Efficiency of 2,2-Dimethoxy-2-phenylacetophenone for the Photopolymerization of Methacrylate Monomers in Thick Sections

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ABSTRACT: The efficiency of 2,2-Dimethoxy-2-phenyl-acetophenone (DMPA) for the photopolymerization of methacrylate monomers in thick sections was assessed. DMPA is an efficient photoinitiator for thick sections (≈ 2 mm) because a fast reaction and high conversions are obtained with concentrations as low as 0.25 wt % DMPA. The polymerization rate increased when the DMPA content increased from 0.125 wt % to 0.25 wt %. However, the conversion versus irradiation time profiles in resins containing 0.25 wt % or 0.5 wt % DMPA were similar. This is attributed to the screening effect caused by excessive levels of DMPA. In addition, the consumption of DMPA under UV irradiation was accompanied by the appearance of light absorbing photoproducts. Because the absorbing species nearest to the light source absorb part of it, the light fails to reach the deeper layers of the sample. The overall effect of light screening is a reduced photoinitiation rate and double bond conversion along the irradiation path. This effect was compensated by the use of irradiation sources of higher intensity; which increased the initiation rate by increasing the production of primary radicals. DMPA is colorless and it does not require the presence of amine as coinitiator. These properties make DMPA attractive as photoinitiator of dental composites. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 418–425, 2012

Key words: photopolymerization; dental polymers; degree of polymerization; methacrylates; 2,2-dimethoxy-2-phenylacetophenone

INTRODUCTION

The camphorquinone (CQ)/amine initiator system is widely used for the free radical photopolymerization of methacrylate-based restorative dental materials. CQ produces free radicals on exposure to 450–500 nm radiation and this process is activated by the redox reaction with tertiary amines.[1–6] CQ is the most common photoinitiator but it possesses a noticeable yellowish color. For the majority of restorative work this is not an issue as natural tooth color also has a yellowish hue, but for cosmetic restoration this yellow color can be a significant factor. Efforts to enhance the quality of the polymer matrix have investigated alternative photosensitizers suitable for dental resins.[7–9]

2,2-Dimethoxy-2-phenylacetophenone (DMPA) is a very efficient and frequently used free radical photo-initiator for thin photocurable coatings ($\sim$ 20 μm).[10,11] The colorless nature of DMPA makes it very attractive for the formulation of dental resins

with improved esthetical properties. The evaluation of a photoinitiator to be used for the polymerization of dental resins is governed by the requirement of a high curing speed ($\sim$ 40–60 s). In addition, since light activated dental composites are normally used in thick section ($\sim$ 2 mm), the effect of the attenuation of the light intensity along the radiation path must be taken account. In a photo-reactive initiator system, there is a spatio-temporal distribution of both light intensity and photoinitiator concentration.[12–17] Initially, the initiator concentration is uniform, and the light intensity will decrease with depth according to the Beer-Lambert law. Immediately after irradiation, the initiator will be consumed at a rate proportional to the local light intensity, thereby leading to an initiator concentration gradient along the beam direction.[16,17] This leads to temporal variation of local light intensity—depending on the nature of the photolysis products, this consumption of the photoinitiator can either lead to an increase in light intensity in the underlying lays (if the photolysis product is more transparent at the irradiating wavelengths) or, in some cases, a reduction in light intensity (if the photolysis product is strongly absorbing. The attenuation of the radiation as a function of depth into the material not

