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# Light absorbing products during polymerization of methacrylate monomers photoinitiated with phenyl-1, 2-propanedione/amine

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ABSTRACT

The efficiency of a novel photoinitiator, phenyl-1,2-propanedione (PPD), of potential use in dentistry was assessed and the performance of PPD was compared with that of traditional photoinitiators used in dental restorative resins. The photodecomposition of PPD and the polymerization of acrylic monomers photoinitiated by PPD in the presence of dimethylamino ethylmethacrylate, ethyl-4-dimethylaminobenzoate and 4-(*N*,*N*-dimethylamino) phenethyl alcohol have been investigated. The photodecomposition of PPD/amine systems in acetonitrile and methacrylate monomers under irradiation at $\lambda = 395$ nm resulted in the appearance of light absorbing by-photoproducts. The absorbing species displayed absorption spectra which overlapped that of PPD and were markedly dependent on the amine structure. Irradiation of methacrylate monomers containing PPD in combination with 4-(*N*,*N*-dimethylamino) phenethyl alcohol resulted in a continuous increase in absorbance. Since the production of photoproducts increases with irradiation time, the light that reaches the deepest layers decreases. The effect of light screening is a reduced overall photoinitiation rate and consequently a reduced double bond conversion. From the results presented it emerges that the selection of the amine to be used in combination with PPD is a crucial step in order to optimize the efficiency of the PPD/amine photoinitiator system.



## 1. Introduction

Light-activated dental composites are widely used in clinical restorative dentistry. Photopolymerization is commonly activated by visible light, using an initiator system comprising a α-diketone in combination with an amine reducing agent. The camphorquinone (CQ)/amine photo-initiating system is the most common one used in the current photoactivated dental materials [1–8]. However, CQ is inherently yellow which causes problems in colour matching to natural teeth [9]. This feature limits the addition of camphorquinone to the composites, since it can turn them excessively yellow, hazarding the final aesthetic result. Efforts to enhance the quality of the polymer matrix have investigated alternative photosensitizers suitable for dental resins [10–12].

Photopolymerization at high initiator concentration is attractive in dental practice because as initiator concentration increases, polymerization rates typically increase. However, the absorption of light by the initiator causes attenuation of the curing light along the beam direction. Light attenuation results in heterogeneous polymerized resins due to the different initiation rates occurring throughout the depth of the sample [13–16]. On the other hand, in polymerizing systems with photobleaching initiators, the initiator is consumed at a rate proportional to the local light intensity, which permits the cure of thicker layers compared with a non-photobleaching system. Therefore, for a thick-section cure; as it is the case of dental restorative resins; it is advantageous to use photobleaching initiators in which light absorption by the initiator products is lower than that by the original photoinitiator molecule, thereby allowing more light to pass through the system. In this context, the study of photobleaching characteristics of photoinitiators used for the polymerization of thick layers is the essential step for a better understanding of the photoinitiation process [13–16].

Differently from CQ, which has been widely studied, reports concerning the photopolymerization of dental resins photoinitiated with PPD are scarce [10–12]. The purpose of the present study was to investigate the photodecomposition of PPD in combination with different amines. The performance of the PPD photoinitiator for the photopolymerization of multifunctional methacrylate monomers was compared with that of the traditional CQ. Light sources were selected in order to achieve an optimum overlap between the spectral irradiance of the curing units and the molar absorption coefficient distribution of the photoinitiators.

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## 2. Experimental

### 2.1. Materials

The resins were formulated from blends of {2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane} (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) at mass fractions 70:30 bis-GMA/TEGDMA. bis-GMA (Esstech, Essington, PA) and TEGDMA (Aldrich) were used as-received. The resins were activated for UV and visible light polymerization by the addition of PPD (Aldrich) or CQ (Aldrich) respectively. The amines used as reducing agent were dimethylamino ethylmethacrylate (DMAEMA, Aldrich), ethyl-4-dimethylaminobenzoate (EDMAB, Aldrich) and 4-(*N*,*N*-dimethylamino) phenethyl alcohol (DMPOH, Aldrich). The solvent acetonitrile (Merk) was employed as-received. The structure of the photoinitiator systems is depicted in Scheme 1.

### 2.2. Light sources

The light sources were assembled from light emitting diodes (Led) with its irradiance centred at 470 nm (LED, OTLH-0090, Optotech. Inc.) and 395 nm (OTLH-0360). The Leds were selected taking into account that the CQ and PPD photoactivators have absorption peaks at 470 and 395 nm respectively. The emission spectrum of the Led source was measured with a calibrated CVI-monochromator (Digikrom 480) and a Si-photodetector. 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. UV Leds having three different irradiances were used: 31.8, 71.3 and 115.8 mW/cm$^2$. The irradiance of the visible blue Led was 38.2 mW/cm$^2$.

