Photobleaching of camphorquinone during polymerization of dimethacrylate-based resins

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ABSTRACT

Objective. The aim of this study was to compare the photobleaching rate of CQ in different dental resins.

Methods. The photodecomposition rate of CQ/amine system in bis-GMA/TEGDMA, bis-EMA and UDMA polymerizing monomers was evaluated at different light intensities. The photobleaching of the CQ was studied by monitoring the decrease in light absorption as a function of continuous irradiation time. The absorption changes were assessed by recording the transmitted light that passed through samples of monomers containing CQ/amine.

Results. Complete photobleaching of CQ was observed in all the monomer tested and the rate constant for the photobleaching was proportional to the radiation intensity. Hydrogen abstraction from amines by the excited CQ state via electron transfer and direct hydrogen abstraction from monomer structures were involved in the CQ photoreduction. CQ was photobleached in the absence of coinitiator in a dimethacrylate monomer containing a carbamate functional group (UDMA). This behavior was attributed to the presence of labile hydrogen atoms in the UDMA monomer. The CQ photobleaching rate constant in UDMA containing CQ/amine was similar to that in UDMA in the absence of amine. Moreover, the efficiency of CQ to photoinitiate the polymerization of UDMA in the absence of amine demonstrated that the radicals derived from the UDMA monomer via hydrogen abstraction are highly reactive toward double bonds.

Significance. CQ photoinitiates the polymerization of the UDMA monomer in the absence of amine and the efficiency of this process is comparable to that of traditional bis-GMA and bis-EMA monomers activated with CQ/amine.

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1. Introduction

Photopolymerization of multifunctional monomers is a method widely applied in clinical restorative dentistry. Polymerization of dental resins is generally initiated by the camphorquinone (CQ)/amine photoinitiating system, which produces free radicals on exposure to 450–500 nm radiation [1–3].

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 triple state and interacts with oxidizable species, thus decomposing into colorless products [1]. The presence of the light absorbing photoinitiator 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 [4,5]. However, when the photoinitiator photobleaches, absorbance decreases and attenuation is reduced since the photoinitiator consumption is accompanied by a deeper penetration of the light through sample thickness. Thus, photobleaching of photoinitiators is particularly important for photopolymerization of thick samples as it is the case of dental restorative resins. Initially, the initiator concentration is spatially uniform, and the light intensity will decrease with depth according to the Beer–Lambert law [6]. Immediately after commencement of irradiation, the initiator will be consumed at a rate proportional to the local light intensity, thereby leading to an initiator concentration gradient along the irradiation path. The evaluation of spatiotemporal variation of photoinitiation rates, which can have profound effects on the final cure of the material and its mechanical properties, requires the knowledge of the photobleaching rate of the photoinitiator [6].

Although extensive research efforts have been devoted to the study of photoreduction of photoinitiators in organic solvents, there is scant information concerning photoinitiators photobleaching rates measured in polymerizing resins [7]. The purpose of this research was to test the hypothesis that the photobleaching of CQ during photopolymerization of dimethacrylate-based monomers is affected by the structure of the monomers.

2. Experimental

2.1. Materials

The resin formulations used for this study were a 70:30 weight ratio of 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane (bis-GMA, from Esstech, Essington, PA) and triethylene glycol dimethacrylate (TEGDMA, from Aldrich), 2,2-bis[4-(2-methacryloxyethoxy)phenyl]propane (bis-EMA, from Esstech, Essington, PA), and 1,6-bis(methacrylyloxy-2-ethoxy-carbonylamino)-2,4,4-trimethyl-hexane (UDMA, from Esstech, Essington, PA). The resins were activated for visible light polymerization by the addition of 1 wt% CQ (Aldrich) in combination with equimolar amounts of ethyl-4-dimethylaminobenzoate (EDMAB, Aldrich) or dimethylamino ethylmethacrylate (DMAEMA, Aldrich). All materials were used as received. The structure of the monomers is shown in Fig. 1.

2.2. Light sources

Two Light Emitting Diodes (LEDs) light sources were used in the present work. These LEDs were selected because their spectral irradiance allows an optimum overlap with the absorption spectrum of CQ. The light source employed in the FT-IR studies was assembled from a LED with a maximum emittance at 470 nm (LED, OTLH-0090-BU, Optotech. Inc.). This unit can only be operated for short (ca. 6 min) periods. The light source

employed in photobleaching studies was assembled from a Luxeon DS45 (Philips) LED which functions in a continuous fashion and also has its emittance centred at 470 nm. The intensity of this LED was set at three different values by varying the electrical voltage through the semiconductor: 24, 35 and 56 mW. The relative emission spectra of the two LED sources were measured with a calibrated CVI-monochromator (Digikrom 480) and were found to be similar and lie within the range 430–520 nm. The absolute, total intensity of both LED sources was measured with the chemical actinometer, potassium ferrioxalate, which is recommended for the 253–577 nm wavelength range [8].

High intensity LEDs units consist of arrays of multiple LEDs and are not prepared to operate continuously during prolonged times (around 3000 s). Conversely, the simple geometry of sources assembled from a single LED permits to replicate the irradiation conditions in different sample specimens. In addition, they can be operated in a continuous fashion and their intensity can be easily and accurately set by varying the electrical voltage through the semiconductor. Unfortunately, the described benefits are accompanied with a lower irradiance compared with high intensity LEDs used in dental practice. The main effect is that the timescales will be reduced.