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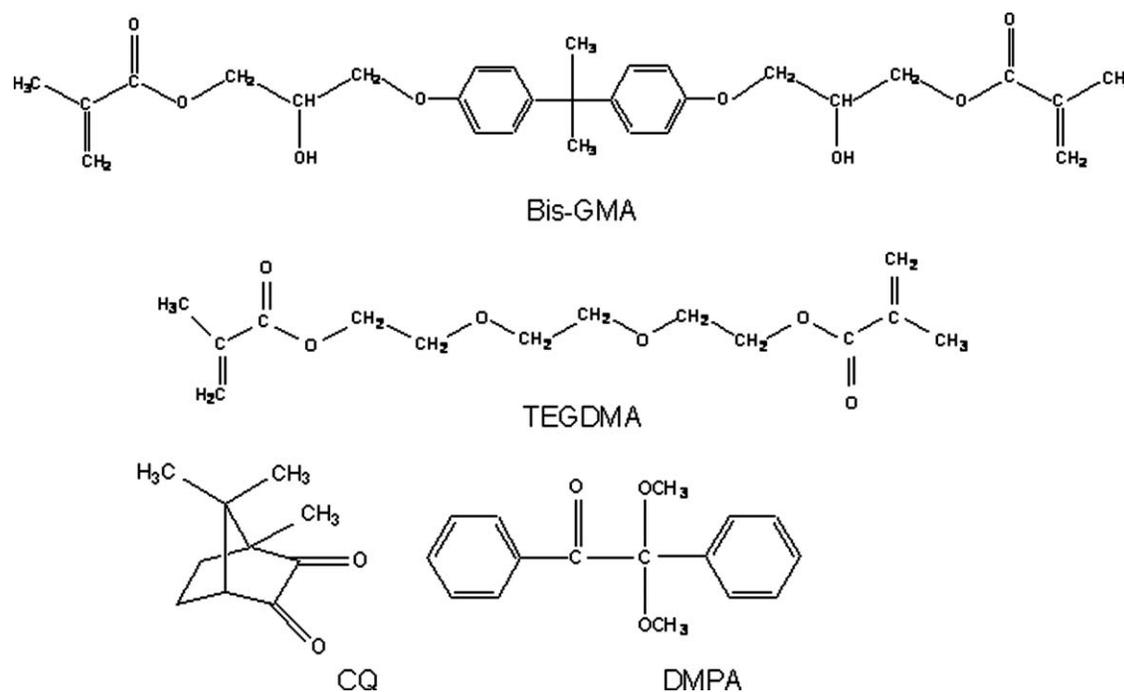
Figure 1 Structure of the monomers and photoinitiator systems studied.

only affects the cure kinetics but also often limits the depth of cure. Since light activated dental composites are normally used in thick section, the depth of cure is important due to its affect on the properties of undercured material and the presence of potentially toxic residual monomer which can be eluted from the resin into the tissues.

Differently from the visible CQ/amine pair photoinitiator, DMPA absorbs in the UV range (310–390 nm). The interest of studying the DMPA for dental applications is motivated by the current availability on the market of curing lights of the Light Emitting Diode (LED) technology. Early LEDs emitted low-intensity red light, but modern versions are available across the visible, ultraviolet, and infrared wavelengths, with very high intensity. In addition, LEDs can emit light of an intended wavelength without the use of filters that traditional UV sources require. It is worth mentioning that prolonged exposure to UV radiation may result in chronic health effects on the eye. However, the assessment of ocular hazards associated with the use of visible dental curing lamps showed that the eyes of the lamp operators are at risk from acute and cumulative effects, mainly due to back-reflection of the blue light. Therefore, the use of eye protectors is recommended for visible radiation as well as UV radiation. It is worth mentioning that the emission spectra of some current commercial dental lamps covers the range 370–460 nm to photopolymerize materials containing different types of photoinitiators.

The purpose of this study was to examine the suitability of DMPA as photoinitiator for the polymerization of dental resins based on methacrylate monomers. The efficiency of DMPA was compared with that of CQ/amine pair which is used in dental restorative formulations.

EXPERIMENTAL

Materials and light sources

The resin formulations used for this study were 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]-propane (bisGMA, from Esstech, Essington, PA), triethylene glycol dimethacrylate (TEGDMA, from Aldrich), and 1,6-bis(methacrylyloxy-2-ethoxy-carbonylamino)-2,4,4-trimethylhexane (UDMA, from Esstech, Essington, PA). BisTEG stands for a blend 70 : 30 bisGMA/TEGDMA. The resins were activated for UV and visible light polymerization by the addition of 2,2-Dimethoxy-2-phenylacetophenone (DMPA, Aldrich) or Camphorquinone (CQ, Aldrich) respectively. The amine used in combination with CQ was ethyl-4-dimethylamino benzoate (EDMAB, Aldrich). The resins and the solvent acetonitrile (Merk) were employed as-received. The structures of the photoinitiators and monomers used are shown in Figure 1. The light sources were assembled from light emitting diodes (LED) with irradiances centered at 470 nm (OTLH-0090, Optotech) and 365nm (OTLH-0480-UV, Optotech). The intensity of the 365 nm LED was set at two different values by varying the electrical voltage through the semiconductor: 95 and 200 mW. The intensity of the 470 nm LED
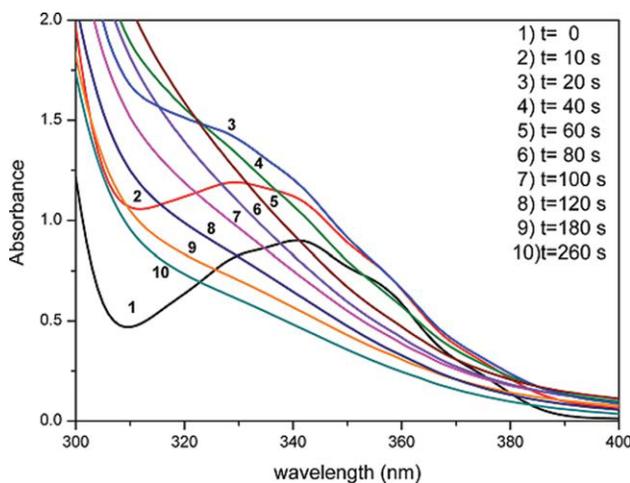
Figure 2 Typical spectral changes during the irradiation of a solution 0.038*M* of DMPA in acetonitrile. The intensity of the LED was 200 mW. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was 30 mW. The absolute value of the light intensity of the LEDs was measured with the chemical actinometer potassium ferroxialate, which is recommended for the 253–577 nm wavelength range.