### 2.3. Photolyses of CQ and PPD

The photodecomposition of the photoinitiators was followed by the changes in absorbance at the wavelength of their maximum absorption. The absorption spectra of CQ and PPD were measured with an UV–vis spectrophotometer 1601PC Shimadzu at room temperature (approximately 20 °C) under air atmosphere in both acetonitrile and bis-GMA/TEGDMA monomers. Bleaching experiments in acetonitrile were carried out in 1 mm thick quartz cuvettes. The concentration of PPD or CQ in acetonitrile was 0.3 M. Photodecomposition studies in bis-GMA/TEGDMA monomers were carried out in 3 ± 0.5 mm thick samples sandwiched between two disposable 3.3 mm thick quartz plates. The concentration of PPD in bis-GMA/TEGDMA monomers was 0.07 M, which is in the range of photoinitiators concentration used in practice in order to optimize polymerization times. UV–vis measurements indicated that the amines used as reducing agents do not absorb in the absorption range of the PPD and CQ.

### 2.4. Measurement of double bond conversion

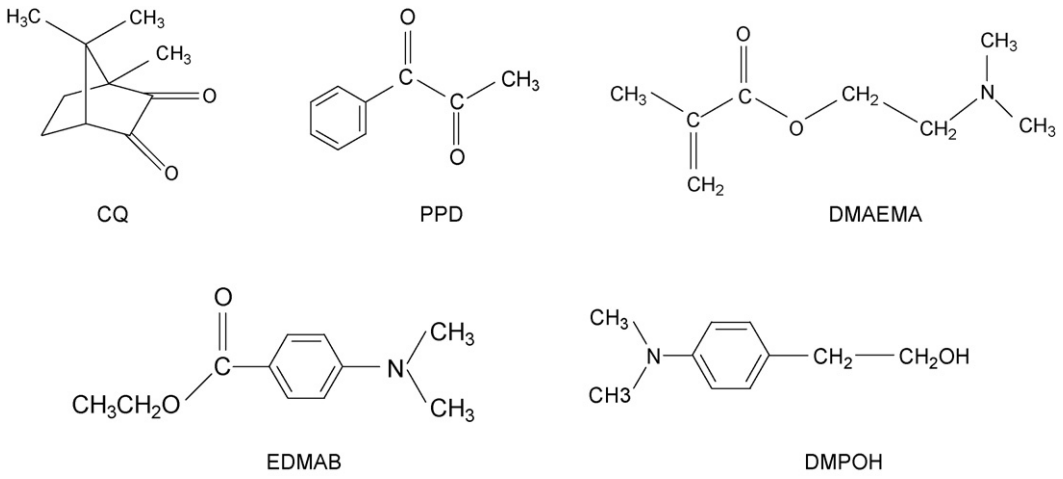
FTIR spectra were acquired with a Genesis II Mattson FT-IR (Madison, WI). The NIR spectra were acquired over the range 4500–7000 cm$^{-1}$ from 16 co-added scans at 2 cm$^{-1}$ resolution. Unfilled resins were sandwiched between two glass plates separated by a 3 mm rectangular rubber spacer and were 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 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$^{-1}$ [8,17]. Two replicates of each of the resins were used in the measurement of conversion.

## 3. Results and discussion

### 3.1. Overlap of the irradiance of the light source and the absorption spectra of CQ and PPD

In practice, the light absorption of photoinitiators should correlate with the spectral emission profiles of light curing units compared on an equivalent basis. Only those wavelengths where the photosensitizer strongly absorbs are useful for the photopolymerization. UV and visible Leds were selected in order to obtain an optimum overlap between the spectral irradiance of the curing units and the molar absorption coefficients of the photoinitiators. Fig. 1 shows the spectral distribution of the light sources along with the molar absorption coefficient distribution of CQ and PPD.

The efficiency of a given curing unit to excite a given photoinitiator, is a function of the spectral irradiance of the curing unit, $I(\lambda)$, and the molar absorption coefficient distribution of the photoinitiator $\varepsilon(\lambda)$. This quantity, termed the photon absorption efficiency (PAE), is assessed as follows [18]: if $I(\lambda)$ (W/cm$^2$) is the energy incident to an area $A$ per unit time, then, the number of photons of a given wavelength, $N(\lambda)$, is equal to the irradiance of the source at




**Scheme 1.** Structure of the photoinitiator systems studied.

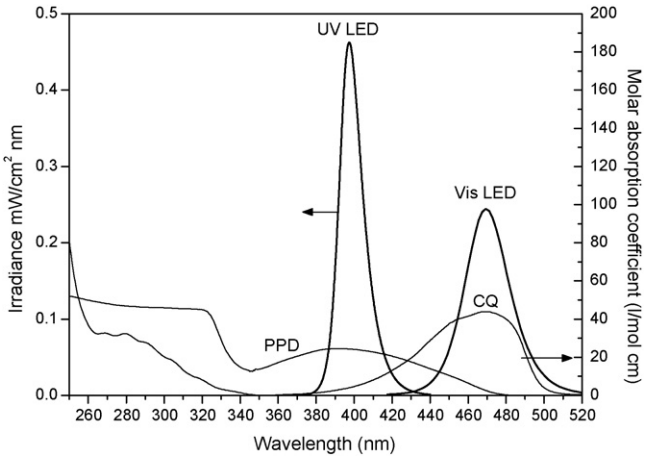



**Fig. 1.** Light irradiance of the UV and visible Led units, and molar extinction coefficients of the photoinitiators PPD and CQ. The values of $\varepsilon$ are 27.8 and 42 l mol$^{-1}$ cm$^{-1}$ for PPD and CQ respectively.