2.3. CQ photobleaching measurements in dimethacrylate resins

The amine and monomers do not absorb significantly between 420 and 520 nm so that the photobleaching of the CQ can be assessed by monitoring the decrease in light absorption as a function of continuous irradiation time. The absorption changes were studied by recording the transmitted light that passed through samples of monomers containing CQ/amine. The resins were contained in a 10 mm diameter well constructed from a rubber gasket material and with a glass slide at the base (Fig. 2). The thickness of the samples was varied in the range 1–2 mm. To monitor the photobleaching of the CQ, the intensity of the transmitted light was measured with an OPHIR PD 2000 photodetector (OPHIR Optronics, Israel), with a 10 mm diameter sensing area, a dynamic range of 2 μW to 200 mW and a precision ±3%. The Luxeon DS45 light source was placed underneath the sample and in contact with the glass substrate. The detector was placed above and at the centre of the sample at a distance less than 1 mm in order to collect and measure all of the transmitted light as a function of irradiation time. The light intensity that passed through the perforation in the rubber gasket, was measured by the actinometer and the resulting irradiances were 11.5, 15.9 and 25.5 mW/cm^2. Bleaching experiments were carried out at room temperature (approximately 20 °C) in an air atmosphere. Measurements were also carried out in resins without photoinitiator to correct for the radiation scattered/reflected at the air/glass/resin/air interfaces. Two replicates of each test were performed.

2.4. Measurement of double bond conversion

Measurements of conversion versus time at room temperature (20 °C) in resins prepared with CQ/EDMAB were carried out in
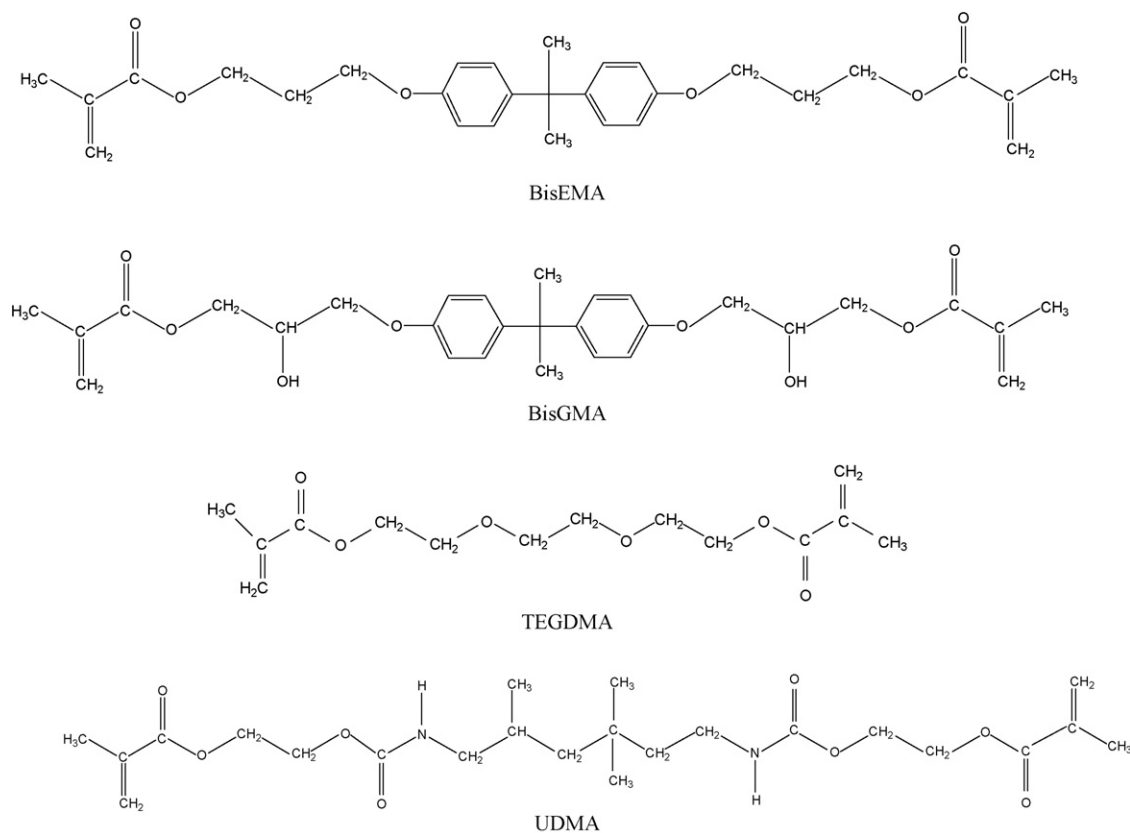
Fig. 1 – Structure of the monomers used in measurements of CQ photobleaching.