Photolysis of DMPA

The absorption spectra of DMPA were measured with an UV-vis spectrophotometer 1601 PC Shimadzu at room temperature (20 ± 2°C) in acetonitrile and methacrylate monomers. The photodecomposition of DMPA was followed by the changes in absorbance at the wavelength of their maximum absorption. Bleaching experiments in acetonitrile were carried out in 1 mm thick quartz cuvettes under nitrogen or air atmosphere. Solutions of DMPA in acetonitrile were deoxygenated by bubbling with nitrogen for about 20 min before irradiation. The concentration of DMPA in acetonitrile was 0.038*M*. Photodecomposition studies in UDMA and BisTEG monomers were carried out in 3 ± 0.5 mm thick samples sandwiched between two glass plates. The concentration of DMPA in methacrylate monomers was 0.01*M*. The molar absorption of DMPA and CQ are 265 (l/mol cm) and 42 (l/mol cm) at 365 nm and 470 nm, respectively.

Degree of conversion

FTIR spectra were acquired with a Nicolet 6700 Thermo Scientific. The NIR spectra were acquired over the range 4500–7000 cm^{-1} from 16 coadded scans at 2 cm^{-1} resolution. Unfilled resins were sandwiched between two glass plates separated by a 2-mm rubber spacer and were tightly attached to the sample holder using small clamps. With the assembly positioned in a vertical position, the light source

was placed in contact with the glass surface. The specimens were irradiated at regular time intervals and spectra were collected immediately after each exposure interval. The background spectra were collected through an empty mold assembly fitted with only one glass slide to avoid internal reflectance patterns. The concentration of DMPA was 0.005*M* (0.125 wt %), 0.01*M* (0.25 wt %), or 0.02*M* (0.5 wt %). The conversion profiles were calculated from the decay of the absorption band located at 6165 cm^{-1}.[5,18] Two replicates of each of the resins were used in the measurement of conversion. Attenuated total reflectance (ATR) spectra were recorded on a Nicolet 6700 Thermo Scientific equipped with a diamond crystal (4 cm^{-1}, 64 scans). The conversion at the surface of 2 mm thick samples was evaluated by following the decay of the band at 1637 cm^{-1} assigned to the methacrylate double bond.

RESULTS AND DISCUSSION

Photolysis of the photoinitiator

2,2-Dimethoxy-2-phenylacetophenone (DMPA) is a photocuring agent widely used for the production of thin films and coatings, and much work has been devoted to the understanding of its photochemistry.[19–23] However, the efficiency of DMPA for the polymerization of thick sections (~ 2 mm) has not received the same attention. In the photopolymerization of thick sections, as it is the case of light activated dental composites, the effect of the attenuation of the light intensity along the radiation path must be taken account.[12–17] The effect of light attenuation caused by excessive levels of light absorbing compounds or thick sections is well known and has been termed the inner filter effect. 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. Thus, when studying the efficiency of a photoinitiator to be used in thick sections, it is relevant to assess changes in absorbance of the sample during irradiation.