the wavelength $\lambda$ divided by the energy of one photon:

$$N(\lambda) = \frac{I(\lambda)\lambda}{hc} \quad \text{and} \quad N_t = \sum_{\lambda_1}^{\lambda_2} \frac{I(\lambda)\lambda}{hc}\, d\lambda \tag{1}$$

where $h$ is the Plank constant, $c$ is the speed of light, $\lambda_1$ and $\lambda_2$ are the limits of the wavelength emission of the source and $hc/\lambda$ is the energy of one photon. The total number of photons of the incident light, $N_t$, is given by the summation of the photons produced at each wavelength. For radiation passing through a layer of sample of thickness $dx$ containing a concentration of photoinitiator PI (mol/cm$^3$), the fraction of absorbed photons ($f_{abs}$) is

$$f_{abs} = 1 - 10^{-\varepsilon(\lambda)\mathrm{PI}dx} \approx 2.302\varepsilon(\lambda)\mathrm{PI}\ dx \tag{2}$$

The right side in Eq. (2) corresponds to the simplification for an infinitely thin layer. Hence, the theoretical number of photons available to be absorbed by the sample per unit time in the volume $A\,dx$ is obtained by combining Eqs. (1) and (2) to give Eq. (3) where $N_{av}$ is the Avogadro's number.

$$\mathrm{PAE} = \frac{2.302\mathrm{PI}N_{av}}{hc} \int_{\lambda_1}^{\lambda_2} I(\lambda)\varepsilon(\lambda)\lambda\, d\lambda \tag{3}$$

This equation provides a means of measuring the efficiency that a particular photoinitiator can utilize the radiation of a given light source to produce an excited state. If these excited states all produce radicals then this is the photocuring efficiency of the source-initiator pair. The visible Led emits at longer wavelengths than the UV Led and the absorption coefficient value of CQ is higher than that of PPD. Therefore, this difference was compensated in photopolymerization studies by using Led sources of different intensities. The values of light intensity of each source were adjusted in order to obtain equivalent values of PAE for both Led/photoinitiator pair.

### 3.2. Photolysis of the photoinitiators in acetonitrile

The mechanism of bimolecular photoinitiation of ketones has been extensively studied and is briefly described here. In these systems, the absorption of radiation promotes the carbonyl group to an excited singlet state. This excited state may return to the ground state by fluorescence or a radiationless transition or it may decompose to another species. The excited singlet may also undergo intersystem crossing to the reactive triplet state PI*.

$$\mathrm{PI} + h\nu \rightarrow \mathrm{PI}* \tag{4}$$

Free radicals are produced simultaneously from different reactions. The PI* acts in combinations with hydrogen donors as tertiary amines (AH), to generate radicals according to a mechanism involving electron and proton transfer through a short-lived charge-transfer intermediate complex (CTC).

$$\mathrm{PI}* + \mathrm{AH} \rightarrow [\mathrm{PI}\cdots\mathrm{AH}]*(\mathrm{CTC}) \tag{5}$$

$$\mathrm{CTC} \rightarrow \mathrm{PIH}^{\bullet} + \mathrm{A}^{\bullet} \tag{6}$$

Alternatively, hydrogen abstraction from a donor (DH) by the PI* results in ketyl and donor derived radicals.

$$\mathrm{PI}* + \mathrm{DH} \rightarrow \mathrm{PIH}^{\bullet} + \mathrm{D}^{\bullet} \tag{7}$$

Depending on the type of initiator and co-initiator, the reaction follows one of these pathways and under certain conditions both mechanisms may be competitively involved.

The decomposition of the PPD and CQ photoinitiators was assessed by monitoring the decrease in absorbance at the wavelength of their maximum absorption. Fig. 2 shows typical plots of the spectral changes during irradiation of PPD in combination with DMAEMA, EDMAB and DMPOH respectively. UV–vis spectra showed that except the PPD/DMPOH system, both CQ and PPD decompose by irradiation giving as result mixtures with decreased absorbance. The band at 467 nm in the CQ spectra decreased monotonically and a complete photobleaching after 90 min irradiation was observed. On the other hand, the consumption of PPD was accompanied by the appearance of a light absorbing photoproduct. Fig. 2 shows that a new band in the near UV appeared, with isosbestic points at 366 and 395 nm for PPD/DMAEMA and PPD/EDMAB respectively whereas the absorbance of PPD/DMPOH increased monotonically with irradiation time.

