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Synthesis and characterization of aliphatic amine co-initiator with different chain length for photopolymerization of dimethacrylate

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Abstract

Four kinds of aliphatic amines co-initiator with different chain length were synthesized via Michael-Addition reaction based on aliphatic amine and methyl acrylate. The addition products were characterized by Fourier transform infrared (FT-IR) and ^{1}H NMR spectroscopy. UV–vis absorption and fluorescence spectroscopy were employed to investigate the photophysical process of combination of camphorquinone (CQ) and the newly synthesized amine. The activity of amine co-initiator was investigated by real-time infrared spectroscopy (RTIR). The results showed that the aliphatic amine with different chain length had no effect on the photoinitiation quantum yield of CQ and the formation of amine free radical. The double bond conversion and the rate of photopolymerization increased as the increase of amine concentration. Although the rate of photopolymerization had a slight decrease with the increase of chain length of aliphatic amine, it had only minor effect on the double bond conversion.

Keywords: Co-initiator; RTIR; Fluorescence; UV–vis spectroscopy; Photopolymerization

1. Introduction

With its unique advantage of 5E (efficient, enabling, economical, energy saving and environmental friendly), photoinitiated free radical polymerization of multifunctional monomers has found a variety of applications over the past few decades, such as curing of coatings, adhesive, medical application and photolithographic materials [1,2]. In photopolymerization, a typical formulation consisted of a vinyl monomer and a photoinitiator system. (Meth)acrylate held a major part in monomer market because of their good physical properties. The photoinitiator for photopolymerization was divided into types I and II. Type II photoinitiators involved hydrogen abstraction or electron transfer reactions according to the mechanisms of radical generation. In the hydrogen abstraction photoinitiator system, the excited state species were usually a diarylketone such as benzophenone, substituted thioxanthone or camphorquinone (CQ), and the hydrogen donor were mainly tertiary amines.

Many commercial photoinitiators have been developed. Most of them had low molecular weight. The photoinitiator with low molecular weight might have good compatibility with monomers and low price. But there were many shortcomings such as bad odor, migration and evaporation. The use of amine co-initiators in formulations was prone to lead to yellowing [3]. The tertiary amine derivatives used as co-initiator were both toxic and mutagenic [4]. The unreacted photoinitiators and amine co-initiators, as well as the photolysis products, might diffuse from the polymer matrix and had an impact on human health or olfaction. All of the drawbacks limited their application in special fields.

In order to overcome some of the shortcomings, much work has been done to modify the photoinitiator and the amine co-initiators. One important method was the synthesis of polymeric photoiniators [5–7] or photoinitiator with covalently bound amine [8,9]. And the other was the synthesis of photoiniator with polymerizable (meth)acrylate functionality [10–12]. These photoiniators have been reported to have significant advantages over low molecular weight photoinitiators, such as low odor, less

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toxicity and a polymer effect. But in all of the studies, most of the amines are *N*-methyl, *N*-ethyl aliphatic or aromatic amine. There were few aliphatic amines with long chain reported.

In the present research, four kind of aliphatic amines co-initiator with different chain length were synthesized via Michael-Addition reaction based on aliphatic amine and methyl acrylate. To investigate the effect of the chain length on the reactivity of aliphatic amine co-initiator, UV–vis and fluorescence spectroscopy of camphorquinone (CQ) and different amine initiator system were undertaken. The co-initiating activity of aliphatic amine with different chain length was tested in the photocuring of a conventional unfilled dental resin mixture which was composed of 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA).

2. Experimental

2.1. Materials

Ethanol and cyclohexane were dried and purified according to standard laboratory methods. Methyl acrylate, Butylamine and dodecylamine were used as received from Sinopharm Group Chemical Reagent Co. Ltd., China. Octylamine (Acros, New Jersey, USA) and hexadecylamine (Alfa Aesar, Lancs, England) were also used as received. 2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (bis-GMA, Sigma–Aldrich Inc., St. Louis, MO, USA) and triethylene glycol dimethacrylate (TEGDMA, donated by Sartomer Company, Warrington, PA, USA) were used without further purification. Camphorquinone (CQ, Sigma–Aldrich) was used as a photoinitiator. Other chemicals were of analytical grade excepted as noted.