Figure 2 shows typical plots of the spectral changes during irradiation of solutions of DMPA in acetonitrile. The absorbance increased during the first 20-s irradiation and decreased with further irradiation. This indicates that the consumption of DMPA was accompanied by the appearance of light absorbing intermediate photoproducts during the initial period of irradiation, which were consumed by secondary photoreactions. Although the trends in the spectra in Figure 2 were not affected by the presence of oxygen, a slower decrease in absorbance was observed in the deoxygenated solutions. Figure 3 is a typical plot of spectral changes during irradiation
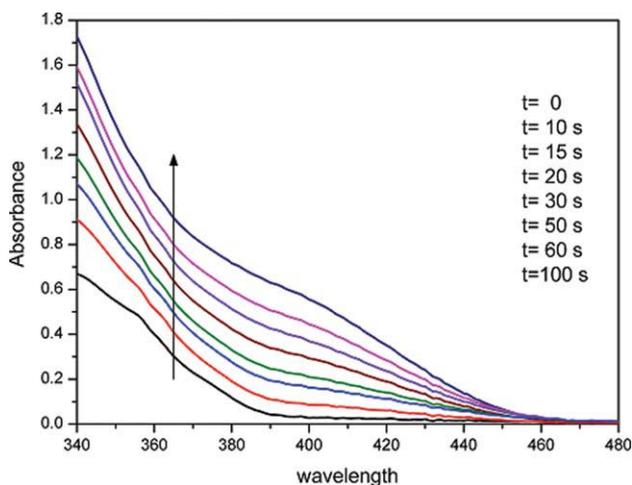
Figure 3 Typical spectral changes during the irradiation of a solution 0.01M of DMPA in UDMA monomer. The intensity of the LED was 200 mW. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of DMPA in UDMA showing a continuous increase in absorbance with irradiation time. Similar spectral changes (not shown here) were observed during photolysis of DMPA in BisTEG monomers. The different trends observed in acetonitrile and dimethacrylate monomers (Fig. 4) are attributed to different mobility of each reacting medium. During photolysis of DMPA in methacrylate monomer, the polymerizing resin is transformed from a viscous liquid to a rigid glass. In vitrifying systems, diffusion of the reactants is strongly suppressed. Therefore, changes in the photofragmentation and secondary photoreactions are expected to occur.

The photochemistry and free radical photofragmentation of DMPA (Fig. 5) was studied by
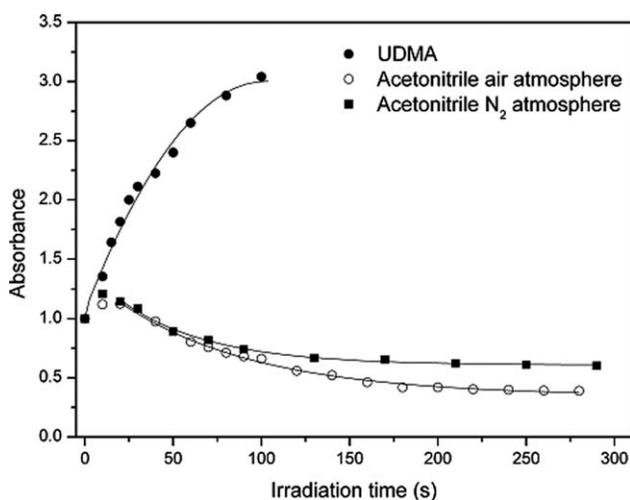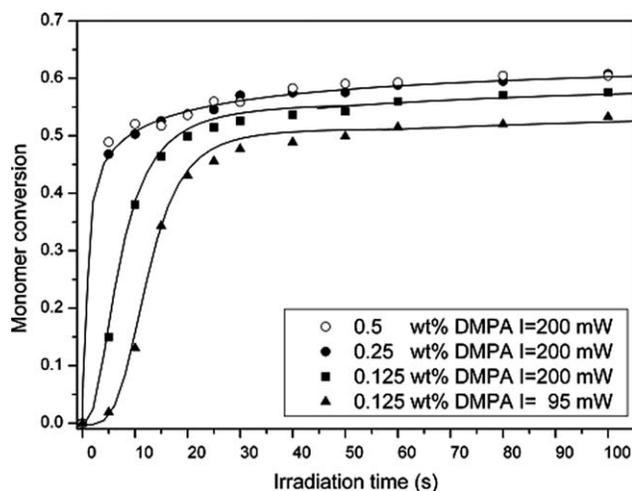

Figure 4 Maximum absorbance versus irradiation time in solutions of DMPA in acetonitrile and UDMA monomer. The intensity of the LED was 200 mW.
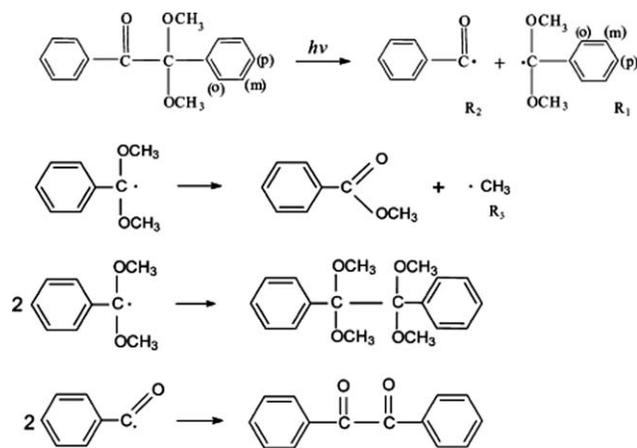
Figure 5 Mechanism of photolysis of DMPA under UV irradiation.