2 mm thick and 1 cm × 1.5 cm rectangular samples using Near-infrared spectroscopy (NIR) with a Genesis II Mattson FT-IR (Madison, WI). Because the present study has direct relevance to real-life photocuring situation, such as dental restorations and fibre composite photocuring which occurs in the presence of air, dissolved oxygen was not excluded from the resins. The irradiance at the resin surface was 4 mW/cm^2. The NIR

Fig. 2 – Experimental setup for transmitted light measurement.

spectra were acquired over the range 4500–7000 cm^{-1} from 16 co-added scans at 2 cm^{-1} resolution 120 s to acquire. Unfilled resins were sandwiched between two 2 mm thick glass plates separated by a 2 mm thickness rubber spacer, which were tightly attached to the sample holder using small clamps. With the assembly positioned in a vertical position, the Optotech photoirradiation source was placed in contact with the glass surface. In order to obtain the double bond conversion as a function of the irradiation time, the samples were irradiated for specific time intervals and the spectra recorded. These spectra were corrected with the background spectrum collected through an empty mould assembly fitted with only one glass slide to avoid internal reflectance patterns. The conversion profiles were calculated from the decay of the absorption band located at 6165 cm^{-1}. Two replicates were used in the measurement of conversion.
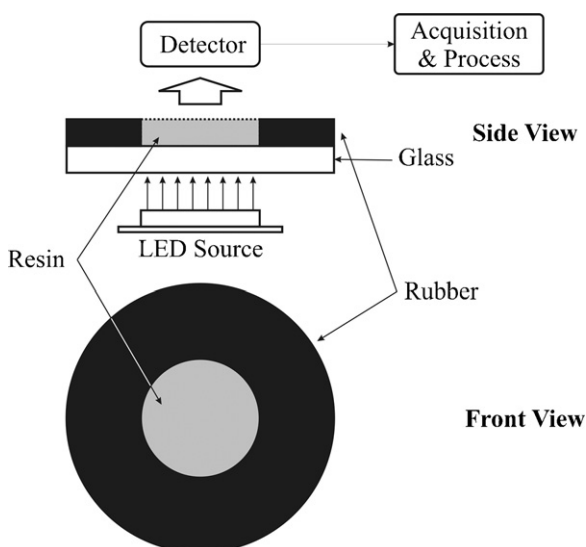
3. Results and discussion

CQ is a widely employed photoinitiator for the photopolymerization of restorative dental composite resins. The mechanism of photodecomposition of CQ/amine systems has been reported in previous research [1,2], and is briefly described here. The CQ is excited under visible light irradiation, to the excited singlet state which converts to the reactive triplet state CQ* via inter-system crossing:

$$CQ + h\nu \rightarrow CQ^* \tag{1}$$
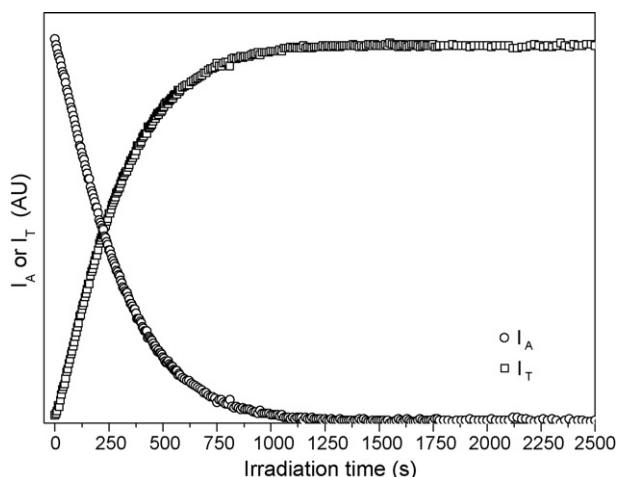
Fig. 3 – Typical plot of corrected transmitted and absorbed light intensity vs. irradiation time during irradiation of the resins. The ordinate is in arbitrary units.

Fig. 4 – Normalized global CQ concentration vs. irradiation time calculated from transmission measurements on bis-EMA and bis-GMA/TEGDMA resins containing 1 wt% CQ in combination with equimolar proportion of EDMAB. The caption includes the irradiance at the surface of the specimen.

Free radicals are produced subsequently from two different reactions. CQ^* can react with hydrogen donors such as tertiary amines (AH), to generate radicals by electron and proton transfer through a short lived charge-transfer intermediate complex (CTC) to give pinicol and amine derived radicals:

$$CQ^* + AH \rightarrow [CQ \ldots AH]^* \quad (CTC) \tag{2}$$

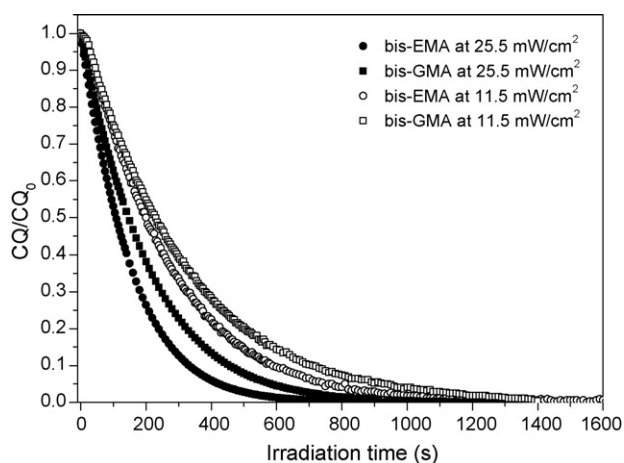$$CTC \rightarrow CQH^\bullet + A^\bullet \tag{3}$$
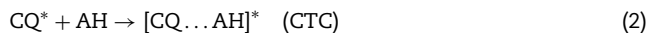
Alternatively, photoreduction of CQ in the absence of coinitiator has been reported in monomers containing hydrogen donor groups such as methylene ether ($-O-CH_2-$) [2], and in these cases hydrogen abstraction can occur from the monomer (MH).