2.2. Synthesis of aliphatic amine co-initiator with different chain length

The aliphatic amine co-initiators (*N*,*N*-di(methoxycarbonylethyl) butyl amine (DBA), *N*,*N*-di(methoxycarbonylethyl) octyl amine (DOA), *N*,*N*-di(methoxycarbonylethyl) dodecyl amine (DDA), *N*,*N*-di(methoxycarbonylethyl) hexadocyl amine (DHA)) were synthesized according to Scheme 1. Methyl acrylate (0.1 mol) and ethanol (25 mL) was added to a 100 mL round-bottom flask and stirred at room temperature using magnetic stirring. Mixtures of 0.05 mol amine (butylamine, octylamine, dodecylamine and hexadecylamine) and 25 mL ethanol were dropped into the stirred solution. Infrared spectroscopy was used to monitor the disappearance of acrylate peak at 1634 cm^{-1} and amine peak at about 3330 cm^{-1}. When the peaks disappeared completely, ethanol was evaporated with rotary evaporation. Then the crude product was purified by silica gel (200–300 mesh) column chromatography using ethyl acetate as an elution. The yields were more than 95%. The product was identified by ^{1}H NMR.

- DBA ^{1}H NMR (CDCl$_3$): δ3.61(s, –O–CH$_3$, 6H), δ2.71(t, CH$_2$–N–CH$_2$, 4H), δ2.40(t, –CO–CH$_2$, 4H), δ2.35(t, –N–CH$_2$, 2H), δ1.35(m, N–CH$_2$–CH$_2$, 2H), δ1.23(m, –CH$_2$–CH$_2$, 2H), δ0.84(t, –CH$_2$–CH$_3$, 3H).
- DOA ^{1}H NMR (CDCl$_3$): δ3.63(s, –O–CH$_3$, 6H), δ2.72(t, CH$_2$–N–CH$_2$, 4H), δ2.40(t, –CO–CH$_2$, 4H), δ2.35(t, –N–CH$_2$, 2H), δ1.36(m, N–CH$_2$–CH$_2$, 2H), δ1.27(m, –CH$_2$–CH$_2$, 2H), δ1.22(m, –CH$_2$–(CH$_2$)$_4$, 8H), δ0.84(t, –CH$_2$–CH$_3$, 3H).
- DDA ^{1}H NMR (CDCl$_3$): δ3.64(s, –O–CH$_3$, 6H), δ2.73(t, CH$_2$–N–CH$_2$, 4H), δ2.41(t, –CO–CH$_2$, 4H), δ2.36(t, –N–CH$_2$, 2H), δ1.37(m, N–CH$_2$–CH$_2$, 2H), δ1.27(m, –CH$_2$–CH$_2$, 2H), δ1.22(m, –CH$_2$–(CH$_2$)$_8$, 16H), δ0.84(t, –CH$_2$–CH$_3$, 3H).
- DHA ^{1}H NMR (CDCl$_3$): δ3.64(s, –O–CH$_3$, 6H), δ2.73(t, CH$_2$–N–CH$_2$, 4H), δ2.41(t, –CO–CH$_2$, 4H), δ2.36(t, –N–CH$_2$, 2H), δ1.37(m, N–CH$_2$–CH$_2$, 2H), δ1.27(m, –CH$_2$–CH$_2$, 2H), δ1.22(m, –CH$_2$–(CH$_2$)$_{12}$, 24H), δ0.84(t, –CH$_2$–CH$_3$, 3H).

2.3. Measurement

2.3.1. Instrumentation

The ^{1}H NMR spectra were recorded on a Bruker AV600 unity spectrometer operated at 600 MHz, with CDCl$_3$ as solvent.

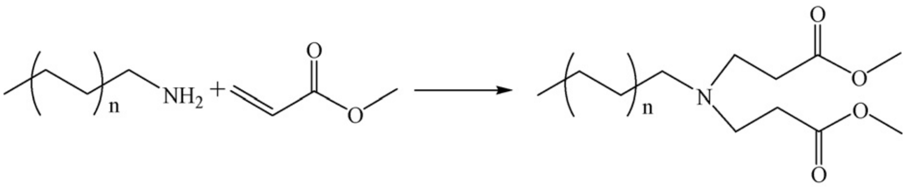
FT-IR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA, USA).

UV–vis absorption spectra were recorded in absolute ethanol or cyclohexane solution on a Hitachi U-3010 UV–vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). A cell path length of 1 cm was employed.

Fluorescence spectra were recorded in anhydrous cyclohexane solution by a Hitachi F-4500 Fluorescence spectrophotometer (Hitachi High-Technologies Corporation, Tokyo Japan).