Differently from CQ, which has been widely studied, reports concerning the photodecomposition of PPD are scarce. Recently, Lopes et al. [19] studied the UV-induced decarbonylation of PPD at $\lambda$ equal to 235 nm. The authors found that upon irradiation, PPD is excited to an excited singlet state and converted, by intersystem crossing, into the triplet state, in which the homolytic cleavage of the inter-carbonyl C–C bond occurred as in the case of the Norrish type I mechanism. The primary photoproducts are then the benzoyl and acetyl radicals. The acetyl radical is considerably less stable than the benzoyl radical and decomposes into $CH_3$ radical and CO upon irradiation. On the other hand, results presented in Fig. 2 demonstrate that similarly to CQ, the photodecomposition of PPD under irradiation at 395 nm is promoted by tertiary amines. In fact, irradiation for 20 min of PPD in acetonitrile without added amine produced no change in the absorption spectrum. This supports the view that, under irradiation at 395 nm, radical production from photo-excited PPD proceeds mainly by a redox mechanism rather than by direct dissociation.

The rate of photodecomposition of each photoinitiator was assessed from measurements of absorbance vs. irradiation time. The variation of the photoinitiator concentration with irradiation time is given by [1,13]:

$$-\frac{\partial \mathrm{PI}(x,t)}{\partial t} = 2.302\Phi\varepsilon I(x,t)\mathrm{PI}(x,t) \tag{8}$$

where PI is the spatiotemporal variation of the photoinitiator concentration, $x$ is the position along the sample thickness, $\Phi$ is the quantum yield of the photoinitiator consumption, and $I(x,t)$ is the spatiotemporal variation of the light intensity. It is worth noting that for an infinitely thin layer $I(x,t) = I_0$, the incident intensity, and $\mathrm{PI}(x,t) = \mathrm{PI}(t)$ is only function of time, therefore the product $2.302\varepsilon I_0\Phi$ is the pseudo-first-order constant rate of decomposition of the photoinitiator. However, if light attenuation cannot be disregarded $I(x,t)$ decreases with sample thickness according to the

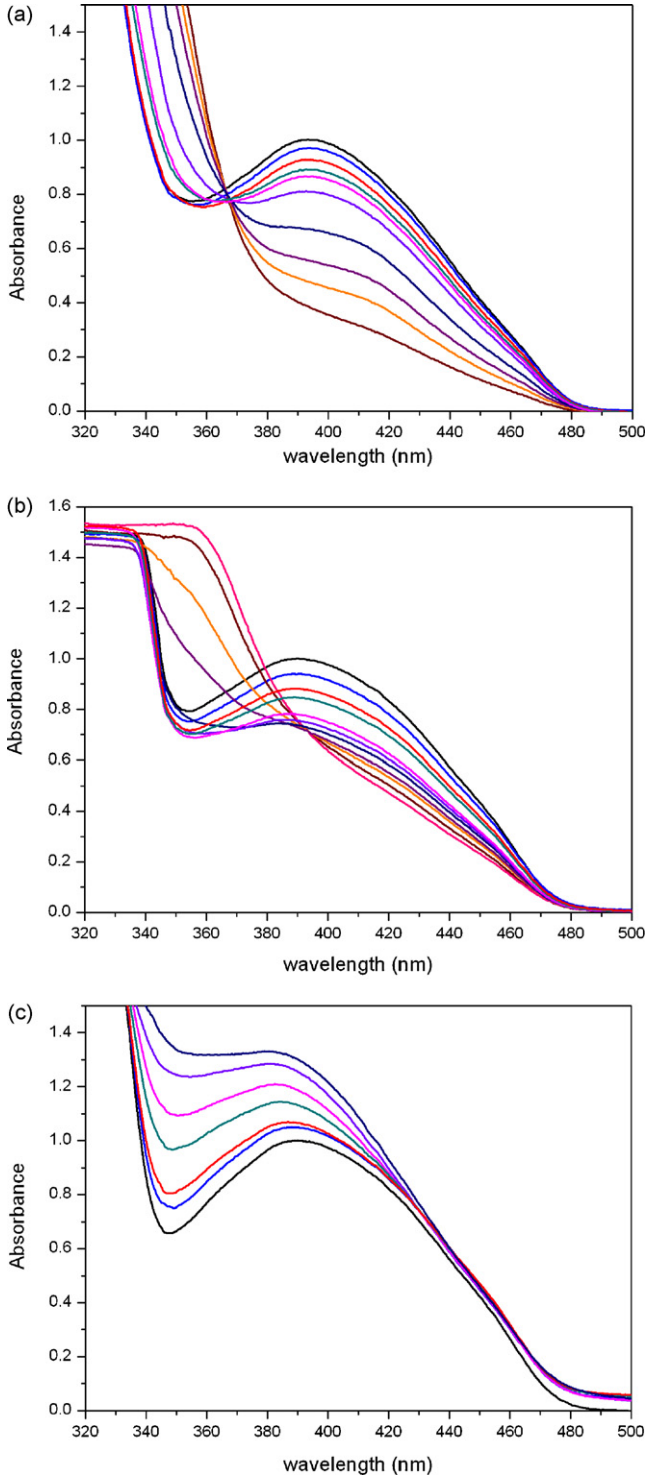



**Fig. 2.** (a) Typical spectral changes during the irradiation of solutions PPD/DMAEMA in cetonitrile with the UV Led at 31.8 mW/cm$^2$. The DMAEMA/PPD molar ratio was 1. The irradiation times were 0, 10, 20, 60, 70, 130, 290, 450, 770 and 1090 s. (b) Typical spectral changes during the irradiation of solutions PPD/EDMAB in acetonitrile with the UV Led at 31.8 mW/cm$^2$. The EDMAB/PPD molar ratio was 1. The irradiation times were 0, 30, 90, 150, 210, 270, 330, 390, 510, 630, 750 and 870 s. (c) Typical spectral changes during the irradiation of solutions PPD/DMPOH in acetonitrile with the UV Led at 31.8 mW/cm$^2$. The DMPOH/PPD molar ratio was 1. The irradiation times were 0, 40, 80, 240, 400, 720 and 1460 s.