$$CQ^* + MH \rightarrow CQH^\bullet + M^\bullet \tag{4}$$

CQ displays an intense dark yellow color due to the presence of the conjugated diketone chromophore that absorbs at 470 nm. During irradiation of CQ and reduction of one of the carbonyl groups, the conjugation is destroyed, causing a blue shift of the remaining ketone's absorption and loss of the yellow color. Thus, the photodecomposition rate of CQ can be assessed by measuring the decrease in absorbance as a function of the irradiation time by UV–vis spectroscopy [1,7]. Alternatively, the photobleaching of CQ in polymerizing resins can be assessed by monitoring the transmitted light intensity under continuous irradiation. Fig. 3 shows a typical plot of the recorded transmitted light and the absorbed light by the CQ as a function of irradiation time (corrected by subtraction of the light lost by scattering at the sample interfaces or absorbed by the resin alone) using the Luxeon LED source. As reported previously, no reduction in irradiance over 3500 s irradiation was observed [9]. Fig. 3 shows that photobleaching occurs from the very commencement of irradiation and so no induction period is observed.

The global (i.e. depth averaged) CQ concentration can be calculated from the incident (I_O) and transmitted (I_T) light intensity, according to the Beer–Lambert law:

$$ABS = \varepsilon L CQ = -\log \frac{I_T}{I_O} \quad \text{and} \quad CQ = -\frac{1}{2.303 \varepsilon L} \ln \left(\frac{I_T}{I_O} \right) \tag{5}$$

where ABS is the absorbance of the sample and L is the thickness of the sample. The consumption of CQ with irradiation time in the polymerizing resins was calculated from Eq. (5) and the data are presented in Figs. 4 and 5.

Figs. 4 and 5 reveal that complete photobleaching was observed in all the monomers investigated, and as a result, at the end of the experiments the samples were colorless and transparent. Fig. 5 shows that CQ is photobleached in UDMA even in the absence of added amine. In the absence of any
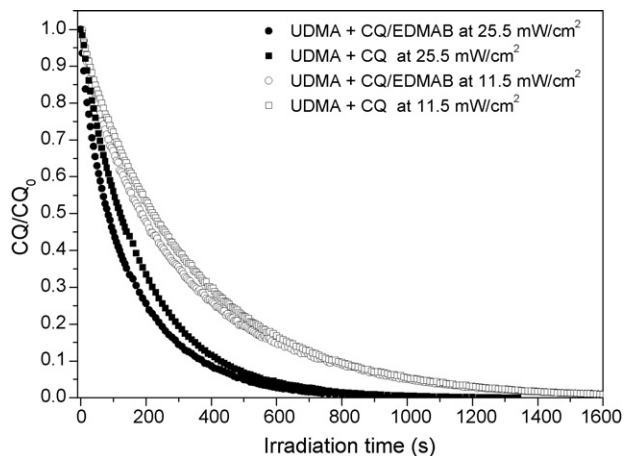
Fig. 5 – Normalized global CQ concentration vs. irradiation time calculated from transmission measurements on UDMA monomer containing 1 wt% CQ either in combination with equimolar proportion of EDMAB or in the absence of amine. The caption includes the irradiance at the surface of the specimen.

coinitiator, the hydrogen donor is the monomer itself, and so the consumption of CQ is attributed to the presence of labile hydrogen atoms in UDMA. From the data in Fig. 5 it is clear that hydrogen abstraction from the amine and the UDMA monomer are competitively involved in the process of CQ photodecomposition.

As was mentioned previously, an important characteristic of photopolymerization reactions is the spatial non-uniformity of the reaction rate, due to the variation of local light intensity throughout the specimen [6]. Initially, the initiator concentration is uniform, and the light intensity will decrease with depth according to the Beer–Lambert law. In addition with photobleaching initiators, as the initiator is consumed, the light penetrates more deeply into the sample. This results in a spatiotemporal variation of the local concentration of photoinitiator (and thus photoinitiation rate), which can be assessed from the photobleaching rate constant of the photoinitiator [6]. The depth averaged rate of photoconsumption of CQ is related to the volumetric rate of absorption of photons averaged over the sample thickness by the following expression [10]:

$$-\frac{dCQ}{dt} = \frac{\Phi I_A}{V} = \frac{\Phi I_O (1 - e^{-2.302\varepsilon CQL})}{AL} \tag{6}$$

where Φ is the quantum yield for the photoinitiator consumption (defined as the number of CQ molecules decomposed per photon absorbed), I_A is the number of photons per unit times absorbed by the sample in unit volume V, I_O is the incident light intensity (in terms of the number of photons irradiating the surface per unit time), ε is the decadic wavelength dependent extinction coefficient of CQ (42 ± 2 l/mol cm) [1,7], CQ is the molar concentration of CQ averaged over the sample thickness, A and L are the area and thickness of the sample respectively and t is the irradiation time. Eq. (6) can be integrated provided that the CQ concentration represents the depth (or volume) averaged concentration. Thus, the decomposition rate constant can be assessed in a thick sample by integrating Eq. (6) [6,11]:

$$-\ln\left[\frac{1 - e^{2.302\varepsilon CQL}}{1 - e^{2.302\varepsilon CQ_oL}}\right] = 2.302\Phi\varepsilon I_o't = kt \tag{7}$$

where CQ_o is the initial concentration of CQ, I_O' is the incident light irradiance (calculated as the incident light intensity I_O divided by the sample area A) and k is the pseudo first order decomposition rate constant of the CQ consumption which is only dependent on I_O. Combination of Eqs. (5) and (7) yields

$$f(I) = -\ln\left[\frac{I_{TO}}{I_T}\frac{(I_O - I_T)}{(I_O - I_{TO})}\right] = 2.303\Phi\varepsilon I_o't \tag{8}$$