The visible light source was Spectrum 800 Curing Light (Dentsply, Milford, DE, USA).

The Visible Light Radiometer was type UV-A radiometer in the range of 400–1000 nm (Photoelectric Instrument Factory, Beijing Normal University, China).



Scheme 1. The synthesis process of amine co-initiators. $n = 1$, *N*,*N*-di(methoxycarbonylethyl) butyl amine (DBA). $n = 3$, *N*,*N*-di(methoxycarbonylethyl) octyl amine (DOA). $n = 5$, *N*,*N*-di(methoxycarbonylethyl) dodecyl amine (DDA). $n = 7$, *N*,*N*-di(methoxycarbonylethyl) hexadocyl amine (DHA).

2.3.2. Real-time infrared spectroscopy (RTIR)

Photocuring unfilled dental resin consisted of bis-GMA/TEGDMA/CQ/amine. A bis-GMA/TEGDMA (75:25 wt%) mixture was employed as the photopolymerizable resin, CQ (0.5 wt%) was used as photoinitiator. Varying concentration of the newly synthesized amines (0.0–0.5 wt%) was used as co-initiator. All samples were photocured in 1.2 mm thick plastic molds with a 6 mm diameter central opening connected by a 3 mm wide channel to one edge. The molds were clamped between two glass slides with spring loaded binder clips [13]. The mixtures were irradiated with a visible light source. The light intensity on the surface of samples was 50 mW/cm^2. Each spectrum was signal of 1 scan with the resolution of 4 cm^{-1} at room temperature. For each sample, the series RTIR runs were repeated three times. 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 change of the absorption peak area was directly proportional to the number of the (meth)acrylate that had polymerized. After baseline correction, conversion of the functional groups could be calculated by measuring the peak area at each time of the reaction and determined as following:

$$\mathrm{DC}\% = \frac{A_0 - A_t}{A_0} \times 100 \tag{1}$$

where DC is the degree of methacrylate double bond conversion at t time, A_0 the initial peak area before irradiation and A_t is the peak area of the double bonds at t time. The rate of photopolymerization is calculated by the differential of conversion of double bond versus irradiation time.

2.3.3. Photoreduction

The photoreduction of CQ and amine was studied by UV absorption spectroscopy. The CQ and amine were dissolved in cyclohexane. The concentrations of CQ and amine were 1.5 and 1.0×10^{-2} mol L^{-1}, respectively. All solutions for measurements were deoxygenated by bubbling nitrogen for 15 min. The relative rate of photoreduction was measured by the decrease of absorbance at 468 nm with irradiation time. The light intensity on the surface of cell was 9 mW/cm^2. The rate of CQ disappearing (R_d) was calculated according to the following equation:

$$R_\mathrm{d} = \frac{-\delta[\mathrm{CQ}]}{\delta t} = -\left(\frac{[\mathrm{CQ}]}{\mathrm{Ab}_0}\right)\frac{\delta[\mathrm{Ab}]}{\delta t} \tag{2}$$

where Ab$_0$ is absorbance of CQ at 468 nm before exposure to the light.

The quantum yield of the CQ photoreduction (Φ_CQ) was calculated from the following equation [14]:

$$\Phi_\mathrm{CQ} = \frac{-\delta[\mathrm{CQ}]}{\delta t} \times I_\mathrm{a} = \frac{-\delta[\mathrm{CQ}]}{\delta t} I_0(1 - 10^{\mathrm{Ab}_{468}})\varepsilon_{468}\frac{[\mathrm{CQ}]}{\mathrm{Ab}_{468}} \tag{3}$$

where I_0 was the incident light intensity at 468 nm (μW cm^{-2}) in the front of the cell, Ab$_{468}$ the total absorbance of CQ, and ε_{468} was 40 in cyclohexane.

3. Results and discussion

3.1. Synthesis of aliphatic amine co-initiator with different chain length

The aliphatic amine co-initiators were prepared according to a general Michael-Addition reaction route involving addition of a primary amine with different chain length to methyl acrylate. The reaction was carried out by controlling the stoichiometry of the reagents in ethanol solution at room temperature with nitrogen purge but without any added catalyst. FT-IR indicated that as soon as the amine was added into methyl acrylate, the N–H peak of amine at 3330 cm^{-1} and C=C peak of acrylate at 1634 cm^{-1} began to disappear and a clear colorless liquid formed at the end of reaction.

