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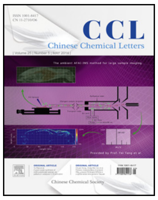

Original article

A thioxanthone-based photocaged superbase for highly effective free radical photopolymerization

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ABSTRACT

Thioxanthone-based *N*-phthalimidoamino acid ammonium salt (thioxanthen-DBU) as a photocaged base was synthesized and characterized. The photochemical properties and initiation mechanism were analyzed. It was found that the compound absorbs over the UV and visible region with relatively high absorption coefficients. Furthermore, the covalent binding of *N*-phthalimidoamino acid and type II chromophores (thioxanthone, TX) remarkably improved the photoreactivity. Specifically, in combination with a benzoyl peroxide initiator, thioxanthen-DBU was able to initiate the amine-mediated redox photopolymerization of trimethylol propane triacrylate (TMPTA), and an excellent photopolymerization profile was obtained.

1. Introduction

Recently, photopolymerization reactions have received revitalized interest as they congregate a wide range of economic and ecological anticipations, while photoinitiators (PIs) or photoinitiating systems (PISs) have been the subject of intense studies [1–9]. However, the light attenuation is a major issue when the photopolymerization is used for the synthesis of photo-screened functional materials. Hence, we recently proposed a redox photopolymerization using a photocaged base and a peroxide, which represents a new free radical PIS [10–13]. The main advantages of the PISs are their longeval active centers and high initiating capability. Remarkably, this PIS leads to significant post conversion due to the persistent interactions of the photogenerated amines with the peroxide. Through this mechanism, the problem of light attenuation that is associated with the conventional free radical photopolymerization has been overcome. This finding may enable the use of PIS as a phototrigger for self-propagating polymerization reactions to access a larger number of opaque composites.

As part of our continuous interest in developing highly effective photocaged bases, herein we design a thioxanthone-based *N*-phthalimidoamino acid ammonium salt (thioxanthen-DBU, Scheme 1), which has taken the following points into consideration. Firstly, the synthesis of thioxanthone (TX) derivatives has recently received interest in photochemistry because of their good absorption characteristics and high photoinitiation efficiency in the visible region [14–19]. This is significant because visible light is cheap, safe, and able to penetrate formulations consisting of UV absorbing monomers, pigments, and substrates. Secondly, there are significant interactions between *N*-substituted maleimides and type II PIs, which lead to enhanced photoefficiency [20,21], thus we would design the new chemical-bonded photosensitive groups comprising of the parent *N*-phthalimidoamino acids and type II chromophores. Finally, both carboxylic acid derivatives of TXs and photolatent amine have been reported to serve as hydrogen bond donors [22].

In the paper, the aim is to establish the mechanism of the primary photocleavage of thioxanthen-DBU and to facilitate the design of future photocaged bases. In order to obtain the clear-cut information on the redox photopolymerization, we extensively studied the photopolymerization of trimethylol propane triacrylate (TMPTA) in the presence of a latent redox initiator combination composed of thioxanthen-DBU and dibenzoyl peroxide (BPO), and the high efficiency has been demonstrated by real-time RTIR measurements.

2. Experimental

Thisosalicyilic acid (99%), *trans*-4-(aminomethyl)cyclohexanecarboxylic acid (98%), polyphosphoric acid (85%), acetic anhydride,

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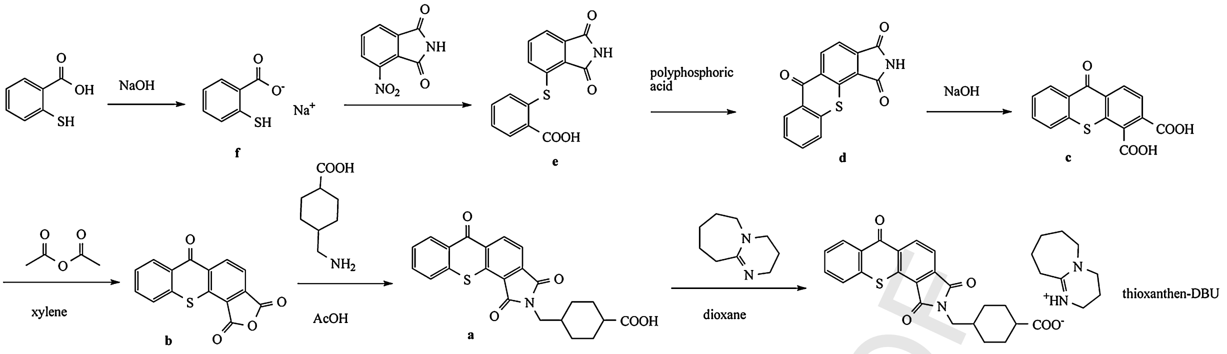