previous authors who reported contradictory results on photolysis products. Sandner and Osborn.[19] reported photolysis products of DMPA in a variety of solvents without exclusion of oxygen. They found methyl benzoate (45–61% yield), benzaldehyde (17–20%), benzil (7–11%), and acetophenone (2–8%). On the other hand, Davidson et al.[20] reported the products of decomposition of DMPA in dinonyl phthalate under aerobic conditions. Besides methyl benzoate they found methyl anisolate, methyl o- and p-benzoylbenzoate and benzoic acid as major components, and benzaldehyde, benzophenone, benzil, acetophenone, and biphenyl in minute amounts. Fischer et al. studied the photofragmentation of DMPA in degassed solutions of DMPA in acetonitrile under irradiation at 360 nm using different light intensity sources.[21] From product studies the authors found that the primary reaction is a photochemical α cleavage from a very short-lived triplet state to α,αdimethoxybenzyl (R_1) and benzoyl (R_2) radicals followed by a fragmentation of the dimethoxybenzyl radical to methyl benzoate, and methyl radicals (R_3). For the low intensity photolysis, the major components observed were methyl benzoate, benzyl, methane, and the methyl benzoylbenzoates from the crosstermination of R_1 and R_2. Acetophenone and benzaldehyde contributed to lower extents. In incompletely deoxygenated samples, the formation of benzoic acid and an increased yield of benzaldehyde was observed. For high intensity irradiation methyl benzoate was virtually the only product of R_1, which indicates nearly quantitative photo-fragmentation. Thus, the contradictory results on photolysis products of DMPA reported by Sandner and Osborn[19] and Davidson et al.[20] are attributed to a strong influence of the light intensity and excitation wavelength employed on the photochemical fragmentation of DMPA. Trends presented in Figure 4 show that the photolysis of DMPA in methacrylate

Figure 6 Conversion versus irradiation time for BisTEG resin containing 0.125, 0.25, or 0.5 wt % of DEABP.

monomers results in an increase in absorbance associated to the presence of photoproducts which absorb in the same wavelength region as DMPA. The effect of increased absorbance during irradiation of DMPA on the degree of conversion of methacrylate monomers is discussed in the following section.

Double bond conversion versus irradiation time

Light absorption by a photoinitiator requires that its absorption band overlaps with the emission line from the light source. If components of the formulation absorb light of the same wavelength important for the photoinitiator excitation, they compete with the latter for incident light, thereby reducing the efficiency of the initiating process. Silica is the most frequently used reinforcing filler in dental composites. It is transparent to visible light but it begins to absorb radiation below about 340 nm. Therefore, the use of a LED source with its emmitance at 365 nm ensures that all the light is absorbed by the DMPA photoinitiator in the polymerization of light-cured dental composites.

The progress of the polymerization reaction was measured in BisTEG and UDMA monomers photoactivated with DMPA. Figure 6 is a plot of monomer conversion versus irradiation time in BisTEG resin containing 0.125, 0.25, and 0.5 wt % of DMPA. Taking into account that dental resins contain about 70 wt % of inorganic filler, the initiator concentrations based in the unfilled resin are equivalent to about 0.036, 0.075, and 0.15 wt % based in the composite resin. Results presented in Figure 6 show that DMPA is an efficient photoinitiator for methacrylate monomers because a fast reaction and high conversions are obtained with concentrations as low as 0.25 wt % DMPA. The polymerization reaction increases when the DMPA content increased from 0.125 wt %

to 0.25 wt %. However, the polymerization rates in resins containing 0.25 wt % or 0.5 wt % DMPA were similar. This is attributed to the filtering or screening effect caused by the increased absorbance in samples containing 0.5 wt % DMPA. Photopolymerization at high initiator concentration is attractive in dental applications because polymerization rates typically increase as initiator concentration increases. However, many studies have shown that polymerization rate reaches a maximum for an optimum level of photoinitiator, and then decreases due to radiation attenuation in the underlying layers.[5,10] Rather, if the extinction coefficient and concentration are both high, a higher proportion of incident light is absorbed in the upper layers and less is available in the lower layers. Thus the surface layer will effectively screen the deeper layer against the penetration of UV light and the light intensity will fall off very rapidly with increasing depth of penetration of the material resulting in undercure or even no cure in the lower layers. An optimum concentration of photoinitiator therefore exists for a given layer thickness, below which the highest rate of cure cannot be attained and above which the overall rate of cure will decline. The intensity of light reaching a depth (x) decreases exponentially with the depth, x, according to the Beer-Lambert law:

