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ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 183 (2006) 154–158
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Synthesis and evaluation of *N*,*N*-dimethyl-*N*′,*N*′-di[2-(methylacryloyl)-ethoxycarbnylethyl] propyldiamine as a coinitiator

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Received 10 November 2005; received in revised form 21 February 2006; accepted 6 March 2006
Available online 17 April 2006

Abstract

The common diluent and coinitiator for current dental resin composite were triethylene glycol dimethylacrylate (TEGDMA) and ethyl-4-dimethylaminobenzoate (EDMAB), respectively. In this study, a polymerisable coinitiator *N*,*N*-dimethyl-*N*′,*N*′-di[2-(methylacryloyl)-ethoxycarbnylethyl] propyldiamine (DMPDA) was synthesized via Michael-Addition reaction. A mixture of 2,2-bis[4-(2-hydroxy-3-methacryloxy propoxy)phenyl]-propane (Bis-GMA)/TEGDMA/camphorquinone (CQ) (75%:25%:0.5% w/w/w) with different coinitiators (i.e. DMPDA, EDMAB or 2-(dimethylamine)ethyl methacrylate (DMEM)) and concentrations were photopolymerized. The kinetics was monitored by real time infrared spectroscopy (RT-IR) and the mechanical properties were measured by dynamic mechanical analyzer (DMA). The results indicated that both the double bond conversion and the rate of polymerization of the resin mixtures increased as increasing the concentration of the DMPDA but were lower than that of EDMAB and DMEM at the same concentration. The modulus and T_g of the cured samples were very close. Water sorption and solubility of the samples were almost the same. It was potential to be used as a coinitiator for dental composite.

Keywords: Coinitiator; Dental composite; Michael-Addition reaction; Polymerizable amine; Photopolymerization

1. Introduction

The conventional dental composite generally contained a mixture of various cross-linking dimethacrylates, a photoinitiator system, glass- and/or silicon dioxide fillers and reactive coupling agent [1]. The selection of monomers had strong effects on the reactivity and viscosity of dental composite, volume shrinkage of polymerization, as well as the mechanical properties, water sorption and solubility of the cured composites. The modern dental composite composed of 2,2-bis[4-(2-hydroxy-3-methacryloxy-propoxy)-phenyl]-propane (Bis-GMA) was firstly introduced by Bowen in 1963 [2]. And it was one of the most used monomer in commercial dental composite. Because of the high viscosity of Bis-GMA, reactive diluent such as Triethylene glycol dimethylacrylate (TEGDMA) was usually added. They were copolymerized when the free radical was produced and formed a cross-linked network [3,4].

The initiator system of dental composite was generally camphorquinone (CQ) and *tert*-amine derivatives coinitiator. However, one of the problems with the photoinitiator system was insufficient curing, leading some amounts of residual unreacted monomer after photopolymerization. Therefore, there was a practical need to understand the curing mechanism and find an efficient photoinitiator for visible light induced curing of dental composite. Various investigations had been performed to study the mechanism of photoinitiating process and to synthesize new photoinitiator or coinitiator for dental composite [3–11].

The *tert*-amine derivative used as coinitiator was both toxic and mutagenic [12–17], but it was a necessary component for the camphorqiunone visible light photoinitiator system. In order to reduce the toxicity and improve the polymerization process, much work had been done to replace the amine coinitiator. A chief way was to synthesize polymerizable and macromolecular photoinitiators or coinitiators. Up to now, some polymerizable and macromolecular photoinitiators or coinitiators had been

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doi:10.1016/j.jphotochem.2006.03.009

reported, which had significant advantages over commercially available low molecular weight photoinitiators, such as good solubility and compatibility in the curable medium, low order and toxicity due to the well-known polymer effect [7–11,18–21].