Scheme 1. Synthesis route for thioxanthen-DBU.

1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, 99%), and dibenzoyl peroxide (BPO) were purchased from Aladdin-reagent (China). BPO was purified by dissolving the commercial material in $CHCl_3$ at room temperature and precipitating by adding an equal volume of MeOH. Trimethylol propane triacrylate (TMPTA, Sartomer Company), isopropyl thioxanthone (ITX, IHT Group) were used as received. All other chemicals used were of analytical grade and used without further purification.

The NMR spectra were obtained on a Varian 300 MHz spectrometer using DMSO-d_6 and TMS as the solvent and internal standard, respectively. Elemental analysis was obtained on an Elementar Vario EL analyzer. Electrospray ionization mass spectra (ESI-MS) were acquired on a Thermo Finnigan LCQ DECA XP ion trap mass spectrometer, equipped with an ESI source. UV–vis absorption spectra were obtained on a Perkin Elmer Lambda 750 UV–visible spectrophotometer. Acrylate conversions were monitored by real-time Fourier transform infrared (RTIR) spectroscopy using a modified Nicolet 5700 spectrometer. Photopolymerization reactions were conducted in a mold from two glass plates and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness, changes in the peak area from 6104 to 6222 cm^{-1} attributed to the stretching vibration were used to monitor the acrylate polymerization kinetics.

Synthesis route for thioxanthen-DBU was given in Scheme 1.

2-(1,3-Dioxoisoindolin-4-ylthio)benzoic acid (**e**) [23]: Thiosalicylic acid (15.4 g, 0.1 mol) in NaOH aqueous solution (200 mL, 1 mol/L) was warmed until the solid dissolved, and then continually warmed to remove water. Ethanol was added into the sticky mixture, and then the white precipitates were collected by filtration, washed with ethanol, and dried in *vacuo* to obtain sodium thiosalicylate (**f**). A mixture of **f** (18.215 g, 0.1034 mol), 3-nitrophthalimide (15.892 g, 0.0827 mol), and DMF (200 mL) was stirred at 80 °C for 8 h. A HCl solution (200 mL, 2 mol/L) was added. The precipitate was filtered, washed with water, dried in *vacuo*, and then recrystallized from dioxane to give a yellow powder. Yield: 95.4%. ^1H NMR (300 MHz, DMSO-d_6): δ 7.29–7.31 (m, 2H), 7.47 (m, 2H), 7.66 (m, 2H), 7.86 (m, 1H). Anal. Calcd. for $C_{15}H_9NO_4S$: C, 60.19; H, 3.03; N, 4.68; S, 10.71; Found: C, 59.48; H, 3.20; N, 4.54; S, 10.51.

Thiochromeno[2,3-e]isoindole-1,3,6(2*H*)-trione (**d**) [23]: A suspension of **e** (6 g, 0.02 mol) in polyphosphoric acid (100 g, 0.30 mol) was stirred at 150 °C for 90 min, and then the mixture was diluted to 500 mL with ice water. The precipitate was filtered, washed several times with H_2O, and dried in *vacuo*. Recrystallisation from xylene gave a yellow powder. Yield: 56.2%. ^1H NMR (300 MHz, DMSO-d_6): δ 7.63 (t, 1H), 7.83 (t, 1H), 7.91 (d, 1H), 7.95 (d, 1H), 8.47 (d, 1H), 8.80 (d, 1H). Anal. Calcd. for $C_{15}H_7NO_3S$: C, 64.05; H, 2.51; N, 4.98; S, 11.40%; Found: C, 64.91; H, 2.81; N, 4.92; S, 11.23.