$$I_x = I_o[1 - exp(-2.303\,Ci\,x)]$$

where Io is the intensity of incident light, ε is the molar extinction coefficient of the photoinitiator, and Ci is the concentration of the photoinitiator. Thus, the difference between I_x and I_o can be extreme for thick sections. Immediately after irradiation, the initiator will be consumed at a rate proportional to the local light intensity. Depending on the nature of the photolysis products, the consumption of the photoinitiator can either lead to an increase in light intensity in the underlying lays (if the photolysis product is more transparent at the irradiating wavelengths) or a reduction in light intensity (if the photolysis product is strongly absorbing).

The presence of oxygen in dental applications is unavoidable; therefore, the samples for measuring monomer conversion versus irradiation time were not deoxygenated. Oxygen generally acts to inhibit radical photopolymerizations by quenching the triplet excited photoinitiator as well as by reaction with radicals. Most (Type I) unimolecular photoinitiators, as it is the case of DMPA, have very short triplet lifetimes, therefore bimolecular triplet quenching is negligible under usual conditions.[10] Nevertheless oxygen inhibition is observed due to scavenging of free radicals. The addition of oxygen to a free radical to yield peroxy radicals competes successfully with the addition of monomer. Once the peroxy
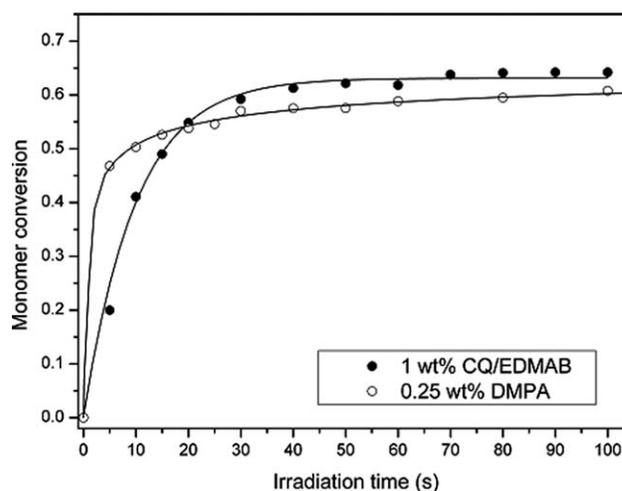
Figure 7 Polymerized samples photoactivated with DMPA or CQ/EDMAB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 Conversion versus irradiation time for BisTEG resin containing either 0.25 wt % of DMPA or 1 wt % CQ/EDMAB. The intensity of the 365 nm LED was 200 mW. The intensity of the 470 nm LED was 30 mW.

radicals form, the addition of monomer to these radicals proceeds so slowly that the chain reaction is virtually stopped. The effect is especially pronounced at surfaces and thin layers where the oxygen consumed is readily replaced by more diffusing in from the surrounding atmosphere.[24] The problem of air inhibition may be eliminated in conducting the photopolymerization in vacuum or in an inert atmosphere, such as nitrogen. Under these conditions, lower intensity light sources and lower photoinitiator concentrations may be used. On the other hand, the use of high intensity sources is a method commonly used to overcome or at least reduce oxygen inhibition. That is clearly seen in the conversion profiles in samples containing 0.125 wt % DMPA irradiated at 95 or 200 mW (Fig. 6).

Efficiency of DMPA compared with that of CQ/amine

The efficiency of the DMPA was compared with that of the CQ/amine pair by monitoring the progress of the polymerization reaction versus the irradiation time. CQ was used in combination with equimolar proportion of ethyl-4-dimethylaminobenzoate (EDMAB), which showed an optimum polymerization rate.[5] Polymerized samples of BisTEG resins photoactivated with CQ/EDMAB or DMPA are shown in Figure 7. Figures 8 and 9 compare the monomer conversion versus irradiation time in BisTEG and UDMA resins activated with either 0.25 wt % DMPA or 1 wt % CQ/EDMAB respectively. During the first 15-s irradiation, the polymerization of BisTEG photoactivated with DMPA (Fig. 8) progressed at higher rate compared with that photoactivated with CQ/EDMAB. After 5 s irradiation, the conversion of BisTEG containing DMPA was