The rate constants for the CQ consumption were calculated from the evolution of the transmitted light during irradiation using Eq. (8). Plots of $f(I)$ against time, give straight lines with a slope equal to the rate constants for the CQ consumption. As reported previously, the photopolymerization reaction is highly exothermic, and consequently, the temperature of the resins increases during the measurements [12]. However,
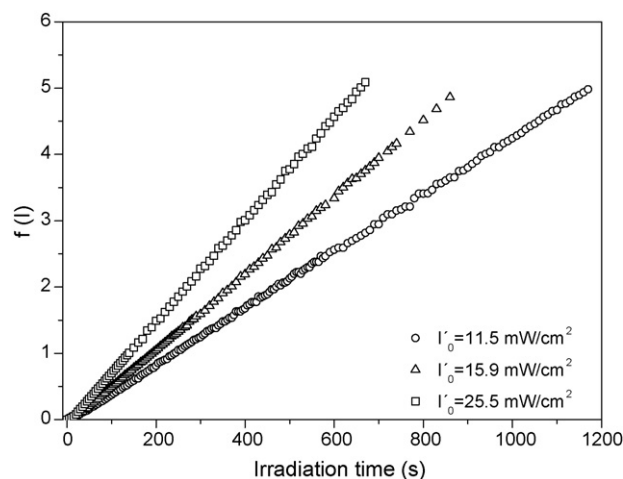

Fig. 6 – Plots of Eq. (8) for the bis-EMA resin containing 1 wt% CQ in combination with equimolar proportion of EDMAB.

in contrast to thermally activated initiators, the decomposition rate of photoinitiators is independent of temperature [10]. Figs. 6–8 show plots of Eq. (8) from measurements of transmitted light versus time during irradiation of different monomers and the rate constant for CQ photobleaching is plotted versus radiation intensity in Fig. 9. It is worth noting that polymerization is accompanied by shrinkage of the resins. In addition, the exothermic nature of free radical bulk polymerization of dimethacrlylate monomers leads to elevated cure temperatures. Consequently, the shrinkage that occurs due to the polymerization reaction is accompanied with volumetric expansions and contractions resulting from the temperature changes. As reported in a previous study the pathlength will change by a small amount (4–5%) and around 80% of that amount occurs during the first 20 s irradiation [12]. After the first stage of fast reaction, the sample shrinkage is very slow and changes in sample thickness can be disregarded.
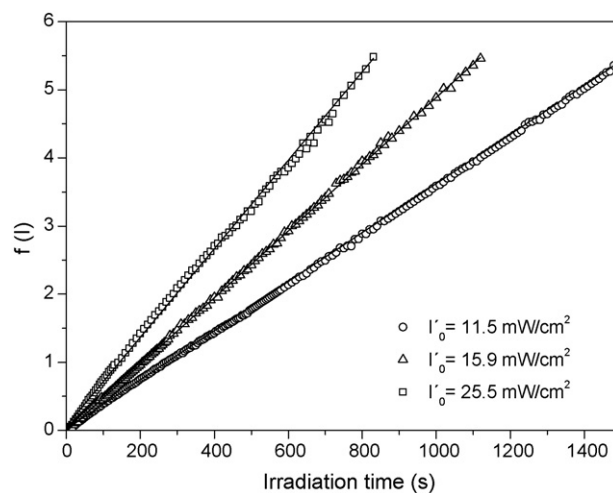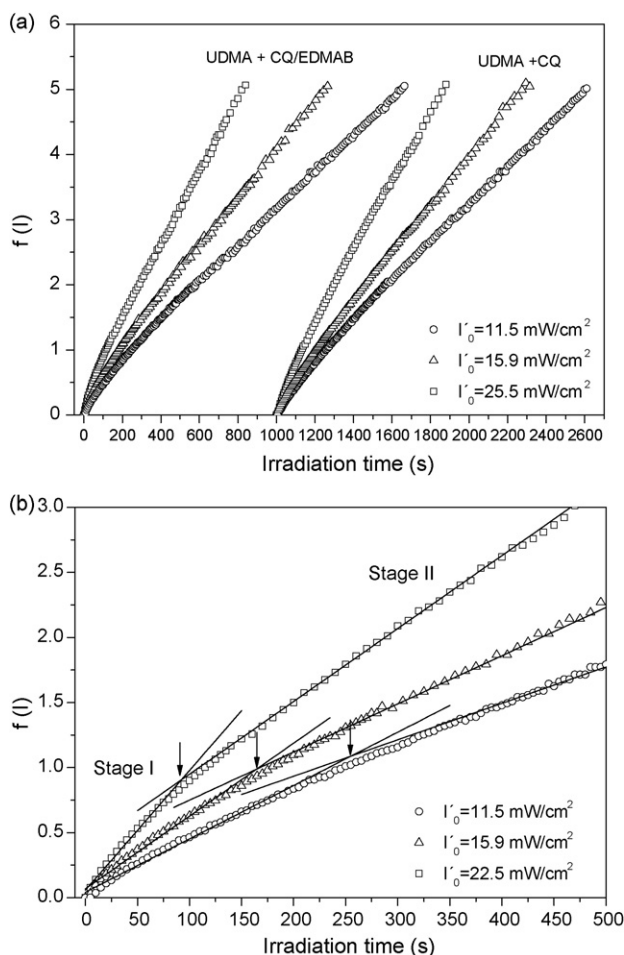

Fig. 7 – Plots of Eq. (8) for the bis-GMA/TEGDMA resin containing 1 wt% CQ in combination with equimolar proportion of EDMAB.

