of epoxy groups per kilogram of UVR and SIB, respectively. The results of conversion in 2-mm-thick samples shown in Figs 1–3 are in agreement with the experimental evidence that the conversion attained by the monomer increases with the cure temperature.[32]

Photolysis of CQ

The photolysis of CQ dissolved in UVR and SIB monomers was examined. During irradiation CQ absorbs visible light due to the n–π^* transition of the α-dicarbonyl chromophore to produce an excited singlet state which passes into an excited triplet state and interacts with oxidizable species, thus decomposing into colourless products.[26] Spectral changes during visible light irradiation of UVR and SIB monomers containing 1 wt% CQ are shown in Figs 5(a) and 5(b). By irradiating the UVR and SIB at 600 mW cm^{-2} for 10 s the absorbance of the CQ was reduced to 84% or 36% of its initial value. The results in Fig. 5 contrast with those reported by Cook et al.[29] who found absence of photobleaching of CQ during irradiation of triethyleneglycol divinyl ether containing 0.25 wt% Ph_2IPF_6 in combination with 0.25 wt% CQ, although

the resin did cure. This observation was ascribed by the authors to the regeneration of the CQ as in Scheme 2. Figures 5(c) and 5(d) show that the photodecomposition of CQ in the presence of EDMAB is accompanied by the appearance of light absorbing by-photoproducts.

The decomposition of CQ in the presence of hydrogen donors obeys first-order kinetics.[21,26] That trend has been confirmed during visible light irradiation of CQ dissolved in methacrylate monomers.[21,26] The rate of photodecomposition of CQ is proportional to the volumetric rate of absorption of photons. The number of photons absorbed per unit time through a sample thickness L is given by[33]

$$I_{abs} = I_0 \left(1 - 10^{-\varepsilon * CQ L} \right) \qquad (3)$$

where CQ is the molar concentration of CQ and ε^* is its extinction coefficient (42 ± 2 L mol^{-1} cm^{-1}). The rate of decomposition of CQ is related to the radiation absorbed:[33]

$$-\frac{d\,CQ}{dt} = \frac{\Phi\,I_{abs}}{L} = \frac{\Phi I_0 \left(1 - e^{-\varepsilon L\,CQ} \right)}{L} \qquad (4)$$

where ε is the absorption coefficient of CQ, equal to 2.302 times its extinction coefficient, I_0 is the irradiance (in moles photons s^{-1} cm^{-2}) at the irradiated surface of the sample and Φ is the fraction of photoinitiator reduced per absorbed photon defined as the quantum yield of the photoinitiator consumption. Integrating Eqn (4) yields

$$\ln\left[\frac{\left(10^{\varepsilon*L\,CQ} - 1 \right)}{\left(10^{\varepsilon*L\,CQ_0} - 1 \right)} \right] = \Phi\,\varepsilon\,I_0\ t \qquad (5)$$

where $\Phi\varepsilon I_0$ is the CQ rate constant for the photobleaching of CQ and CQ_0 is the initial concentration of CQ. The CQ concentration versus irradiation time is given by the following expression:[33]

$$\frac{CQ}{CQ_o} = \frac{1}{\varepsilon\ L\,CQ_o} \ln\left[1 - \left(1 - e^{\varepsilon\ L\,CQ_o} \right) e^{-\Phi\,\varepsilon\,I_o\,t} \right] \qquad (6)$$