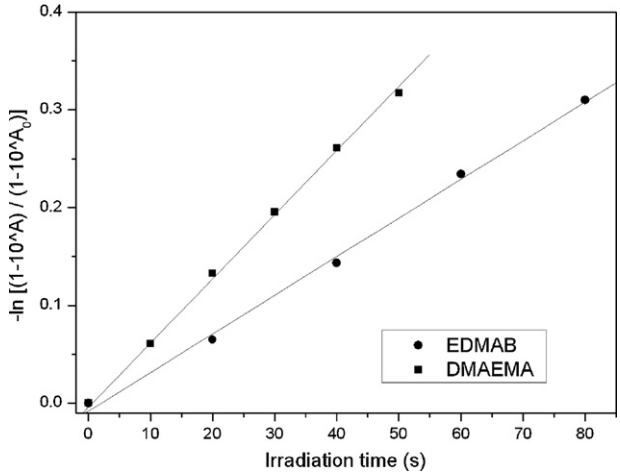



**Fig. 3.** Typical plots of Eq. (11) for PPD in combination with DMAEMA and EDMAB.

integrated form of the Lambert-Beer law.

$$I(x,t) = I_0 \exp\left[-\sum_{i=1}^{N}\int 2.302\varepsilon_i C_i(x,t)dx\right] \quad (9)$$

where $\varepsilon_i$ and $C_i$ are the molar absorption coefficient and the concentration of the $i$ light absorbing compound respectively. If only the photoinitiator absorbs then the concentration of photoinitiator averaged over the sample thickness, PI, is given by the following analytic solution of Eqs. (8) and (9), where $x$ is the sample thickness [13]:

$$\frac{\mathrm{PI}}{\mathrm{PI}_0} = \frac{1}{2.302\varepsilon \mathrm{PI}_0 x}\ \ln[1-(1-e^{2.302\varepsilon \mathrm{PI}_0 x})e^{-\varepsilon\Phi I_0 t}] \quad (10)$$

and

$$-\ln\left[\frac{1-e^{2.302\varepsilon \mathrm{PI} x}}{1-e^{2.302\varepsilon \mathrm{PI}_0 x}}\right] = 2.302\Phi\varepsilon I_0 t \quad (11)$$

Thus, a plot of Eq. (11) will give a straight line which slope is proportional to the pseudo-first-order rate constant for the photoinitiator consumption. The analysis for the PPD/amine systems is complicated by the fact that light absorbing compounds, which overlaps with the PPD spectra, are produced during irradiation. In order to minimize interferences due to light absorption by the photoproduct, only the absorbance values measured during the initial irradiation were used to calculate the rate of decomposition of PPD. Plots of Eq. (11) for PPD in combination with different amines are depicted in Fig. 3 and values of the rate constant for the photoinitiators decomposition are presented in Table 1.

A satisfactory fit of experimental measurements of absorbance to a first-order kinetics for the decomposition of PPD is observed. In addition, measurements of decomposition rate of PPD/DMAEMA and PPD/EDMAB carried out at different light irradiances indicate that similarly to direct photolysis processes, the decomposition rate of PPD increased linearly with $I_0$ (Table 2).

**Table 1**
Apparent first-order constant rate for PPD and CQ consumption in combination with different amines.

| Amine | PPD | CQ |
|---|---|---|
| DMAEMA | 0.0071 | 0.0016 |
| EDMAB | 0.0038 | 0.0005 |
| DMPOH | – | 0.0003 |

The irradiances the UV and Vis Leds sources were 71.3 and 38.2 mW/cm$^2$ respectively. The values are in s$^{-1}$.

**Table 2**
Apparent first-order constant rate for PPD/DMAEMA and PPD/EDMAB consumption as a function of light irradiance, $I_0$.

| $I_0$ (mW) | EDMAB | DMAEMA |
|---|---|---|
| 25 | 0.00235 | 0.0038 |
| 56 | 0.0038 | 0.0071 |
| 91 | 0.0067 | 0.0121 |

The values are in $s^{-1}$.

These results are in agreement with trends reported by Cook [1] for the photodecomposition of CQ/amine systems. The effect of amine concentration on the decomposition rate of PPD was examined by measuring the PPD consumption in samples with different PPD/DMAEMA molar proportions, *r*, irradiated under identical conditions. Values of the decomposition rate presented in Table 3 demonstrate that for the range of amine concentration studied, the rate of decrease in absorbance was independent of the amine concentration. This trend is similar to that reported by Cook [1] for the photodecomposition of CQ/amine systems. The author found that at low amine concentration, the rate of CQ decomposition was dependent on the amine concentration and reactivity whereas at high concentrations of amine, the rate of CQ consumption was independent of amine concentration and only depended on the amine reactivity. According with the kinetic scheme proposed by the author, if the intersystem crossing of the excited singlet to the triplet state is the rate determining step, the resulting kinetic expression is simplified and the resulting expression for the consumption of CQ is independent of the amine concentration.