Michael-Addition reaction between acrylate and amine had been drawn many attentions because the reaction was very fast and was essentially quantitative. Muh and coworkers synthesized a series of organic–inorganic hybrid bis-methacrylate monomers via Michael-Addition potentially used in dental composite because of their low viscosity and low volume shrinkage [22]. Mathias and coworkers used Michael-Addition reaction for the synthesis of new hydroxylated methacrylate monomers with higher rates of polymerization [23].

In this study, *N*,*N*-dimethyl-*N*′,*N*′-di[2-(methylacryloyl)-ethoxycarbnylethyl] (DMPDA) was synthesized via Michael-Addition reaction. There were two different kinds of functional groups in this monomer. One group was the methacrylate, which could be polymerized by free radical chain growth process, linking the DMPDA to the crosslinking network; and the other group was amine, which served as the coinitiators for hydrogen abstraction. Since the DMPDA was incorporated into the polymer chain, it was difficult to leach out from the polymer matrix after polymerized.

The detailed synthesis and characterization of the novel material were reported in this work. FTIR and NMR were used to identify the structure of the monomer structure. Real time IR (RTIR) technique was employed to monitor the extent of the polymerization. The DMA technique was used to measure the glass transition temperature (T_g) and modulus of the novel resin system. Water sorption and solubility were measured according to ISO 4049's standards. A conventional Bis-GMA/TEGDMA/CQ/EDMAB and Bis-GMA/TEGDMA/CQ/DMEM photopolymerization systems were examined for comparison.

2. Experimental

2.1. Materials

2-(Dimethylamine)ethyl methacrylate (DMEM), camphorquinone (CQ), 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (Bis-GMA), Ethyl-4-dimethylaminobenzoate (EDMAB), and 3-dimethylamine-1-propylamine (DMAPA) (Aldrich, USA), Triethylene glycol dimethylacrylate (TEGDMA, donated by Sartomer Company, USA) were used without further purification.

2.2. Synthesis of N,N-dimethyl-N′,N′-di[2-(methylacryloyl)-ethoxycarbnylethyl] propyldiamine

9.20 g of ethylene glycol acrylate methacrylate (EGAMA, 0.05 mol) was dissolved in 25 ml of methanol. Mixture of 2.55 g of 3-dimethylamine-1-propylamine (0.025 mol) dissolved in 25 ml methanol was added droplet at 0–5 °C under magnetic stirring in N_2 atmosphere. FTIR was used to monitor the process of the reaction. When the N–H peaks at 3363 and 3288 cm^{-1} were disappeared, methanol was removed with rotary evaporation. Then the crude product was purified by silica gel (200–300 mesh) column chromatography using ethyl acetate: hexane = 50: 50(V/V) as an eluent. Fig. 1 depicted the synthesis process. The final product was identified by ^{1}H NMR.

^{1}H NMR ($CDCl_3$): δ 6.09(2H), δ 5.56(2H), δ 4.29(8H), δ 2.72–2.74(4H), δ 2.40–2.44(6H), δ 2.18–2.20(2H), δ 2.16(6H), δ 1.91(6H), δ 1.54(2H).

2.3. Measurement

2.3.1. NMR

^{1}H NMR spectra were recorded on a Bruker AV600 unity spectrometer operated at 600 MHz using TMS as an internal reference, with $CDCl_3$ as the solvent.

2.3.2. FTIR

FTIR were recorded on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Company, USA). Series RTIR were used to determine the conversion of double bond. The mixture of resin, diluent, initiator and coinitiator was placed in a mold made from glass slides and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness and irradiated with a visible light source (Spectrum 800 Curing Light, Densply, USA). The light intensity on the surface of samples was 50 mW/cm^2, which was detected by Visible Light Radiometer (400–1000 nm, Beijing Normal University, China). The double bond conversion of the mixtures was monitored using near IR spectroscopy with the resolution of 4 cm^{-1}. The absorbance change of the =C–H peak area from 6100.70 to 6222.50 cm^{-1} was correlated to the extent of polymerization. For each sample, the series RTIR runs were repeated three times.