Computation of the CQ concentration versus time from Eqn (6) requires knowledge of the value of the photobleaching rate constant ($\Phi\varepsilon I_0$), which is calculated from the slope of the lines resulting from Eqn. (5). Figure 6 shows that the photolysis of CQ in UVR monomer is satisfactorily fitted to first-order kinetics. Conversely, the values calculated from the photolysis of CQ in SIB do not fit first-order kinetics over the entire range of irradiation time. A straight line is seen during the first 10 s irradiation and then the values deviate from linearity. The rate of decomposition of CQ in the presence of EDMAB could not be computed due to interference caused by the light absorbing photoproducts. Figure 7 shows the molar concentration of CQ as a function of irradiation time calculated from Eqn (6). The value of $\Phi\varepsilon I_0$ to be used in Eqn (6) was calculated from the slope of the linear part of Eqn (5). Again, the experimental measurements of the concentration of CQ in UVR are in good agreement with those predicted from Eqn (6). On the other hand, the consumption of CQ during irradiation of SIB monomer was slower than that predicted by first-order kinetics. This disagreement may be caused by the regeneration of CQ during the photolysis. As shown in Scheme 2, the ketyl radicals are oxidized by the diaryliodonium salt thereby regenerating the CQ and yielding a Brønsted acid, which initiates the cationic polymerization. The rapid photolysis of CQ in UVR accompanied by absence of polymerization might be attributed to a rapid dimerization of the ketyl radicals which inhibits the production of
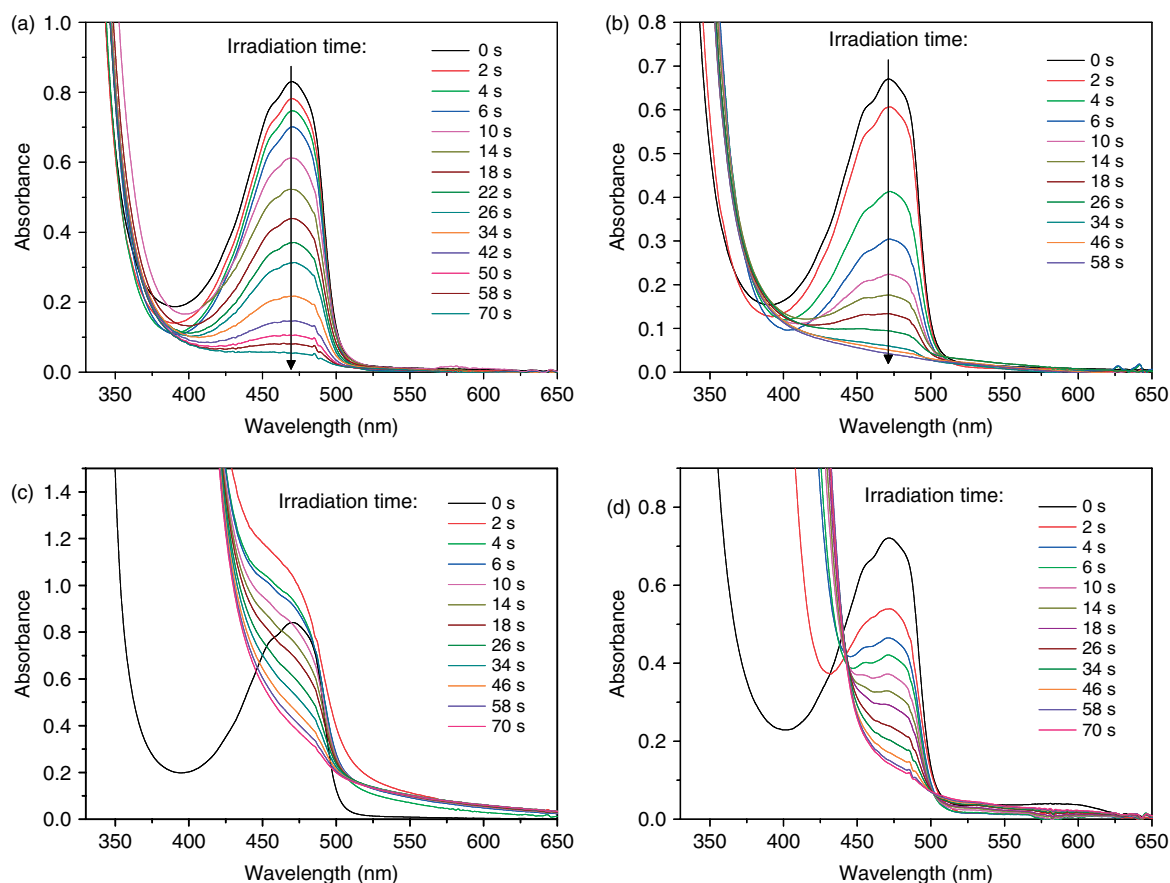
Figure 5. Spectral changes during irradiation of (a) UVR containing 2 wt% Ph$_2$ISbF$_6$ and 1 wt% CQ, (b) SIB containing 2 wt% Ph$_2$ISbF$_6$ and 1 wt% CQ, (c) UVR containing 2 wt% Ph$_2$ISbF$_6$ and 1 wt% CQ in combination with 1 wt% EDMAB and (d) SIB containing 2 wt% Ph$_2$ISbF$_6$ and 1 wt% CQ in combination with 1 wt% EDMAB.
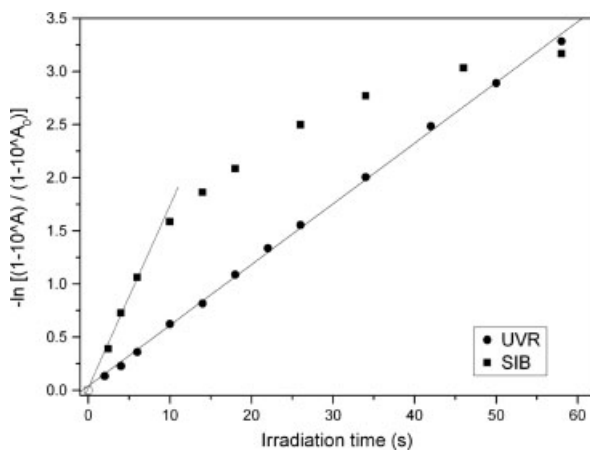

