

Synthesis and photopolymerization characteristics of amine coinitiator

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Abstract

Four different amines were synthesized by Michael addition using different space length of acrylate with octylamine. The structure was identified by ¹H NMR. The photopolymerization kinetics of 2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA)/camphorquinone (CQ)/amine system was monitored by “Real Time Fourier Transform Infrared” (RTIR). The primary photoreaction of CQ/amine was investigated by UV spectra and fluorescence quenching. The results indicated that the chain length only had slight effect on the photopolymerization process.

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1. Introduction

Photopolymerization technique is one of the fastest developed polymerization technology has been used in a lot of fields such as coatings, inks, adhesives, photolithography, biomedical materials because of the advantages such as low energy consumption, environmental friendly, and high efficiency [1–5]. Visible light polymerization which use visible light source as energy to induce the polymerization has a lot of advantages for the biomedical application, because the traditional UV polymerization could cause the damage of the human tissue. One of the successful applications of visible light polymerization is the dental composite which used as restorative filling materials for the human tooth [6–9]. One of the most popular used photoinitiator systems for the visible light polymerization is camphorquinone (CQ) and amine. Because of the toxicity of the amine, a lot of research has focused on the development of novel amine which

has low toxicity and good biocompatibility [10–13]. Nie and his coworkers have synthesized a series of novel polymerizable and unpolymerizable amines [14–17]; the photopolymerization kinetics results showed that the novel amines have very close reactivity.

In our previous studies, a series of amines with different chain length via Michael-addition reaction have been synthesized based on different aliphatic amine and methyl acrylate [17]. The previous investigation showed that the longer the aliphatic amine chain length, the lower the solubility and the higher the price of the synthesized coinitiator. On the other hand, when the amine chain length is longer than eight, the yellowing possibility is reduced greatly. The main aim of this research was to synthesize a series of amine via Michael-addition reaction based on octylamine and different acrylate, which might have good solubility and lower yellowing effect and reasonable price. The coinitiating activity of aliphatic amine with different chain length was tested in the photocuring of a conventional dental resin mixture which was composed of 2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA).

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2. Experimental

2.1. Materials

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

The photopolymerization resin was composed of Bis-GMA/TEGDMA = 75/25 (wt%), with designed different concentration of CQ and amine as photoinitiator system.

2.2. Synthesis of amine

N,N-Di(methoxycarbonyl) ethyl octylamine (DMOA), *N,N*-di(ethoxycarbonyl) ethyl octylamine (DEOA), *N,N*-di(butoxycarbonyl) ethyl octylamine (DBOA) and *N,N*-di(octoxycarbonyl) ethyl octylamine (DOOA) were synthesized according to the literatures [14–17]. A brief description was octylamine reacted, respectively, with methyl acrylate, ethyl acrylate, butyl acrylate and octyl acrylate in an ethanol solution. The crude products were purified by silica gel (200–300 mesh) column chromatography using ethyl acetate and hexane as elution. The product was identified by ^1H NMR. The structure of the amines was illustrated in Fig. 1.

- $n = 0$: *N,N*-di(methoxycarbonyl) ethyl octylamine (DMOA).
- $n = 1$: *N,N*-di(ethoxycarbonyl) ethyl octylamine (DEOA).
- $n = 3$: *N,N*-di(butoxycarbonyl) ethyl octylamine (DBOA).
- $n = 7$: *N,N*-di(octoxycarbonyl) ethyl octylamine (DOOA).

DMOA ^1H NMR (CDCl_3): δ 3.63 (s, $-\text{O}-\text{CH}_3$, 6H), δ 2.72 (t, $\text{CH}_2-\text{N}-\text{CH}_2$, 4H), δ 2.40 (t, $-\text{CO}-\text{CH}_2$, 4H), δ 2.35 (t, $-\text{N}-\text{CH}_2$, 2H), δ 1.36 (m, $\text{N}-\text{CH}_2-\text{CH}_2$, 2H), δ 1.27 (m, $-\text{CH}_2-\text{CH}_2$, 2H), δ 1.22 (m, $-\text{CH}_2-(\text{CH}_2)_4$, 8H), δ 0.84 (t, $-\text{CH}_2-\text{CH}_3$, 3H).