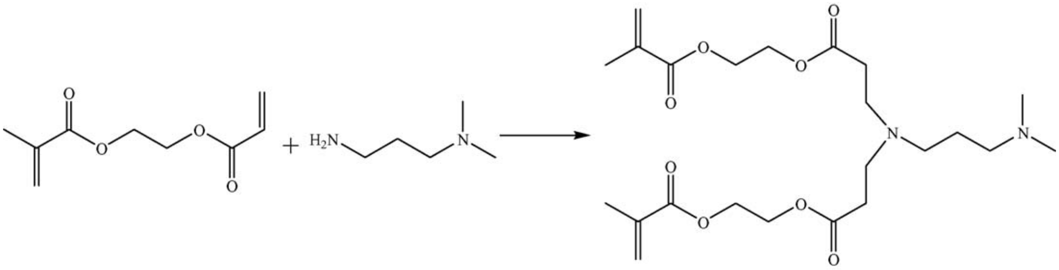

Fig. 1. Synthesis process of *N*,*N*-dimethyl-*N*′,*N*′-di[2-(methylacryloyl)-ethoxy carbnylethyl] propyldiamine.

2.3.3. DMA

A dynamic mechanical analyzer (DMA) (Rheometyic, USA) was used to perform the mechanical properties measurement. The samples were photocured with a visible light source (Spectrum 800 Curing Light, intensity ≈ 800 mW/cm^2) for 5 min in a mold made from glass slides and spacers. The polymerized samples were put at room temperature for 5 days after curing to ensure that post-polymerization process was complete. The samples used for DMA were thin rectangular films of approximately 1.2 mm thickness and dimensions of 7 mm × 35 mm. Dynamic mechanical analysis was performed over a temperature range from −50 to 200 °C with a ramping rate of 5 °C/min using extension mode. The loss and storage modulus and the loss tangent (tan δ, ratio of loss to storage modulus) were recorded as a function of temperature, and the glass transition temperature (T_g) was taken to be the maximum of the loss tangent versus temperature curve.

2.3.4. Water sorption and solubility

Water sorption and solubility were measured according to ISO4049. Specimens, 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness, were stored in a desiccator that contained anhydrous calcium chloride. The samples were maintained at 37 ± 1 °C for 24 h. The temperature was then decreased to 23 °C for 1 h and the samples were subsequently weighed to an accuracy of ±0.2 mg. This process was repeated until a constant mass m_1 was obtained.

The specimen were then immersed in water and maintained at 37 °C for 7 days. After this time, the samples were took out, washed with water, blotted to remove surface water, waved in air for 15 s, and weighed 1 min after removed from water. This measurement was recorded as m_2. Following this weighing, the specimens were replaced into the desiccator, and the cycle described previously was repeated until a final constant mass was obtained (m_3). For every polymer system, the value was average of five specimens. The specimen volumes (V) were also measured.

To calculate the water sorption (w_{sp}) and solubility (w_{sl}), the following equations were used:

$$W_{sp} = \frac{(m_2 - m_3)}{V} \quad (1)$$

$$W_{sl} = \frac{(m_1 - m_3)}{V} \quad (2)$$

All samples were cured with a visible light source (Spectrum 800 Curing Light, Densply, USA, intensity ≈ 800 mW/cm^2) for 5 min.

3. Results and discussion

3.1. DMPDA used as a coinitiator

Generally, photocuring dental composite consisted of Bis-GMA/TEGDMA/CQ/amine. To compare the photopolymerization characteristics at different concentrations of amine, RTIR was used to determine the extent of double bond as a function of time. The real time IR (RTIR) technology had been widely used to measure the double bond conversion of (meth)acrylate monomers under irradiation [24–26]. Upon irradiation, the decrease of the =C–H absorption peak area from 6100.70 to 6222.50 cm^{-1} accurately reflected the extent of the polymerization since the absorption of the peak area was directly proportional to the number of the (meth)acrylate functionalities that had polymerized. At the same time, the rate of polymerization could be calculated by the time derivative of the double bond conversion.