Figure 6. Plots of Eqn (5) for UVR and SIB monomers containing 2 wt% Ph$_2$ISbF$_6$ and 1 wt% CQ.
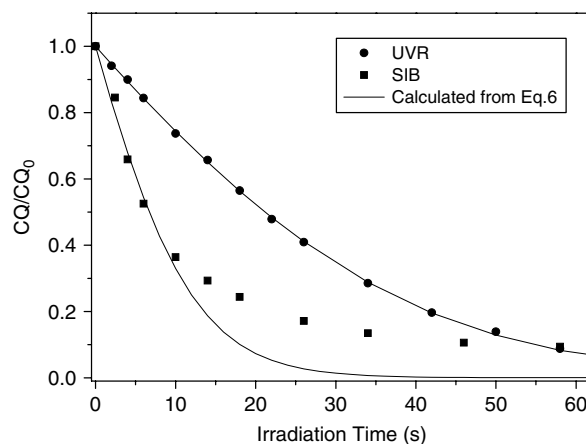

Figure 7. Molar concentration of CQ *versus* irradiation time in UVR and SIB monomers containing 2 wt% Ph$_2$ISbF$_6$ and 1 wt.% CQ.

the Brønsted acid in addition to the retarding effect of the ester carbonyl group described previously. Further studies are certainly needed to explain the initiating mechanism in more detail.

Mechanical properties

Figure 8 shows typical registers of compression tests of the UVR and SIB monomers. Table 1 summarizes the compressive yield strength (σ_y), the flexural modulus (E) and the flexural strength