0.45 while the value in the monomer containing CQ/EDMAB was 0.2. At 20 s irradiation the reversed trend was observed and the conversion of BisTEG photoactivated with CQ/EDMAB was slightly greater than that of BisTEG containing DMPA. On the other hand, the polymerization rate of UDMA photoinitiated with CQ/EDMAB was faster than that of the UDMA photoactivated with DMPA (Fig. 9). After 10-s irradiation, the conversion of UDMA containing DMPA was 0.65 while the value in UDMA containing CQ/EDMAB was 0.56. These trends can be explained in terms of the mechanisms of initiation of each photoinitiator. Figure 5 shows that the photolysis of DMPA involves Norrish type I unimolecular photocleavage to give initiating
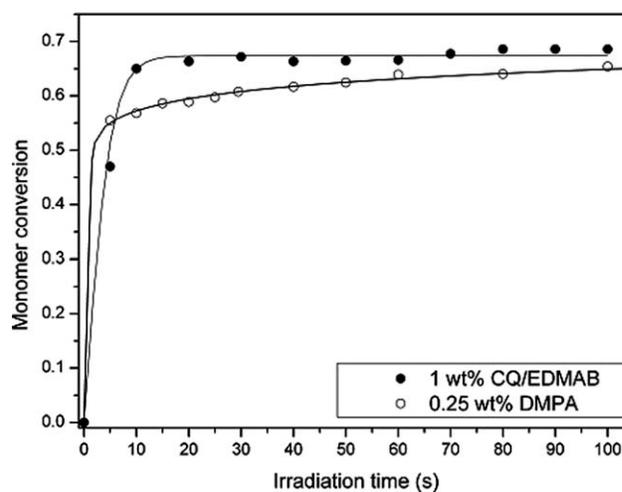

Figure 9 Conversion versus irradiation time for UDMA resin containing either 0.25 wt % of DMPA or 1 wt % CQ/EDMAB. The intensity of the 365 nm LED was 200 mW. The intensity of the 470 nm LED was 30 mW.

TABLE I
### Conversion after 100-s Irradiation of BisTEG Resin Containing DMPA or CQ/EDMAB

System	NIR	ATR irradiated surface	ATR nonirradiated surface
0.25 wt % DMPA	0.54	0.45	0.37
1 wt % CQ/EDMAB	0.57	0.47	0.40

The intensity of the UV and visible LED was 200 mW and 30 mW, respectively.

radicals. The mechanism of photodecomposition of CQ/amine systems has been reported in previous research,[1,3] 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 intersystem crossing:

$$CQ + h\upsilon \rightarrow CQ^*$$
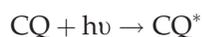
CQ* can react with hydrogen donors such as tertiary amines (AH), to generate radicals by electron and proton transfer through a short lived charge-transfer intermediate complex (CTC) to give pinacol and amine derived radicals:

$$CQ^* + AH \rightarrow [CQ..AH]^*(CTC)$$
$$CTC \rightarrow CQH^{\bullet} + A^{\bullet}$$
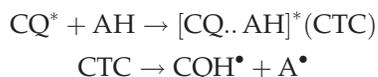
UDMA possesses labile hydrogen atoms in its structure, i.e., two methylene units adjacent to the carbamate functionality. Thus, UDMA reacts with the CQ* to give UDMA derived radicals, which are highly reactive toward double bonds.[16] This is supported by the observation that UDMA photosensitized with CQ polymerizes in the absence of amine.[16] This feature contrasts with the lack of polymerization observed in BisTEG photosensitized with CQ in the absence of amine.[16] From results presented in Figures 8 and 9 it emerges that under the experimental conditions used in this study, DMPA photoinitiates the polymerization of BisTEG and UDMA monomers and the efficiency of this process is comparable to that of the CQ/amine pair.

In practice, the light absorption of photoinitiators should correlate with the spectral emission profiles of light curing units. Only those wavelengths where the photosensitizer strongly absorbs are useful for photopolymerization. The efficiency that a particular photoinitiator can utilize the radiation of a given light source to produce an excited state is given by the photon absorption efficiency (PAE)[25]:

$$PAE = I(\lambda)\ \varepsilon(\lambda)\ Ci$$

According to the molar absorption coefficients and the concentration of DMPA and CQ at 365 nm and