9-Oxo-9*H*-thioxanthene-3,4-dicarboxylic acid (**c**) [23]: Compound **d** (0.55 g, 1.95 mmol) in NaOH aqueous solution (60 mL, 0.1 mol/L) was refluxed for 90 min, and then acidified with concentrated HCl. The mixture was refluxed with stirring for 18 h. The crude diacid **c** was filtered, washed with water, dried in *vacuo* to give a yellow powder. Yield: 56.2%. ^1H NMR (300 MHz, DMSO-d_6): δ 7.66 (t, 1H), 7.85 (t, 1H), 8.01 (d, 1H), 8.10 (d, 1H), 8.48 (d, 1H), 8.90 (d, 1H). Anal. Calcd. for $C_{15}H_8O_5S$: C, 60.12; H, 2.75; S, 10.58%; Found: C, 64.91; H, 2.81; N, 4.92; S, 11.23.

9-Oxo-9*H*-Thioxanthene-3,4-anhydride (**b**) [23]: A mixture of **c** (0.58 g, 0.0017 mol) and acetic anhydride (8.5 mL, 0.09) in xylene (80 mL) was heated to reflux for 90 min. The precipitated powder was filtered, washed with water, dried in *vacuo* to give a yellow powder **b**. Yield: 87.3%. ^1H NMR (300 MHz, DMSO-d_6): δ 7.67 (t, 1H), 7.86 (t, 1H), 8.02 (d, 1H,), 8.12 (d, 1H), 8.49 (d, 1H), 8.92 (d, 1H). Anal. Calcd. for $C_{15}H_6O_4S$: C, 63.83; H, 2.14; S, 11.36%; Found: C, 63.63; H, 2.04; S, 11.16.

4-((1,3,6-Trioxothiochromeno[2,3-e]isoindol-2(1*H*,3*H*,6*H*)-yl)methyl)cyclohexanecarboxylic acid (**a**): A solution of **b** (5 mmol) and *trans*-4-(aminomethyl)-cyclohexanecarboxylic acid (0.785 g, 5 mmol) in acetic acid (20 mL) was refluxed for 3 h. The reaction mixture was cooled to room temperature, poured into ice cooled water (50 mL), and stirred for 15 min. A white crystalline product was obtained, filtered and dried. Yield: 66.1%. ESI-MS (negative mode): m/z 420.1 (M−H⁻) (calcd. for M−H⁻: 420.1). ^1H NMR (300 MHz, DMSO-d_6): δ 1.05 (m, 2H), 1.23 (m, 2H), 1.73 (m, 3H), 1.90 (m, 2H), 2.14 (m, 1H), 3.44 (d, 2H), 7.63 (t, 1H), 7.82 (t, 1H), 7.95 (t, 2H), 8.44 (d, 1H), 8.80 (d, 1H). Anal. Calcd. for $C_{23}H_{19}NO_5S$: C, 65.54; H, 4.54; N, 3.32; S, 7.61%; Found: C, 64.34; H, 4.59; N, 3.27; S, 7.46.

4-((1,3,6-Trioxothiochromeno[2,3-e]isoindol-2(1*H*,3*H*,6*H*)-yl)methyl)cyclohexanecarboxylic acid DBU salt (thioxanthen-DBU): To **a** (5 mmol) in dioxane (30 mL) was slowly added excess DBU (10 mmol) in dioxane (20 mL) and the mixture was stirred at room temperature for 24 h. The mixture was poured into water (100 mL), filtered, washed thrice with water, and dried to give the white powder. The product can be further purified by silica gel column chromatography using hexane: EtOAc (1:5) to give a pure product. Yield: 85%. ESI-MS (negative mode): m/z 420.1 ($M-H^-$) (calcd. for $M-H^-$: 420.5); (positive mode): m/z 153.4 ($M+H^+$) (calcd. for $M+H^+$: 153.14). ^1H NMR (300 MHz, DMSO-d_6): δ 1.04 (m, 2H), 1.26 (m, 2H), 1.61 (m, 9H), 1.77 (m, 4H), 2.13 (m, 1H), 2.66 (d, 2H), 3.24–3.55 (m, 6H), 3.62 (m, 2H), 7.64 (t, 1H), 7.83 (t, 1H), 7.96 (t, 2H), 8.45 (d, 1H), 8.81 (d, 1H). Anal. Calcd. for $C_{32}H_{35}N_3O_5S$: C, 66.99; H, 6.15; N, 7.32; S, 5.59%; Found: C, 65.67; H, 6.28; N, 7.22; S, 5.47.