In these studies, a Bis-GMA/TEGDMA (75%:25% w/w) mixture was employed as the photopolymerizable resin, CQ was used as a photoinitiator. Varying concentration of the DMPDA (0.0–0.5 wt.%) was used as the coinitiator. Under the irradiation of visible light, CQ absorbed the photon energy and was excited. The excited CQ combined with the amine coinitiator to form an exciplex. Then the exciplex led to produce a camphorquinone-kety (CQH$^\bullet$) radical and an amine radical (Am$^\bullet$) by electron and proton transfer process [3,4]. The polymerization of (meth)acrylate was usually initiated by the amine radical. It was obviously the concentration of CQ and the amine had great effect on the rate of photopolymerization and final double bond conversion. Fig. 2 graphically illustrated the double bond conversion versus visible light irradiation time of resin mixture initiated by different concentration of CQ and DMPDA. It clearly indicated that increasing the concentration of CQ and DMPDA increased both the double bond conversion of the resin and the rate of polymerization. For Bis-GMA/TEGDMA/CQ (75%:25%:0.5% w/w/w) system, the final double bond conversion of the mixture without amine was very low (approximately 24%) and the rate of polymerization was almost constant. When the concentration of DMPDA was increased from 0.1 to 0.5 wt.%, the final double bond conversion reached approximately from 41.5% to 50.7% and the rate of polymerization increased as well.

Fig. 3 presented the double bond conversion of the Bis-GMA/TEGDMA/CQ (75%:25%:0.5% w/w/w) with different amines (EDMAB, EMDM and DMPDA 0.5 wt.%) as a function of irradiation time. The results indicated that the commercial aromatic amine coinitiator (0.5 wt.% EDMAB) had the rapidest rate of polymerization and highest double bond conversion. For the 0.5 wt.% DMPDA, it had lowest final double bond conversion (50.7%) and the slowest rate of polymerization. This could attribute to the structure of amine. It had been reported that the aromatic amines were more efficient coinitiators in (meth)acrylate system than aliphatic amines [5]. It was reasonable that the double bond conversion and the rate of polymerization of EDMAB (aromatic amine) were higher than that of DMPDA and DMEM (aliphatic amine). While DMPDA was less efficient coinitiator than DMEM, it may be due to its higher molecular weight and the steric hindrance.

3.2. DMA characteristics

The final double bond conversion and type of polymerization had much effect on the mechanical properties of cured samples. The DMA results for several different resin mixtures were shown in Fig. 4. The storage modulus of Bis-GMA/TEGDMA/CQ/