Fig. 8 – (a) Plots of Eq. (8) for the UDMA monomer containing 1 wt% CQ either in combination with equimolar proportion of EDMAB or in the absence of amine. The time in the UDMA without amine is shifted 1000 s to make the plot more clear. **(b)** Magnification of the initial part of (a) for the UDMA resin containing 1 wt% CQ in combination with equimolar proportion of EDMAB.

This gives support to the calculus of the rate constants for CQ consumption using Eq. (8).

The photobleaching of CQ in the bis-EMA and bis-GMA/TEGDMA monomers resulted in linear plots with regression coefficients greater than 0.992 during the total period of irradiation (Figs. 6–7), and the rate constant for the photobleaching of CQ was proportional to the radiation intensity (Fig. 9), extrapolating to zero at zero intensity as expected. Since the polymerizing bis-EMA and bis-GMA/TEGDMA resins change from relatively viscous materials to glassy networks during the irradiation period, the linearity of the plots in Figs. 6–7 shows that the rate of photobleaching of CQ in these monomers is not very sensitive to the mobility of the medium. On the other hand, the photobleaching data for the UDMA monomer in the absence of amine and presence of amine was non-linear (see Fig. 8). As an approximation, this behavior can be divided into two regions during the irradiation. A more rapid decomposition of CQ occurred during the first part of the irradiation (stage I), and the intensity
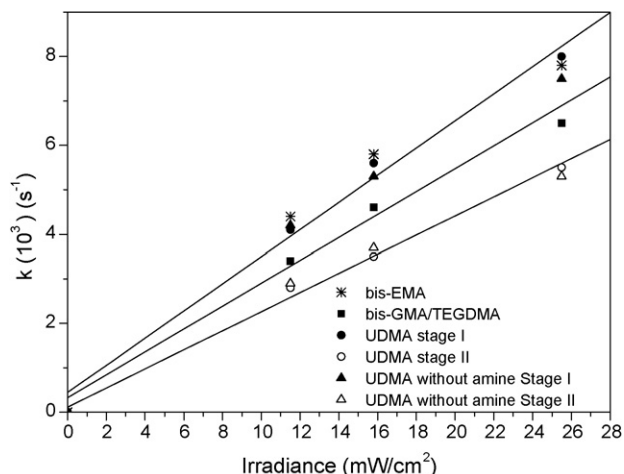
Fig. 9 – Apparent first order rate constant for CQ photobleaching in different monomers at different irradiances.

dependent decomposition rate constant was similar to that of the bis-EMA monomer. For prolonged irradiation times (stage II), the CQ decomposition rate constant was markedly reduced. The time of the transition from stage I to stage 2 decreases when the light irradiance increases, suggesting that the decrease in the CQ reduction rate in UDMA is associated with changes in the molecular mobility in the resin during irradiation, probably the vitrification of the network. Thus, the existence of two rate constants may be interpreted by the presence of two mechanism of CQ consumption operating at different levels of polymerization. As it will be shown later, the double bond conversion in UDMA reaches a plateau after 100 s radiation at 4 mW/cm^2 due to vitrification of the network. Thus, during UDMA polymerization CQ photobleaches with the constant rate value in stage I. Concentrating for the moment on the initial part of the irradiation (stage I), which also corresponds to the period where most of the polymerization occurs, the results in Fig. 9 and Table 1 demonstrate that the for the systems containing 1 wt% CQ in combination with equimolar proportion of EDMAB, the photobleaching constant rate was not markedly affected by the structure of the polymerizing monomer since it varied less than 20%. In order to examine the role of the amine on the CQ photobleaching rate, measurements of transmitted light were carried out in bis-GMA/TEGDMA and bis-EMA monomers containing CQ in combination with an equimolar amount of the DMAEMA aliphatic amine. The photobleaching constant rates presented in Table 1 demonstrate that the

Table 1 – Rate constants for CQ photobleaching in different monomers. The samples contained 1 wt% CQ in combination with equimolar amount of EDMAB or DMAEMA amine. The values are in s^{-1}. The irradiance was 25.5 mW/cm^2.

Monomer	EDMAB	DMAEMA
bis-EMA	7.7×10^{-3}	7.2×10^{-3}
bis-GMA/TEGDMA	6.5×10^{-3}	6.3×10^{-3}

consumption rate of CQ was not very sensitive to the amine reactivity.