3.2. Photoreduction

UV–vis absorption spectrum of CQ in cyclohexane solution showed two peaks, peak in the region of 200–300 nm due to π–π* transition and peak at 400–500 nm due to the n–π* transition of dicarbonyl group. There was significant difference of ε_max for the two transitions, with ε_max being about 10,000 for the π–π* transition and 40 for the n–π* transition (measured in cyclohexane) [14–16]. This reflected the fact that the n–π* transition was symmetry forbidden, while the π–π* transition was freely allowed.

The photoreduction studies were conducted with visible light irradiation in the region of 350–550 nm because UV irradiation might damage oral tissues in dental restoration. During the visible light irradiation of CQ/DBA in cyclohexane, the absorption band of CQ in the range of 400–500 nm decreased significantly, which was shown in Fig. 1. Likewise, spectral of CQ/DOA, CQ/DDA and CQ/DHA at the same condition showed almost the same trend. The decrease of maximum absorbance of CQ at 468 nm in the present of amine and no amine were presented in Fig. 2. It could be clearly seen that the observed absorbing peak of CQ alone was almost constant with irradiation. The additions

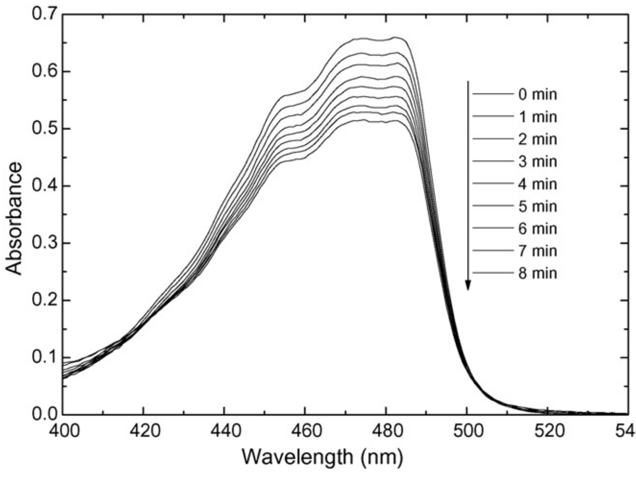


Fig. 1. Change of the UV–vis absorption spectra of CQ in the presence of DBA in cyclohexane during irradiation at 468 nm after nitrogen bubble of 15 min ([CQ] = 1.5×10^{-2} mol L^{-1}, [DBA] = 1.0×10^{-2} mol L^{-1}, I = 9 mW/cm^2).

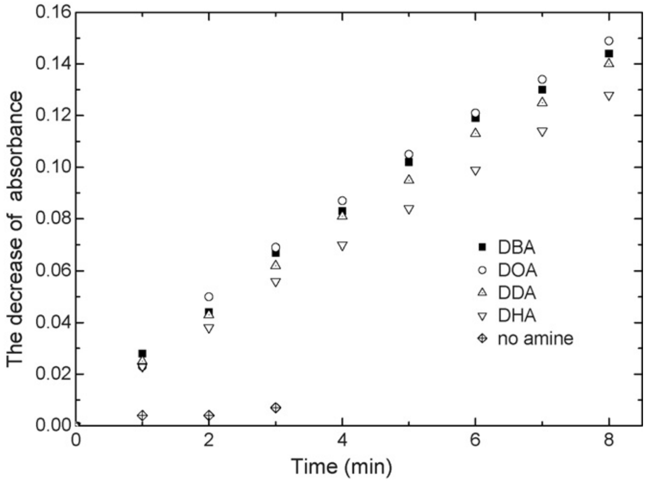


Fig. 2. Kinetics of the disappearance of the CQ absorption band at 468 nm in the presence of aliphatic amine co-initiators with different chain length in cyclohexane during irradiation after nitrogen bubble of 15 min ($[CQ] = 1.5 \times 10^{-2}$ mol L^{-1}, $[amine] = 1.0 \times 10^{-2}$ mol L^{-1}, $I = 9$ mW/cm^2).

of any kind of amine made the maximum absorbance peak of CQ decrease dramatically. The decrease was proportional to the irradiation time.