DEOA ^1H NMR (CDCl_3): δ 4.11 (q, $-\text{O}-\text{CH}_2-\text{CH}_3$, 4H), δ 2.75 (t, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CO}$, 4H), δ 2.41 (t, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CO}$, 4H), δ 2.41 (t, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2$, 2H), δ 1.39 (m, $\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2$, 2H), δ 1.28–1.23 (m, CH_3-CH_2- , 2H; t, $-\text{O}-\text{CH}_2-\text{CH}_3$, 6H; m, $\text{N}-(\text{CH}_2)_7-\text{CH}_3$, 8H), δ 0.86 (t, $-\text{CH}_2-\text{CH}_3$, 3H).

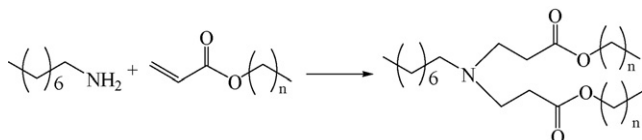


Fig. 1. The synthesis process of amine cointiators.

DBOA ^1H NMR (CDCl_3): δ 4.05 (t, $-\text{O}-\text{CH}_2-\text{CH}_2$, 4H), δ 2.75 (t, $\text{CH}_2-\text{N}-\text{CH}_2$, 4H), δ 2.42 (t, $-\text{CO}-\text{CH}_2$, 4H), δ 2.42 (t, $-\text{N}-\text{CH}_2$, 2H), δ 1.59 (m, $-\text{O}-\text{CH}_2-\text{CH}_2$, 4H), δ 1.38 (m, $-\text{N}-\text{CH}_2-\text{CH}_2$, 2H), δ 1.36 (m, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2$, 4H), δ 1.36 (m, $-\text{CH}_2-\text{CH}_2-\text{CH}_3$, 2H), δ 1.25 ($-\text{N}-(\text{CH}_2)_4-$, 8H), δ 0.85–0.93 (t, $-(\text{CH}_2)_4-\text{CH}_3$, 3H; t, $\text{O}-(\text{CH}_2)_3-\text{CH}_3$, 6H).

DOOA ^1H NMR (CDCl_3): δ 3.97 (t, $\text{O}-\text{CH}_2-\text{CH}_2$, 4H), δ 2.76 (t, $-\text{N}-\text{CH}_2-\text{CH}_2-\text{CO}$, 4H), δ 2.42 (t, $-\text{CO}-\text{CH}_2$, 4H; t, $\text{N}-\text{CH}_2-\text{CH}_2-$, 4H), δ 1.56 (m, $-\text{O}-\text{CH}_2-\text{CH}_2-$, 4H), δ 1.33 (m, $-\text{O}-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_3$, 4H; m, $-\text{N}-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_3$, 2H), δ 1.26 (m, $-\text{O}-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_3$, 16H; m, $-\text{N}-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_3$, 8H), δ 0.85–0.89 (t, m, $-\text{O}-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_3$, 6H; m, $-\text{N}-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_3$, 3H).

2.3. Instrumentation

The ^1H NMR spectra were recorded on a Bruker AV600 unity spectrometer operated at 600 MHz, using CDCl_3 as solvent.

RTIR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA, USA) equipped with an extended range KBr beam splitter and on MCT/A detector.

UV–vis absorption spectra were recorded in cyclohexane solution by Hitachi U-3010 UV–Vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). The cell path length was 1 cm.

Fluorescence spectra were recorded in anhydrous cyclohexane solution by 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 main wavelength is located at 475 nm.

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

2.4. Real-time infrared spectroscopy (RTIR)

A Bis-GMA/TEGDMA (75/25 wt%) mixture was employed as the photopolymerizable resin, varying concentration of CQ (0.1–0.5%) and the newly synthesized amines (0.0–0.5 wt%) was used as photoinitiator and coinitiator. 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 on one edge at room temperature upon visible light irradiation [18]. The decrease of the $=\text{C}-\text{H}$ absorption peak area from 6100.70 to 6222.50 cm^{-1} accurately reflects the extent of the polymerization since the change of the absorption peak area was directly proportional to the number of the methacrylate 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 the following: each sample was repeated three times:

$$\text{DC}(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

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.