In the photoreduction of the excited CQ species, three steps can be distinguished, namely, diffusion of the CQ and reducer (usually the amine) into a state of encounter, electron transfer with the formation of a donor–acceptor charge-transfer complex and the decay of the complex by proton transfer resulting in radical production. Thus, the photoinduced electron transfer reaction of the excited CQ with amines depends on the rate constant of diffusion of the reactants which may be highly dependent on the viscosity or rigidity of the medium. During measurements of CQ photobleaching by irradiation of monomer samples, the polymerizing resin is transformed from a viscous liquid to a rigid glass. Because the photoinduced electron transfer is strongly diffusion controlled, its effectiveness decreases as the polymerization progresses and then, CQ is consumed by another simultaneous mechanism. Direct hydrogen abstraction from the monomer is expected to be less dependent on the mobility of the medium due to the close vicinity of both reactive species. Consequently, as the mobility of the media is reduced, hydrogen abstraction from monomer structures competes with the electron transference reaction of the excited CQ with the amine. If the electron transfer process is slowed down, then the photochemical process involves a hydrogen abstraction mechanism leading to the CQ photoreduction accompanied by the formation of radical species deriving from the monomers.

The monomers studied, exhibit different chemical structures which are expected to result in different intra- and intermolecular interactions. The presence of these interactions can cause a decreased mobility of the medium during polymerization and also increased rigidity of the corresponding polymeric network. For a better understanding of this effect, it is worth mentioning the main characteristics of the monomers studied. For bis-GMA, weaker hydrogen bonds are formed between the OH group and methacrylate carbonyls, while stronger hydrogen bonding interactions arise between bis-GMA hydroxyl groups [13]. In the UDMA monomer, NH hydrogen bonded interactions can be differentiated into weaker associations with the methacrylate carbonyls and stronger bonds formed with the more electron rich urethane carbonyl. In addition, a combination of intra- and intermolecular associations is possible with the more flexible aliphatic UDMA structure. The lack of hydrogen bonding in bis-EMA allows a greater degree of mobility and is considered responsible of its low viscosity. The viscosity of the monomers, which is indicative of the degree of molecular interactions, is around 1, 8 and 20 Pa for bis-EMA, bis-GMA/TEGDMA (70/30) and UDMA respectively [14,15]. From comparison of this values it emerges that UDMA displays a viscosity value 20 times higher than that of bis-EMA whereas CQ photobleaches in both monomers at a similar rate during the initial part of the irradiation. For efficient reduction of CQ, the bimolecular hydrogen abstraction reaction must compete with side reactions that lead to deactivation of the CQ excited states. In viscous media, where the diffusion of the reactants is restricted, the rate constants of the steps involved in the reduction of CQ and the deactivation of the CQ excited states are reduced in the same way by diffusion effects. This explains the observation
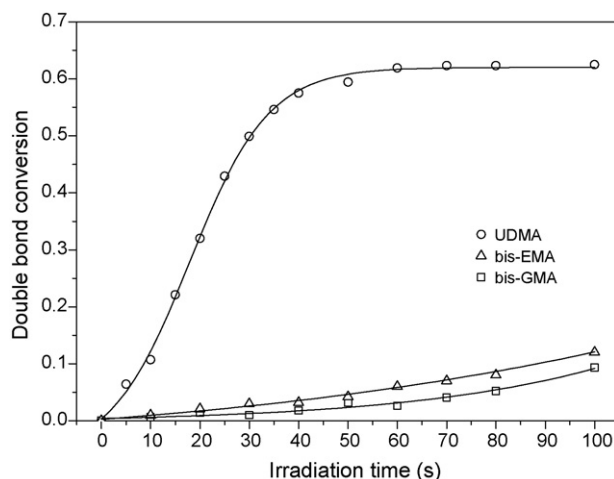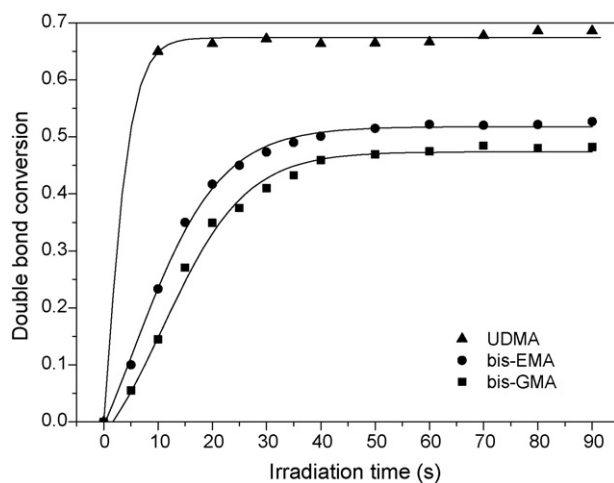

Fig. 10 – Double bond conversion vs. irradiation time for resins containing 1 wt% CQ in the absence of amine. The irradiance was 4 mW/cm^2.

that the photobleaching rate of CQ during the initial part of irradiation is not very sensitive to the medium mobility. This is in agreement with spectroscopic studies reported by Cook on CQ reduction in glassy and elastomeric matrixes [1].