It was generally accepted that the visible light irradiation led to the formation of the excited singlet $^1CQ^*$, by the intersystem crossing (ISC), to the triplet $^3CQ^*$ state:

$$CQ + h\nu \rightarrow {}^1CQ^* \tag{4}$$

$$^1CQ^* \xrightarrow{ISC} {}^3CQ^* \tag{5}$$

$^3CQ^*$ could directly abstract a hydrogen atom from any hydrogen atom donor. In the presence of amine (AmH), the photoreduction of $^3CQ^*$ with AH occurred via a short-lived charge transfer complex (CTC), followed by a proton transfer with the formation of the ketyl radical (CQH$^\bullet$) and amino alkyl radical (Am$^\bullet$):

$$^3CQ^* + AmH \rightarrow [CQ \cdots AmH]^* \, (CTC) \tag{6}$$

$$CTC \rightarrow CQH^\bullet + Am^\bullet \tag{7}$$

The CQH$^\bullet$ did not initiate the polymerization because of the steric hindrance, whereas the Am$^\bullet$ was an effective radical that initiated the polymerization through an addition reaction on the monomer double bond [14–16].

The rate of CQ disappearing and the quantum yield of CQ photoreduction for the four systems in cyclohexane were dependent on the amine structure and were presented in Table 1. It was notable that the data of CQ/DBA, CQ/DOA and CQ/DDA were almost the same except CQ/DHA. These indicated that the chain length of aliphatic amine had slight effect on the charge transfer and proton abstraction between $^3CQ^*$ and amine.

Table 1
The rate of CQ disappearing and the quantum yield of CQ photoreduction for the four systems in cyclohexane

	DBA	DOA	DDA	DHA
$R_d \times 10^6$ (mol L^{-1} S^{-1})	6.76	6.96	6.49	5.97
$\Phi_{CQ} \times 10^2$	4.07 ± 0.16	4.24 ± 0.19	3.91 ± 0.15	3.65 ± 0.13

3.3. Fluorescence quenching

Fluorescence spectra always used to illustrate the reaction of excited state molecular. Fig. 3(a) presents the fluorescence quenching spectra of CQ in the presence of DBA at different concentration, where the emission intensity of fluorescence decreased as the increase of DBA concentration. The Stern-Volmer plots of CQ/DBA, CQ/DOA, CQ/DDA and CQ/DHA systems were shown in Fig. 3(b). The $k_q\tau_0$ values for the fluorescence quenching of the four systems were 60.87, 56.81, 58.63 and 55.72, respectively, where k_q was the bimolecular quenching rate constant and τ_0 was the lifetime of CQ in the absence of a quencher. The singlet state lifetime τ_0 of CQ was reported as 18 ns [16,17]. The $\log k_q$ values calculated were 9.53, 9.50, 9.51 and 9.49, respectively, for four synthesized amines. The $\log k_q$ values of aliphatic amines with short chain length such as *N*,*N*′-dimethylethylamine, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 1-methylpiperidine were reported as