2.5. 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 1.5×10^{-2} 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 in absorbance at 468 nm with irradiation time. The rate of CQ disappearing (R_d) was calculated according to the following equation:

$$R_d = \frac{-\delta[\text{CQ}]}{\delta t} = - \left(\frac{[\text{CQ}]}{A_{b_0}} \right) \frac{\delta[A_b]}{\delta t} \quad (2)$$

where A_{b_0} was absorbance of CQ at 468 nm before exposure to the light.

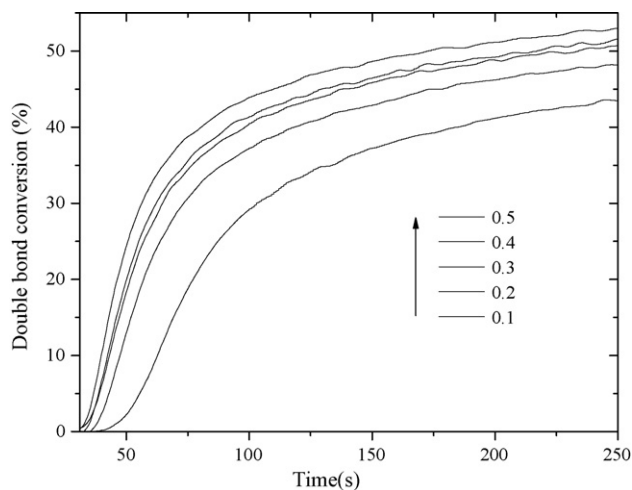


Fig. 2. The effect of CQ concentration on photopolymerization of Bis-GMA/TEGDMA system (DBOA = 0.5 wt%; $I = 50$ mW/cm²).

The quantum yield of the CQ photoreduction (Φ_{CQ}) was calculated from the following equation [19]:

$$\Phi_{\text{CQ}} = \frac{-\delta[\text{CQ}]}{\delta t} I_a = \frac{-\delta[\text{CQ}]}{\delta t} I_0 (1 - 10^{-A_{b_{468}}}) \epsilon_{468} \frac{[\text{CQ}]}{A_{b_{468}}} \quad (3)$$