The decomposition of the PPD in combination with different amines in acetonitrile solvent is faster than that of CQ indicating a more efficient photochemical event (Table 1). In fact, the rate constant of the PPD/DMAEMA pair was four times greater than that of the CQ/DMAEMA while the value for the PPD/EDMAB was eight times greater than that of the CQ/EDMAB. In addition, results presented in Table 1 indicate that the consumption of CQ and PPD in combination with DMAEMA is more rapid than that of the photoinitiators combined with EDMAB. For substrates possessing both high ionization potential and strong bond energy such as acetonitrile, hydrogen abstraction is extremely inefficient and the photodecomposition of the ketones in the presence of amines takes place through a short-lived charge-transfer intermediate complex. The efficiency of this mechanism is enhanced for amines which readily undergo electron transference and which are capable of transferring a proton. Thus, the difference in the decomposition rate measured with different amines is consistent with the fact that, due to a great localization of the free electron pair of the amino group, tertiary aliphatic amines are more efficient electron donors than aromatic amines.

### 3.3. Photolysis of the photoinitiators in bis-GMA/TEGDMA

Since the initiator decomposition is assisted by association with tertiary amines and involves some ionic intermediates, the rate of reaction is expected to be affected by the polarity of the solvent. Thus, the photodecomposition of each photoinitiator was studied in bis-GMA/TEGDMA resin. Fig. 4 shows typical plots of the spectral

**Table 3**
Apparent first-order constant rate for PPD consumption, *k*, in combination with different PPD/DMAEMA molar proportions, *r*.

| *r* | $k$ ($s^{-1}$) |
|---|---|
| 0.25 | 0.0116 |
| 0.5 | 0.0122 |
| 1 | 0.0118 |

The concentration of PPD was 0.3 M. The irradiance of the UV Led was 115.8 mW/cm$^2$.