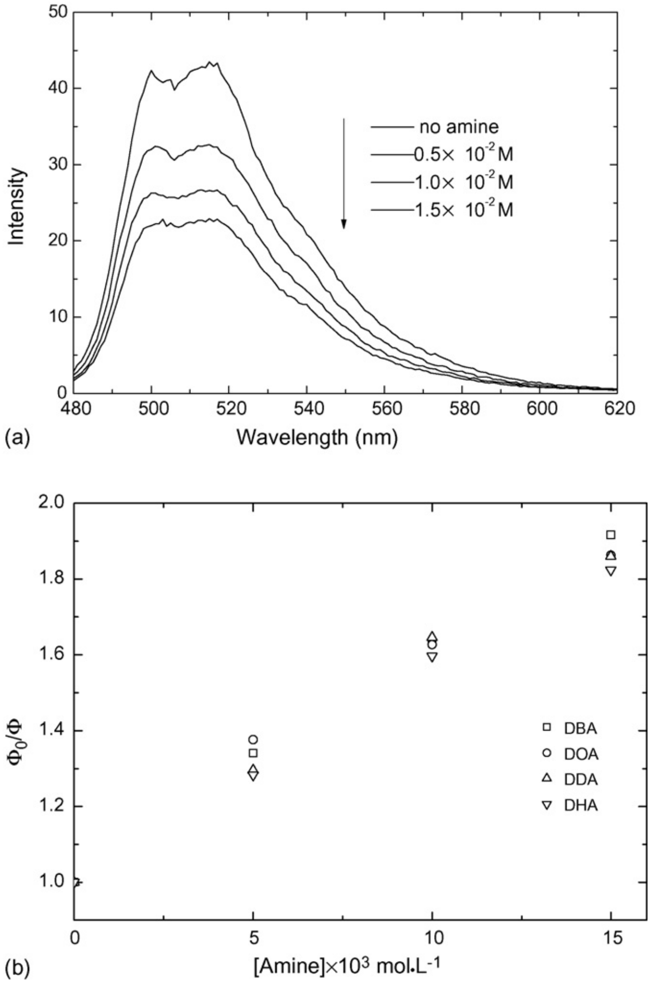


Fig. 3. (a) Fluorescence spectra of CQ in the presence of DBA at different concentrations and (b) Stern-Volmer plots of the quenching of fluorescence of CQ* (1.5×10^{-2} mol L^{-1}) by amine co-initiators with different chain length in cyclohexane ($\lambda_{ex} = 468$ nm, $[CQ] = [amine] = 1.5 \times 10^{-2}$ mol L^{-1}).

9.2, 9.4 and 9.2, respectively [16]. It indicated that the chain length had no effect on the formation of CTC and the proton abstraction.

3.4. Photopolymerization

Real-time infrared spectroscopy (RTIR) had become an important method for obtaining kinetics data. Conversion versus time profiles for all mixtures were determined by real-time near infrared (RT-NIR) spectroscopy [13,18,19]. Conversion data were obtained by monitoring the decay of the methacrylate double bond =C–H peak at 6165 cm^{-1}. Fig. 4 shows the effect of DBA concentration on the double bond conversion and rate of photopolymerization during visible light irradiation. The photopolymerization proceeded slowly and the rate of photopolymerization was almost constant in the condition of CQ alone as photointiator. The addition of small amount of DBA accelerated photopolymerization dramatically. This attributed to the formation of amine radical according to Eqs. (4)–(7). The double bond conversion and the rate of photopolymerization increased as the DBA concentration increased. The time to reach the maximum photopolymerization rate decrease with the increase of DBA concentration (Fig. 4(b)). The same results were obtained when DOA, DDA, or DHA was used as co-initiator, and were tabulated in Table 2. The maximum photopolymerization rate was related to the formation of the gel structure. There would produce fewer amine radicals in the condition of low DBA concentration than in high DBA concentration by the incident of visible light. Thus it led to the requirement of longer time for gel formation.

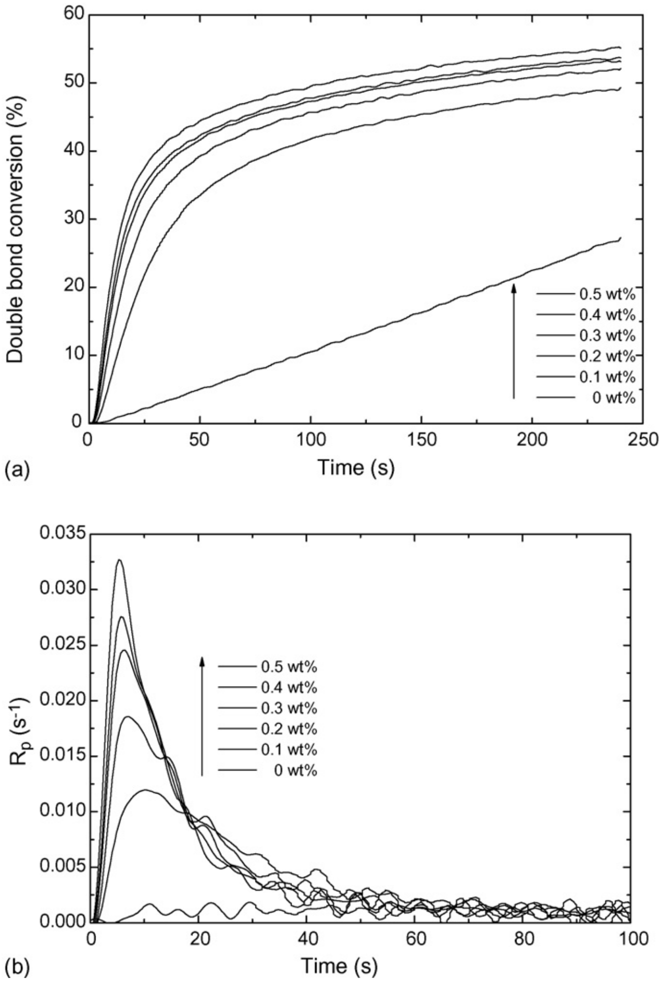


Fig. 4. (a) The double bond conversion and (b) the rate of photopolymerization as a function of irradiation time for polymerization of dental composite in the presence of different concentration of DBA at room temperature (CQ = 0.5 wt%, I = 50 mW/cm^2).