of the materials cured in air at room temperature and materials subjected to a post-curing treatment. The polymerization in the absence of external heating leads to glassy resins in which only some of the available double bonds are reacted. Before the completion of conversion, the vitrification phenomenon decelerates the reaction to a hardly perceptible rate. The presence of non-reacted monomer can have a plasticizing effect on the polymer, thereby altering the physical and mechanical properties
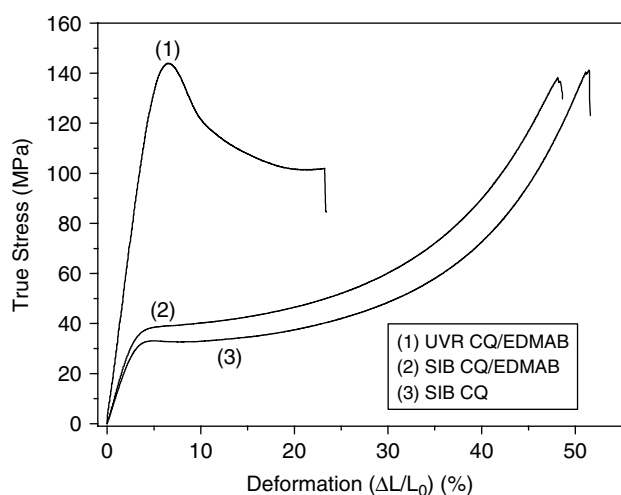
Figure 8. Typical plots of the compression tests of UVR and SIB monomers containing different photoinitiator systems.

Table 1. Flexural and compressive properties of monomers cured in air at 22 °C

	ERL CQ/EDMAB	SIB CQ	SIB CQ/EDMAB
Cured in air at 22 °C			
σy (MPa)	132.3 ± 8.2	33.7 ± 0.4	37.9 ± 0.2
E (GPa)	4.16 ± 0.05	1.37 ± 0.13	1.47 ± 0.07
σf (MPa)	129.9 ± 13.9	53.3 ± 5.4	52.2 ± 4.4
Post-cured 2 h at 150 °C			
σy (MPa)	145.7 ± 3.2	36.4 ± 0.6	38.2 ± 0.5
E (GPa)	3.96 ± 0.15	1.54 ± 0.09	1.43 ± 0.05
σf (MPa)	154.5 ± 19.9	56.0 ± 1.8	50.4 ± 3.9

of the hardened material.[34] The post-curing treatment at 150 °C increases monomer conversion and reduces the plasticizing effect of the non-reacted monomer on the mechanical behaviour of the polymers.[34] Thus, the higher values of flexural modulus and compressive strength of samples of SIB subjected to a post-curing treatment are attributed to a reduced amount of non-reacted monomer.[23] In contrast, no significant differences in mechanical properties of UVR monomer cured at room temperature or subjected to an additional post-curing treatment are observed. This is attributed to the fact that the UVR monomer reached almost complete conversion during irradiation and consequently the plasticizing effect of the residual monomer is absent. It is interesting to note that the polymer resulting from irradiation of UVR monomer displays higher compressive and flexural properties compared with those of the polymer derived from SIB. Again, this is explained in terms of a higher density of crosslinking points. As described in the temperature evolution experiments, the moles of epoxy groups per kilogram in UVR and SIB are 7.94 and 5.22 respectively. Thus, the UVR monomer results in a more densely crosslinked polymer and therefore a material with higher compressive and flexural properties.[35]

CONCLUSIONS

A three-component visible light sensitive cationic photoinitiator system has been examined for the polymerization of selected epoxy monomers. The system is based on an iodonium salt in combination with CQ and EDMAB as donor molecule. Visible light is used to excite the CQ which then abstracts hydrogen atoms from the EDMAB. The resulting α-amino radicals are oxidized by the diaryliodonium salt to yield the respective cations, which initiate the polymerization. In the absence of EDMAB, the hydrogen donor is either the monomer or an impurity. The excited CQ molecule is initially reduced to the ketyl radical which in turn is oxidized back to CQ by the iodonium salt. The resulting strong Brønsted acid derived from this process initiates the cationic ring-opening polymerization.

The extent of reaction of UVR and SIB monomers was markedly affected by the sample thickness. The conversion reached in thin films of UVR is higher than that of SIB with the same photoinitiator system. However, the opposite trend was observed in polymerizations carried out in thick samples. This discrepancy is attributed to thermal effects, which are present in thick samples but can be disregarded in thin films. The polymerization reaction is highly exothermic, which results in an increase in the sample temperature during the process, and this effect becomes more important as the sample thickness increases. A higher sample temperature induces an increase of the mobility of the reaction environment (i.e. monomer, propagating species and polymer) and consequently increases the reaction rate.

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