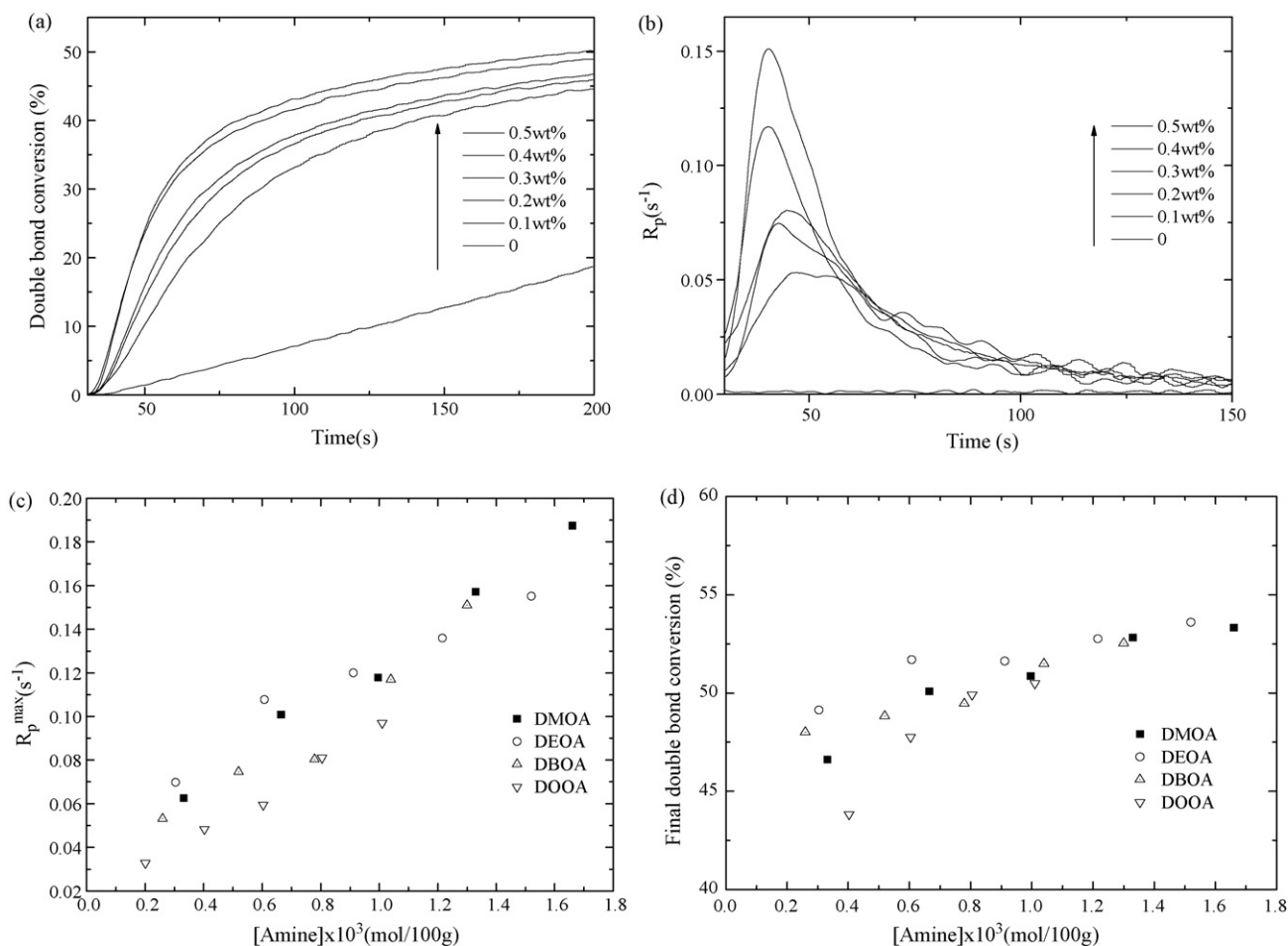


Fig. 3. Effect of concentration of DBOA on (a) the double bond conversion, (b) the rate of photopolymerization; effect of amine structure on (c) maximum rate of polymerization and (d) final double bond conversion at room temperature (CQ = 0.5 wt%; $I = 50$ mW/cm²).

where I_0 was the incident light intensity at 468 nm ($\mu\text{W cm}^{-2}$) in the front of the cell, Ab_{468} was the total absorbance of CQ, and ε_{468} was 40 when cyclohexane was used as solvent.

Excited state of CQ could be quenched by amine easily. The quantum yield for fluorescence emission from excited molecule in the absence of quencher is given by Eq. (4):

$$\Phi_0 = \frac{k_L}{k_L + k_D} \quad (4)$$

where k_L is the rate constant for emission from excited molecule and k_D is rate constant for deactivate.

The quantum yield for emission from excited molecule in the presence of quencher is given by Eq. (5):

$$\Phi_Q = \frac{k_L}{k_L + k_D + k_q[Q]} \quad (5)$$

where k_q is the rate constant for quenching of molecule by a quencher molecule (Q)

Dividing Eqs. (4) by (5) gives the Stern–Volmer equation (6):

$$\frac{\Phi_0}{\Phi_Q} = \frac{k_L + k_D + k_q[Q]}{k_L + k_D} = 1 + k_q\tau_0[Q] \quad (6)$$

where $\tau_0 = 1/(k_L + k_D)$. τ_0 is the measured lifetime of an excited molecule in the absence of quencher. The plot of $\Phi_0/[Q]$ versus concentration of quencher produces a straight line with a slope of $k_q\tau_0$. So it is easily to get the data of $k_q\tau_0$ and $\log k_q$ from the fluorescence quenching spectra.

3. Results and discussion

3.1. Effect of CQ concentration on polymerization

CQ as an initiator, it absorbed the visible light and caused the CQ be excited to its excited state. The excited CQ reacted with coinitiator (amine) to form amine free radical to induce the photopolymerization of acrylate monomer. The ketyl free radical (CQH^*) had lower reactivity and tends to dimerize. The concentration of the CQ, in most of the case, would have great effect on the polymerization process. Fig. 2 showed the results of the CQ concentration on the photopolymerization of Bis-GMA/TEGDMA system. It demonstrated that when the concentration of CQ increased, the rate of polymerization increased gradually, the induction time decreased, the final double conversion increased. The reason could be that the increase of CQ concentration would produce more excited CQ and it reacted with amine to form more free radical during the visible light irradiation, which caused the increase of polymerization rate, and shortened the induction time.