Table 2

The final double conversion (DC$_f$), the maximum rate of photopolymerization (R_{max}), and the time at the maximum rate (t_{max}) for polymerization of dental composite in the presence of aliphatic amine with different chain length at room temperature (CQ = 0.5 wt%, I = 50 mW/cm^2)

	wt%	DC$_f$ (%)	R_{max} (s^{-1})	t_{max} (s)
DBA	0.1	49.3	0.012	10.3
	0.2	52.1	0.019	7.2
	0.3	53.1	0.025	6.4
	0.4	53.7	0.028	5.6
	0.5	55.1	0.033	5.3
DOA	0.1	46.5	0.009	12.6
	0.2	50.0	0.015	9.1
	0.3	50.8	0.019	7.2
	0.4	52.9	0.025	6.4
	0.5	53.0	0.027	5.6
DDA	0.1	46.3	0.008	11.5
	0.2	50.0	0.013	10.7
	0.3	51.6	0.018	6.4
	0.4	52.1	0.022	6.4
	0.5	53.0	0.023	6.4
DHA	0.1	45.7	0.008	14.6
	0.2	47.4	0.013	9.5
	0.3	50.5	0.016	7.6
	0.4	51.3	0.019	6.4
	0.5	51.9	0.022	6.4

The rate of photopolymerization could be expressed by the following equation [20]:

$$R_{\mathrm{p}} = \frac{-\delta[\mathrm{M}]}{\delta t} = \frac{k_{\mathrm{p}}}{k_{\mathrm{t}}^{1/2}}[\mathrm{M}](\Phi_i \varepsilon I_0[\mathrm{PI}_0])^{1/2} \tag{8}$$

where k_p and k_t were the propagation and termination rate constants, respectively; [M] the molar concentration of the (meth)acrylate group; Φ_i the photoinitiation quantum yield; ε the mole extinction coefficient of initiator; I_0 the incident light intensity, and [PI$_0$] was the concentration of photoinitiator.

For the bimolecular hydrogen abstraction photoinitiator systems, Φ_i was given by Eq. (9) [21]:

$$\Phi_i = \Phi^* f \alpha \beta \tag{9}$$

where Φ^* was the quantum yield of the excited state formation; f the fraction of excited states that were deactivated by the hydrogen donor; α the fraction of radical produced in the quenching process, and β was the fraction of radical that added onto the monomer.

For the CQ/amine photoinitiator system, the fraction of excited states that were deactivated by amine was given by

$$f = \frac{k_q[\mathrm{Am}]}{k_q[\mathrm{Am}] + k_0} \qquad (10)$$

where k_q was the quenching rate constant and k_0 was the decay rate constant of the excited state in the absence of amine. When the amine concentration was very low, Eq. (10) could be simplified as Eq. (11):

$$f = \frac{k_q[\mathrm{Am}]}{k_0} \qquad (11)$$

So, Eq. (8) led to Eq. (12):

$$R_p \propto [\mathrm{Am}]^{0.5} \qquad (12)$$

Fig. 5 presents the plot of the maximum rate of photopolymerization versus $[\mathrm{DBA}]^{0.5}$. It was a very good straight line ($R = 0.995$) with an intercept of -4.6×10^{-3} and a slope of 0.817. Similar behavior had been observed in the photopolymerization of unfilled dental resin initiated by the benzoyl/amine photoinitiator system [22].

Fig. 6 shows the effect of the chain length of amine co-initiator on the photopolylmerization. Although it made a slightly decrease of the rate of photopolymerization, the increase of the aliphatic chain length had little effect on the double bond conversion. The plots of the maximum rate of photopolymerization versus $[\mathrm{Am}]^{0.5}$ were presented in Fig. 5, and they were in agreement with Eq. (12). Each of them was a very good straight line. The slopes were 0.817 for DBA, 0.816 for DOA, 0.774 for DDA and 0.714 for DHA. This meant the aliphatic amine with different chain length had similar effect on the photoinitiation quantum yield according to Eq. (8) and the formation of $\mathrm{Am}^{\bullet}$ according to Eqs. (6) and (7). The chain length had some effect on the activity of the $\mathrm{Am}^{\bullet}$ radical with similar structure. The smaller radical had the less steric hindrance and the faster diffusion rate. So the bulker $\mathrm{Am}^{\bullet}$ radical had lower activity. On the other hand, the lower photopolymerization rate of DHA and DDA owed to their higher molecular weight, which meant less concentration of radical generated.