As it was shown in Figs. 6–8, the photobleaching processes were described by a single rate constant for bis-EMA and bis-GMA/TEGDMA and two rate constants for UDMA. In order to gain a further insight on these different trends, the progress of the polymerization in different monomers was studied by measuring the progress of double bond conversion versus irradiation time. Measurements in absence and presence of amine are depicted in Figs. 10 and 11 respectively.
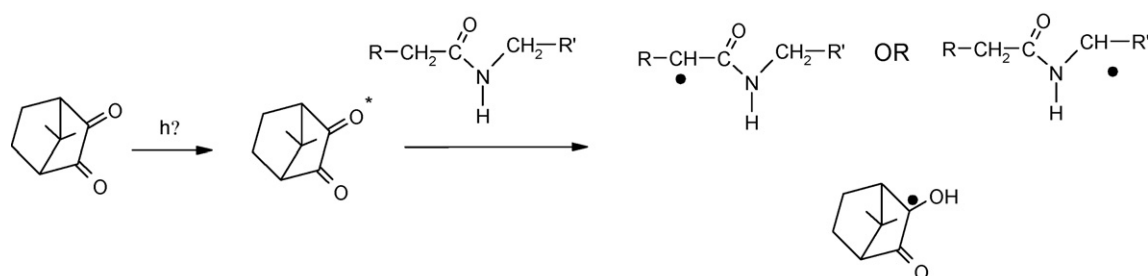
The photopolymerization kinetics of these monomers has been reported by previous researches [13–16]. The different factors that affect the photoinitiation efficiency include the rate constants for the formation and deactivation of the

Fig. 11 – Double bond conversion vs. irradiation time for resins containing 1 wt% CQ in combination with equimolar proportions of DMAEMA. The irradiance was 4 mW/cm^2.

excited triplet state and its exciplex with the reducer, the fraction of excited states that leads to radicals, and the proportion of these radicals that add to the monomer [1,17,18]. As can be seen from Fig. 10, the most striking difference between polymerizations initiated by CQ in the three monomer systems occurs when no coinitiator was present. CQ affords a negligible photoinitiating activity when used alone in bis-GMA/TEGDMA and bis-EMA monomers. It is well known that the ketyl radical does not initiate the polymerization because of steric hindrance effects [1], therefore, the very slow polymerization of either bis-GMA/TEGDMA or bis-EMA in the absence of amine (see Fig. 10) indicates that radicals derived from the monomers are ineffective at initiating the polymerization process. These results are in agreement with previous research on the photopolymerization of TEGDMA with CQ in the absence and presence of amine coinitiator [2]. The markedly increased polymerization rate of bis-GMA/TEGDMA and bis-EMA monomers containing CQ/DMAEMA (Fig. 11) is attributed to the formation of reactive amine radicals which initiate the polymerization reaction. On the other hand, in the absence of added amine, CQ can itself photoinitiate the polymerization of the UDMA monomer (Fig. 10) and the efficiency of this process is comparable to that of the bis-GMA/TEGDMA and bis-EMA monomers activated with CQ/amine. This suggests that CQ oxidizes the UDMA monomer and that the radicals derived from the UDMA monomer via hydrogen abstraction are highly reactive toward double bonds so that a similar level of double bond conversion can be achieved (Figs. 10 and 11).

The trends observed in the CQ photobleaching in UDMA can be analyzed in conjunction with polymerization studies, which showed that hydrogen abstraction from the tertiary amine is in competition with hydrogen abstraction from the UDMA monomer. It is generally accepted that methine hydrogens are more abstractable than methylene which in turn are more abstractable than methyl hydrogens. The UDMA monomer contains two methylene units adjacent to the carbamate functionality, and these could be responsible of the efficient photobleaching of CQ as well as the efficient polymerization in the absence of coinitiator as shown by the mechanism:

irradiation time in UDMA may be attributed to a restricted mobility of the network, which favor the deactivation of the CQ excited states and lead to a reduced CQ photobleaching rate after the vitrification of the UDMA monomer [19,20].

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4. Conclusions

The photobleaching rate of CQ in polymerizing monomers was assessed by monitoring the decrease in light absorption as a function of continuous irradiation time. Hydrogen abstraction from monomer structures and electron transference of the excited state of CQ with the amine were competitively involved in the CQ photoreduction. The consumption rate of CQ in polymerizing resins was not markedly affected by the amine reactivity. This behavior was attributed to a strongly diffusion controlled photoinduced electron transference process.

The photobleaching processes for bis-EMA and diluted bis-GMA were not sensitive to the mobility of the medium, which changed from relatively viscous resins to glassy networks. However, the CQ reduction in UDMA was described by two constant rates. A more rapid decomposition of CQ occurred during the first part of the irradiation, and the CQ decomposition rate constant value was similar to that of the bis-EMA and bis-GMA. For prolonged irradiation times the CQ decomposition rate constant in UDMA was markedly reduced. This behavior may be attributed to a restricted mobility of the network, which favor the deactivation of the CQ excited states and lead to a reduced CQ photobleaching rate. This conclusion is supported by the observation that the time at which the reduction in the rate constant occurred decreased when the light irradiance increased.

CQ was photobleached in UDMA in the absence of amine due to the presence of labile hydrogen atoms in UDMA. Moreover, radicals derived from the UDMA monomer via hydrogen abstraction were highly reactive toward double bonds. This feature contrasts with the lack of polymerization observed in bis-GMA/TEGDMA and bis-EMA monomers photosensitized with CQ in the absence of amine.

According with results on UDMA polymerization in the absence of amine (Fig. 10), the monomer derived radical is reactive, then it can cause the initiation of polymerization and thereby offer an alternative path of continuation of polymerization. Consequently, the formed network is expected to be more rigid than the predicted structure considering as crosslinking sites only those of the two vinyl groups. Thus, the observed decrease in the CQ consumption rate with

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