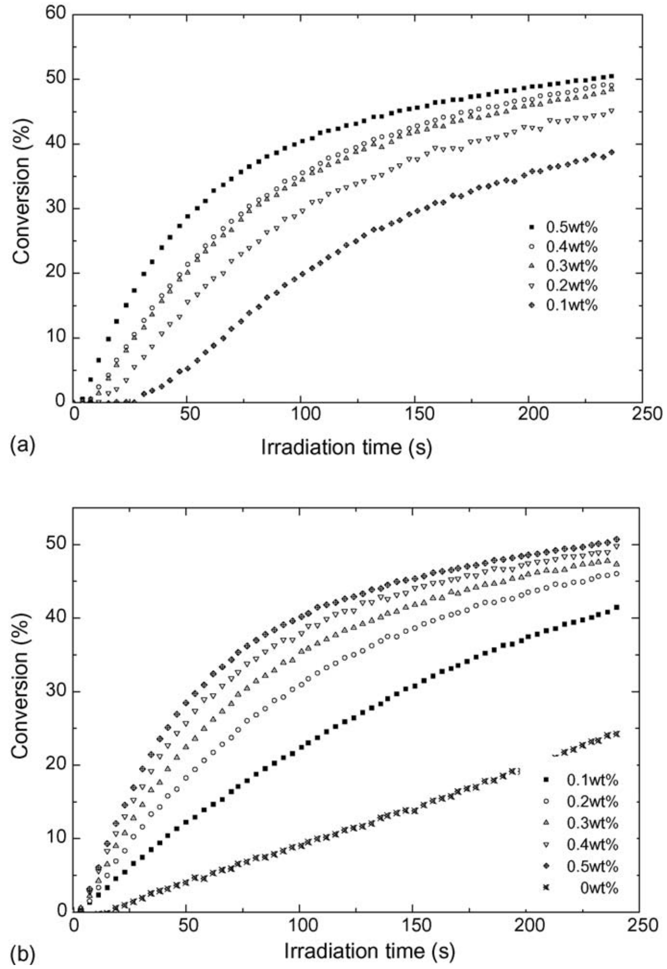

Fig. 2. Double bond conversion as a function of irradiation time for (a) Bis-GMA/TEGDMA/DMPDA (75%:25%:0.5% w/w/w) with different concentration of CQ and (b) Bis-GMA/TEGDMA/CQ (75%:25%:0.5% w/w/w) with different concentration of DMPDA.

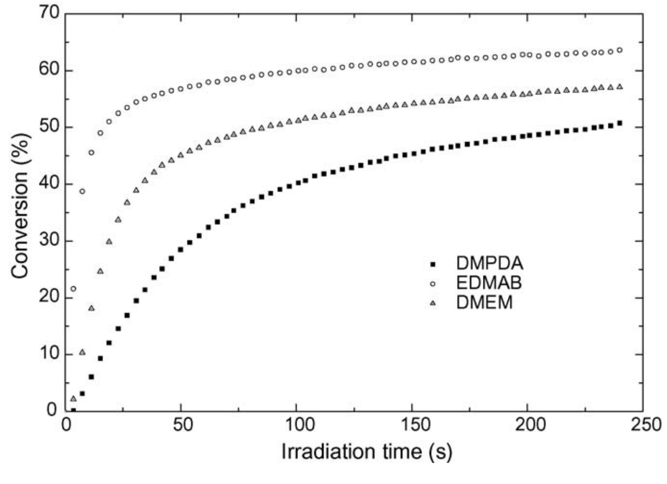

Fig. 3. Conversion of double bond as a function of irradiation time for Bis-GMA/TEGDMA/CQ (75%:25%:0.5% w/w/w) with different amines (EDMAB, DMEM and DMPDA) with the concentration of 0.5 wt.%.