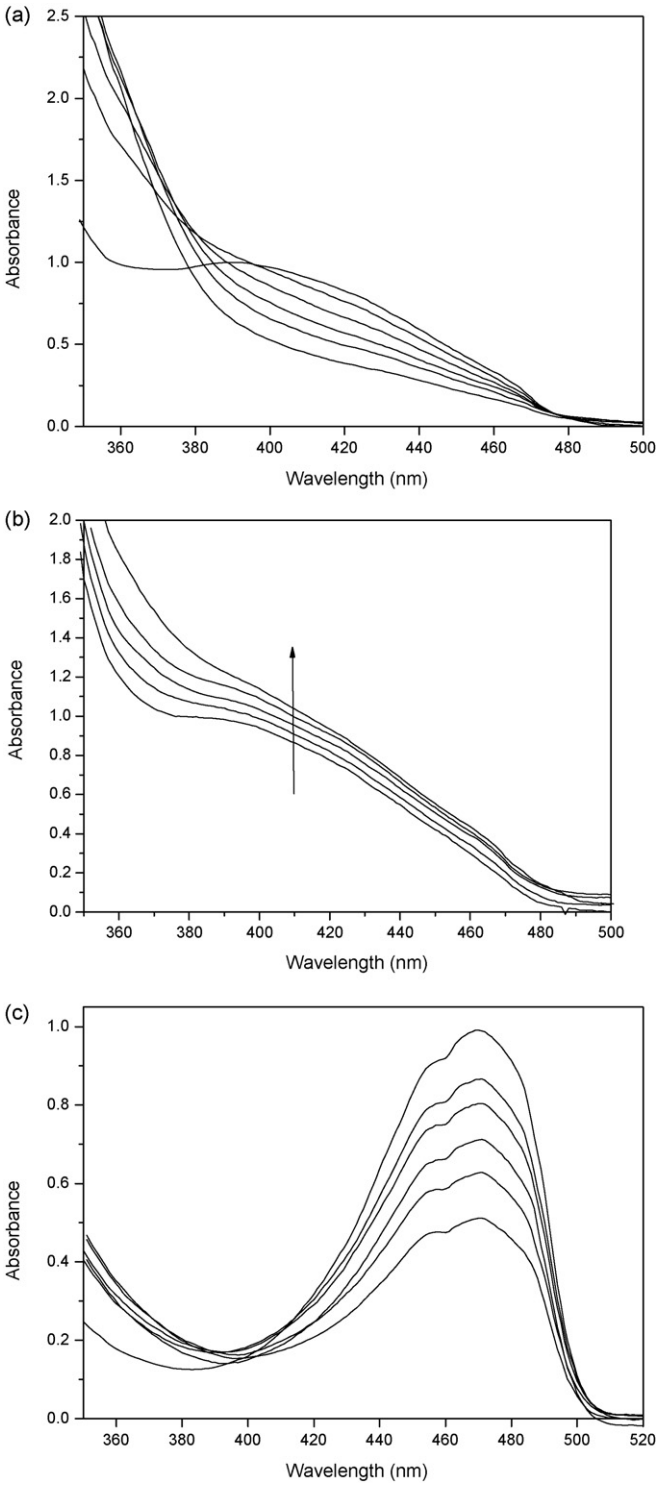



**Fig. 4.** (a) Typical spectral changes during the irradiation of solutions PPD/DMAEMA in bis-GMA/TEGDMA with the UV Led at 31.8 mW/cm$^2$. The DMAEMA/PPD molar ratio was 1. The irradiation times were 0, 60, 120, 240, 300 and 420 s. (b) Typical spectral changes during the irradiation of solutions PPD/DMPOH in bis-GMA/TEGDMA with the UV Led at 31.8 mW/cm$^2$. The DMPOH/PPD molar ratio was. The irradiation times were 0, 60, 120, 240, and 300 s. (c) Typical spectral changes during the irradiation of solutions CQ/DMAEMA in bis-GMA/TEGDMA with the Vis Led at 38.2 mW/cm$^2$. The DMAEMA/CQ molar ratio was 1. The irradiation times were 0, 80, 160, 320, 800 and 1120 s.

changes during irradiation of PPD in combination with DMAEMA and DMPOH. Spectral changes for the CQ/DMAEMA are also shown for comparison.

Similarly to studies in acetonitrile, the PPD/DMPOH pair showed a continuous increase in absorbance with irradiation time. Polymerizing resins containing CQ/amine irradiated during prolonged periods of time were transparent and colourless whereas the cured resins containing PPD/amine remained yellow.

In the reduction of photoinitiators through the electron transfer process, two sub-steps can be distinguished, namely, electron transfer with the formation of a donor–acceptor charge transfer complex and the decay of the complex by proton transfer. In the encounter complex the reactants must reorient themselves until a favourable geometry is reached. Thus, the photo-induced electron transference reaction of the initiator with amines depends on the mutual orientation of the reactants, the rate constant of diffusion of the reactants and the rate constant of dissociation of the encounter complex. All these factors are highly dependent on the viscosity or rigidity of the medium. Acetonitrile is a low viscosity solvent and hydrogen abstraction in this particular solvent is extremely inefficient, therefore, disregarding diffusion effects, the photoreduction process occurs by electron transfer through a charge transfer intermediate complex and the efficiency of this mechanism is dictated by the amine reactivity. In contrast, in photobleaching measurements by irradiation of monomer samples, the polymerizing resin is transformed from a viscous liquid to a rigid glass. Because the photo-induced electron transference is strongly diffusion controlled, its effectiveness decreases as the polymerization progresses and then, the photoinitiator 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, hydrogen abstraction from monomer structures and electron transference of the photoinitiator with the amine are competitively involved in the photoreduction of CQ and PPD. TEGDMA contains three oxyethylene units which may serve as a source of abstractable hydrogens. Radical formation is then possible because the lowest excited triplet state of PPD and CQ has n, $\pi^*$ character which enables it to react efficiently with ethers [20]:

$$-O-CH_2-CH_2- + PPD*/CQ* \rightarrow -O-C^{\bullet}H-CH_2- + PPD^{\bullet}H/CQ^{\bullet}H$$

### 3.4. Double bond conversion vs. irradiation time

The progress of double bond conversion vs. irradiation time was measured in bis-GMA/TEGDMA (70:30) containing 0.07 mol/l (around 1 wt.%) of either PPD or CQ in combination with equal molar ratios of amine. This concentration of photoinitiator is commonly used in dental resins formulations in order to obtain polymerization rates appropriate to clinical practice. UV and Vis Led sources of 71.3 and 38.2 mW/cm$^2$ respectively were used in order to compensate the lower value of the molar absorption coefficient of PPD. In that way, equivalent values of PAE for each Led/photoinitiator pair were achieved.

It is seen that the radicals produced by the photodecomposition of CQ or PPD in the absence of amine induce polymerization. In the absence of any co-initiator, the hydrogen-donor molecule is the monomer itself; thus, the polymerization occurs due to the presence of labile hydrogen atoms of the TEGDMA monomer. A significantly higher degree of polymerization in the resins containing PPD compared with CQ is observed in Fig. 5. It is well known that the ketyl radical derived from the CQ is an inefficient photoinitiator because of steric hindrance effect [1,2]. On the other hand, PPD can form two different ketyl radicals. The radical derived from the carbonyl group attached to the aromatic ring is expected to exist