470 nm, and the light intensity of each LED, the PAE of DMPA and CQ was 286 and 86, respectively. Therefore, to achieve comparable rates of polymerization in resins photoinitiated with 0.25 wt % DMPA or 1 wt % CQ/EDMAB, the intensity of the 365 nm source (200 mW) was about seven times the intensity of the 470 nm source (30 mW). The rate of photoinitiation depends on several factors such as the constant for the deactivation of excited states of the photoinitiator, the fraction of the exciplets that leads to radicals, and the proportion of these radicals that add to the monomer. In addition, the filtering or screening effect caused by the photoproduct resulting from irradiation of photoinitiators must be taken into account. CQ photobleaches by conversion to moieties transparent at the wavelength of interest and, therefore, the incident radiation progressively penetrates deeper into the sample.[1,16–17] On the contrary, the absorbance of resins photoactivated with DMPA increases monotonically with irradiation due to the appearance of light absorbing compounds (Fig. 3). As a result, the light fails to reach the deeper layers of the sample because the absorbing species nearest to the light source absorb part of it. The overall effect of light screening is a reduced photoinitiation rate and double bond conversion along the irradiation path. However, this effect is compensated by the use of irradiation sources of higher intensity; which increase the initiation rate by increasing the production of primary radicals such that it becomes much greater than their consumption by oxygen. Figure 6 shows an induction time in the polymerization of BisTEG with a low intensity LED (95 mW). As it was described previously, if oxygen is present, the polymerization cannot proceed until the propagation reaction competes with the inhibition reaction. In resins photoactivated with CQ/EDMAB an induction time is not observed because amines suppress oxygen inhibition by the consumption of oxygen in a radical chain process:[3,4]

$$A^{\bullet} + O_2 \rightarrow AOO^{\bullet}$$
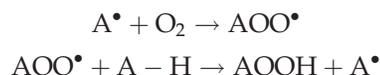$$AOO^{\bullet} + A-H \rightarrow AOOH + A^{\bullet}$$

Table I shows the monomer conversion at both the irradiated and the nonirradiated surfaces measured by ATR. The lower conversion of methacrylate groups at the irradiated surface (ATR measurements) compared to that in the core of the sample (transmission measurements) may be attributed to thermal effects. During polymerization process, higher temperature is reached in the core of the sample compared to the sides where thermal exchanges are favored, leading to higher extent of conversion in the center of the sample. As a result of light attenuation through sample thickness, the values of conversion at the irradiated surfaces are about

17.5 and 20% higher than those at the nonirradiated surfaces in monomer samples photoactivated with 1 wt % CQ/EDMAB and 0.25 wt % DMPA respectively. Results presented in Table I show that the conversion profile along the irradiation path is a resin photoactivated with 0.25 wt % DMPA is similar to that photoactivated with 1 wt % CQ/EDMAB. Again, the similar value of conversion is attributed to the use of a UV LED of higher intensity than that of the visible LED; which compensates the light screening effect in resins photoactivated with DMPA.

From results presented in this study it emerges that DMPA exhibits properties that make it attractive as photoinitiator of dental composites. It exhibits a strong absorption at 340 nm ($265 \text{ L mol}^{-1} \text{ cm}^{-1}$), is an efficient photoinitiator of methacrylate monomers for thick sections ($\approx$2 mm) and is colorless. It is worth mentioning that biocompatibility requirements have limited the number of compounds which can be used as coinitiators of CQ and research has therefore been directed towards the use of amines with reduced toxicity.[25] Thus, an additional benefit associated to the use of DMPA is that it does not require the presence of amine as coinitiator.

CONCLUSIONS

DMPA is an efficient photoinitiator for thick sections ($\approx$2 mm) because a fast reaction and high conversions are obtained with concentrations as low as 0.25 wt % DMPA.

The rate of photopolymerization increased with the incident light intensity, but not with initiator concentration.

An optimum concentration of photoinitiator therefore exists for a given layer thickness, below which the highest rate of cure cannot be attained and above which the overall rate of cure will decline. The polymerization rate increased when the DMPA content increased from 0.125 wt % to 0.25 wt % and decreased with further addition of DMPA. This is attributed to the screening effect caused by excessive levels of DMPA.

The consumption of DMPA under UV irradiation was accompanied by the appearance of light absorbing photoproducts. Because the absorbing species nearest to the light source absorb part of it, the light fails to reach the deeper layers of the sample. The overall effect of light screening is a reduced photoinitiation rate and double bond conversion along the irradiation path. This effect was compensated by the use of irradiation sources of higher intensity; which increased the initiation rate by increasing the production of primary radicals.

Comparable rates of polymerization in resins photoinitiated with 0.25 wt % DMPA or 1 wt % CQ/EDMAB were achieved by using UV sources of intensity about seven times the intensity of the visible source.

DMPA is colorless and it does not require the presence of amine as coinitiator. These properties make DMPA attractive as photoinitiator of dental composites.

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