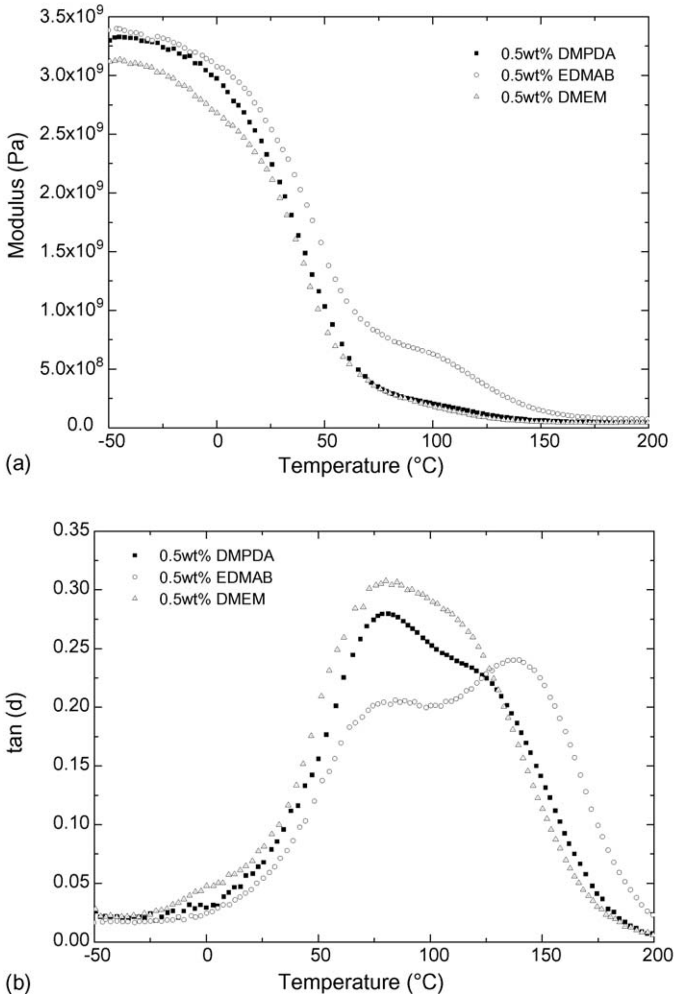

Fig. 4. (a) Storage modulus as a function of temperature and (b) tan δ as a function of temperature for Bis-GMA/TEGDMA/CQ (75%:25%:0.5% w/w/w) with different amines (EDMAB, DMEM and DMPDA) at the concentration of 0.5 wt.%.

DMPDA samples were just between that of the Bis-GMA/TEGDMA/CQ/EDMAB and Bis-GMA/TEGDMA/CQ/DMEM samples. The glass transition temperatures (T_g) of Bis-GMA/TEGDMA/CQ/DMPDA was 80 °C, and lower than that of Bis-GMA/TEGDMA/CQ/EDMAB and Bis-GMA/TEGDMA/CQ/DMEM (91 °C). There were much difference among the efficiency of initiators and the final double bond conversion of the cured samples. For systems initiated by EDMAB, there were two peaks in Fig. 4(b). It attributed to the post-cure during heat. For systems initiated by DMPDA and DMEM, there was only a wide peak. This might be heterogeneous polymerization.

3.3. Water sorption and solubility

The properties of water sorption and solubility were very important for dental restorative materials. Materials with high water sorption and solubility were not suitable for use as dental materials. ISO 4049's standards for dental restorative resins were: water sorption (<50 μg/mm^3) and water solubil-

Table 1
Water sorption and solubility of Bis-GMA/TEGDMA/CQ (75%:25%:0.5% w/w/w) with different amines (EDMAB, DMEM and DMPDA) at the concentration of 0.5 wt.%, average of five samples ± standard deviation (μg/mm^3)

	Water sorption	Solubility
Bis-GMA/TEGDMA/CQ/DMPDA (0.5 wt.%)	36.78 ± 1.28	3.65 ± 0.97
Bis-GMA/TEGDMA/CQ/EDMAB (0.5 wt.%)	35.84 ± 1.39	2.12 ± 0.27
Bis-GMA/TEGDMA/CQ/DMEM (0.5 wt.%)	37.73 ± 2.73	2.64 ± 0.63

ity (<5 μg/mm^3). Table 1 gave the results of water sorption and solubility for several mixture resins initiated by CQ and different *tert*-amines system. The results indicated that Bis-GMA/TEGDMA/CQ with different amines (EDMAB, DMEM and DMPDA) at the concentration of 0.5 wt.% had almost the same water sorption and solubility.

4. Conclusions

DMPDA was synthesized as a polymerizable coinitiator. As the increasing of the concentration of CQ and DMPDA, the double bond conversion and the rate of photopolymerization of resin mixtures increased. When the concentration of DMPDA was 0.5 wt.%, the rate of polymerization and the final double bond conversion were lower than that of both the aromatic amine EDMAB and aliphatic amine DMEM. The modulus, T_g, water sorption and solubility of the samples were very close.

DMPDA could be synthesized by Michael-Addition reaction of amine and acrylate. It could be used potentially as a coinitiator for dental restoration, because the photopolymerization characteristics and the physical properties of the polymer formed were comparable to aliphatic coinitiator DMEM.

Acknowledgements

The authors would like to thank the National Natural Science Foundation of China (50473024) for its financial support.

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