3.2. Effect of amine on the polymerization

The structure of amine should affect the reactivity of the amine free radical. Four different amines were used as coinitiator in this study. The results shown in Fig. 3(a) and (b) was the effect of DBOA concentration on double bond conversion and

rate of polymerization. It indicated that the rate of polymerization and final double bond conversion increased with the increase of concentration, which was because that the free radical concentration increased when the amine concentration increased, then the polymerization rate and final conversion increased. The other three amines showed the same trend. Fig. 3(c) and (d) showed the effect of amine structure on polymerization. The results illustrated that the maximum rate of polymerization and final double bond conversion of various amines were different at lower concentration. But the rate of polymerization and final double bond conversion turn to be the same at higher concentration ($>1 \times 10^{-3}$ mol/100 g). This meant that the reactivity of the amine with different space length was concentration depended, the space length only had slight effect on polymerization kinetics. The results were similar to our previous work [17].

3.3. UV spectra

In order to investigate the reactivity of different amines, the UV–vis spectroscopy was employed to measure the absorp-

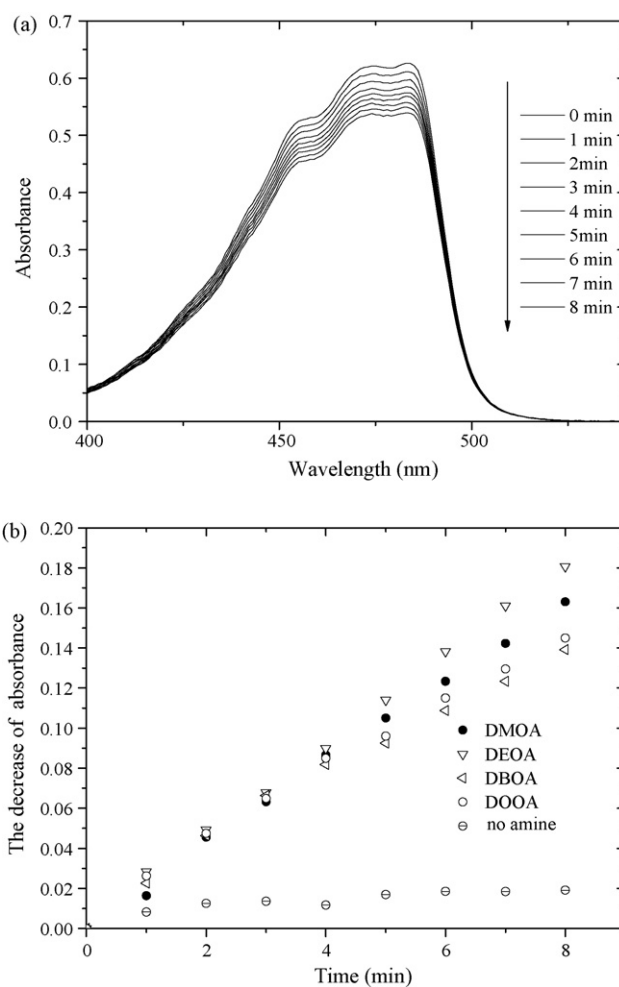


Fig. 4. The disappearance of CQ absorption band at 468 nm in the presence of DBOA during irradiation (a); and the kinetics of the disappearance of CQ absorption with different amine (b) in cyclohexane ($[\text{CQ}] = 1.5 \times 10^{-2}$ mol L $^{-1}$; $[\text{Amine}] = 1.0 \times 10^{-2}$ mol L $^{-1}$; $I = 9$ mW/cm 2).

Table 1
 R_d and Φ_{CQ} values of different amines

	DMOA	DEOA	DBOA	DOOA
R_d ($\times 10^6 \text{ mol L}^{-1} \text{ s}^{-1}$)	4.77	5.04	4.13	4.28
Φ_{CQ} ($\times 10^2$)	3.00 ± 0.08	3.22 ± 0.12	2.69 ± 0.06	2.72 ± 0.07

tion peak decrease of the CQ/amine system during irradiation. The results in Fig. 4(a) indicated that the CQ absorption peak decreased gradually during irradiation when DBOA was added, which meant that the CQ reacted with DBOA during the irradiation. The other three amines showed the similar trend. Fig. 4(b) showed the decrease of absorbance of four different amines during irradiation. The four lines located almost at the same position, except the derivative after 5 min irradiation. This might be the effect of oxidation of the leaked oxygen in the system or side effect during long time irradiation. The results supported the kinetics results in this paper. The reactivity of the four amines was very close. Table 1 lists the calculated results of R_d and Φ_{CQ} according to Eqs. (2) and (3). It showed that the R_d and Φ_{CQ} values were very close to each other.