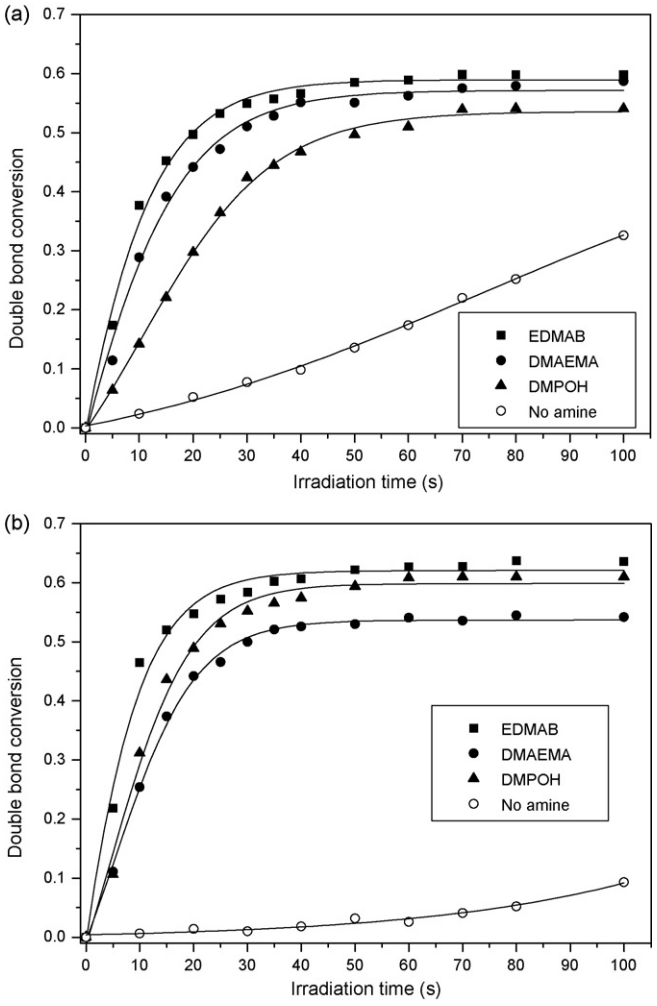



**Fig. 5.** (a) Conversion vs. irradiation time for bis-GMA/TEGDMA resins containing 0.07 mol/l PPD in combination with equimolar proportion of DMAEMA, EDMAB and DMPOH and in absence of added amine. The irradiance of the UV Led was 71.3 mW/cm$^2$. (b) Conversion vs. irradiation time for bis-GMA/TEGDMA resins containing 0.07 mol/l CQ in combination with equimolar proportion of DMAEMA, EDMAB and DMPOH and in absence of added amine. The irradiance of the visible Led was 38.2 mW/cm$^2$.

in higher proportion due to its great resonance stabilization. Thus, the higher polymerization rate of the resin containing PPD in the absence of amine could be attributed to a more efficient hydrogen abstraction from the monomer by the PPD* compared with the CQ*. Fig. 5 also shows that the polymerization rate with PPD and CQ is markedly increased by the presence of amine. It is generally considered that in polymerization reactions photoinitiated by ketone/amine systems, the amine radical is responsible for initiating the polymerization. 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 [20]. Consequently, the different photoinitiation efficiencies of formulation containing different amines may be attributed to structural effects on the recombination rate of radicals and on the radical reactivity toward the monomer double bond [6,21,22]. It is interesting to note that the polymerization rate photoinitiated with PPD/DMPOH was markedly lower than that photoinitiated with the CQ/DMPOH system. This may be attributed to the filtering or screening effect caused by the photoproduct resulting from irradiation of PPD/DMPOH pair (Fig. 4a). As a result of the presence of light absorbing compounds, the light fails to reach the deeper layers of

the sample because the absorbing species nearest to the light source absorb part of it. Since the production of light absorbing compounds increases with irradiation time, the light that reaches the deeper layers decreases and the distribution of initiating radicals along the thickness becomes less uniform. The overall effect of light screening is a reduced photoinitiation rate and consequently a reduced double bond conversion averaged over the sample thickness. The characterization of the photodecomposition products of PPD/amine is beyond the purpose of the present work, which aims to compare the efficiency of the PPD and CQ to initiate the polymerization of dental monomers. Nevertheless, from the results obtained, it is clear that the presence of side reactions derived from PPD/amine decomposition result in light absorbing species and in no case a complete photobleaching was observed. This effect was more marked in PPD/DMPOH system, in which a continuous increase of absorbance with irradiation time was observed. Thus, the slowest polymerization rate in the PPD/DMPOH photoinitiated resin is explained in terms of light absorption by the resulting photoproduct, which reduces the photoinitiation rate along the irradiation path.

## 4. Conclusions

Similarly to CQ, the photodecomposition of PPD under irradiation at 395 nm is promoted by tertiary amines according to a Norrish type II mechanism. UV–vis measurements showed that the photodecomposition of PPD/amine in both acetonitrile and bis-GMA/TEGDMA monomer was accompanied by the appearance of light absorbing species overlapping the absorption range of PPD. Irradiation of monomer samples containing PPD in combination with DMAEMA or EDMAB results in decreased absorbance whereas irradiation of PPD in combination with DMPOH produces a continuous increase in absorbance. Light absorption by the resulting photoproduct reduces the photoinitiation rate along the sample thickness, which is consistent with the slowest polymerization rate observed in the PPD/DMPOH photoinitiated resin. From the results presented it emerges that the selection of the amine to be used in combination with PPD is a crucial step in order to optimize the efficiency of the PPD/amine photoinitiator system.

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