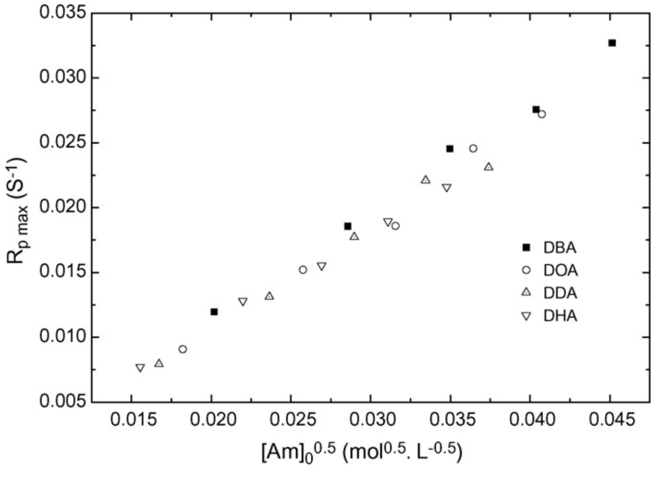


Fig. 5. Calculation of the maximum rate of photopolymerization vs. $[\mathrm{Am}]^{0.5}$ for polymerization of dental composite at several initial amine concentration at room temperature (CQ = 0.5 wt%, I = 50 mW/cm^2).

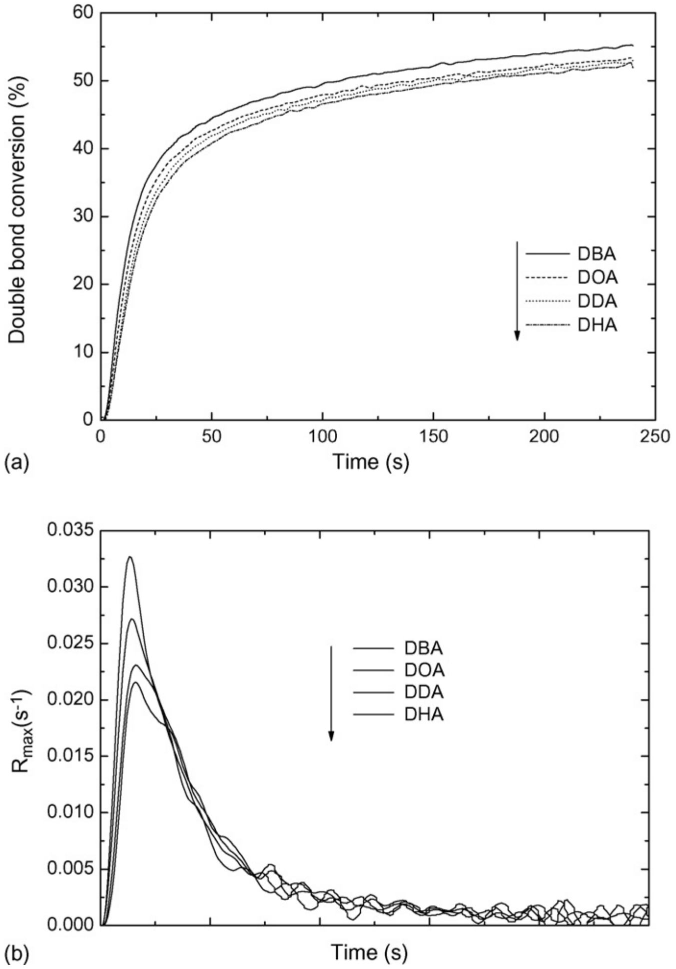


Fig. 6. (a) The double bond conversion and (b) the rate of photopolymerization as a function of irradiation time for polymerization of dental composite in the presence of aliphatic amine with different chain length at room temperature (CQ = 0.5 wt%, Am = 0.5 wt%, I = 50 mW/cm^2).

4. Conclusions

DBA, DOA, DDA and DHA could successfully synthesize through Michael-Addition reaction. Photoreduction and fluorescence quenching results indicated that the aliphatic amine with different chain length had no effect on the photoinitiation quantum yield of CQ and the formation of free radical. The double bond conversion and the rate of photopolymerization increased as the increase of amine concentration. Although the rate of photopolymerization had a slight decrease with the increase of chain length of aliphatic amine, it had only minor effect on the double bond conversion. The plot of the maximum rate of photopolymerization versus $[\mathrm{amine}]^{0.5}$ was a very good straight line.

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