Table 2
 $k_q\tau_0$ and $\log k_q$ values of different amines

	DMOA	DEOA	DBOA	DOOA
$k_q\tau_0$	51.5	50.0	46.9	42.6
$\log k_q$	9.46	9.44	9.42	9.37

3.4. Fluorescence quenching

Fluorescence spectra always used to illustrate the reaction of excited state molecular. Fig. 5(a) presents the fluorescence quenching spectra of CQ in the presence of DBOA at different concentration, where the emission intensity of fluorescence decreased as the increase of DBOA concentration. The Stern–Volmer plots of CQ/DMOA, CQ/DEOA, CQ/DBOA and CQ/DOOA systems were shown in Fig. 5(b).

The $k_q\tau_0$ values and $\log k_q$ values were calculated according to Eq. (6) and showed in Table 2. All the results indicated the four synthesized amines had very close reactivity. 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 9.2, 9.4 and 9.2, respectively [20]. The values were very close to our results. It indicated that the chain length only had slight effect on the formation of CTC and the proton abstraction.

4. Conclusions

DMOA, DEOA, DBOA and DOOA could be synthesized by Michael-addition reaction. The kinetics data, UV spectra and fluorescence quenching results showed that the chain length only had slight effect on the photopolymerization process.

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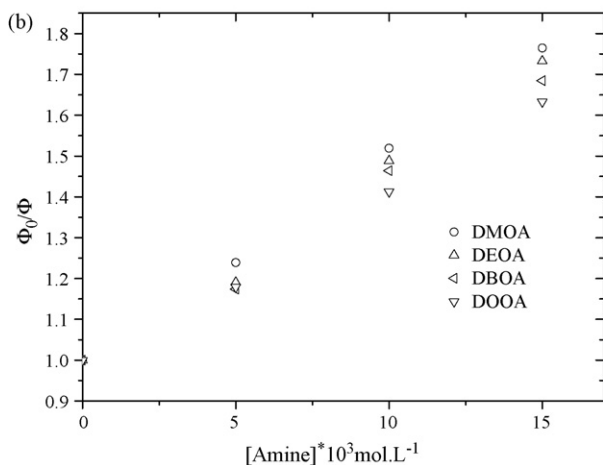
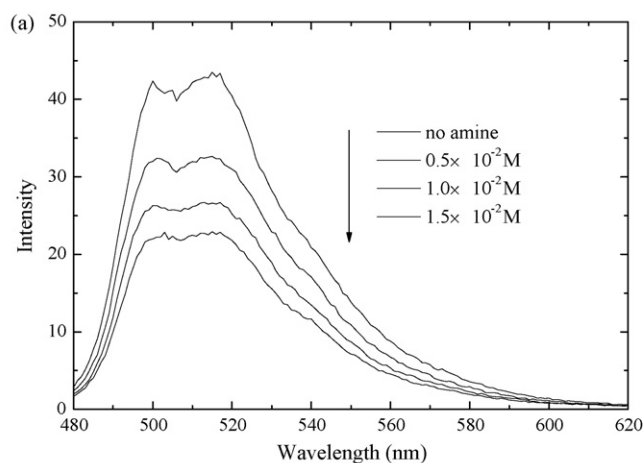


Fig. 5. (a) Fluorescence spectra of CQ in the presence of DBOA at different concentrations and (b) Stern–Volmer plots of the quenching of fluorescence of CQ* ($1.5 \times 10^{-2} \text{ mol L}^{-1}$) by amine cointiators with different chain length in cyclohexane ($\lambda_{\text{ex}} = 468 \text{ nm}$, $[\text{CQ}] = [\text{Amine}] = 1.5 \times 10^{-2} \text{ mol L}^{-1}$).

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