Photopolymerization: PIs (3×10^{-5} mol) composed of thioxanthen-DBU, BPO, or ITX were dissolved in DMSO (0.5 mL) under ultrasonication, and then TMPTA (1 g) was added to this solution. The mixture was injected into a mold, and irradiated with an optical cable-directed UV lamp in the 200–400 nm range (RW-UVA-Φ200U, Runwing Co., China). The light intensity at the surface level of the cured samples was measured to be 20 mW/cm^2

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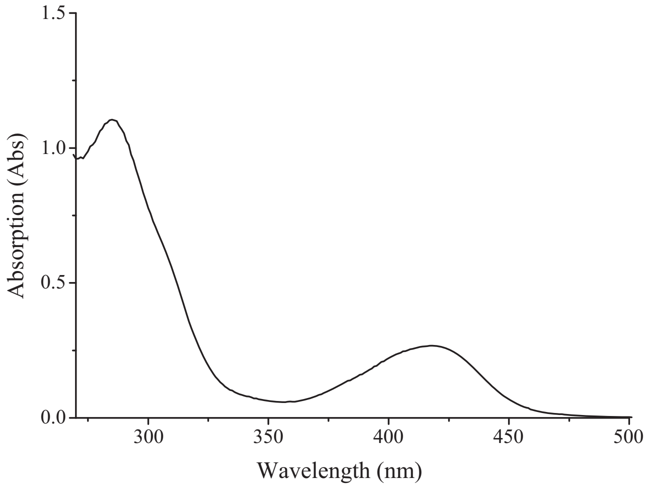

Fig. 1. UV–vis absorption spectra of thioxanthen-DBU (1×10^{-5} mol/L) in DMSO.

Table 1
Photopolymerizations of TMPTA initiated by BPO, thioxanthen-DBU, and thioxanthen-DBU&BPO combination.

Entry	Initiator	T_{start} (min)[a]	R_{pmax} (min^{-1})[b]	Final conversion (%)
1	BPO	–	–	0[c]
2	BPO	–	–	0
3	Thioxanthen-DBU	0.3	378	83.3
4	Thioxanthen-DBU&BPO	0.03	580	85.6
5	ITX	0.1	30	40.8

[a] The induction period, can be expressed by irradiation duration required for initiating the photopolymerization.
[b] The maximum initiation rate.
[c] Irradiation time is 0 min, reaction time is 30 min.

by a UV-radiometer (type UV-A, Photoelectric Instrument Factory, Beijing Normal University).

Photo-generated DBU detected by ESI-MS: A thioxanthen-DBU solution in DMSO (0.01 mmol/L) was irradiated for 30 min, and then isometric water was added, nonphotolytic thioxanthen-DBU was filtered off. ESI-MS spectrum of the filtrated solution was then measured.

3. Results and discussion

Synthesis of the photocaged base thioxanthen-DBU was achieved according to the procedures given in Scheme 1. Firstly, the NO_2 group in 3-nitrophthalimide was displaced by salicylic acid sodium salt (**f**), followed by an intramolecular acylation of the obtained intermediate **e** in polyphosphoric acid (PPA). Secondly, the hydrolysis of **d** in alkaline aqueous solution gave the dicarboxylic acid **c**, which reacted with acetic anhydride to produce the 9-oxo-9*H*-thioxanthene-3,4-anhydride **b**. Finally, thioxanthone-based *N*-phthalimidoamino acid ammonium salt (thioxanthen-DBU) was synthesized from *trans*-4-(aminomethyl)-cyclohexanecarboxylic acid and the anhydride **b**, followed by a salt formation reaction with 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU). The obtained thioxanthen-DBU was characterized by ^{1}H NMR, elemental analysis, and ESI-MS spectra.

TX derivatives have extended absorption up to 420 nm depending upon the type of substitutions [22]. Fig. 1 demonstrates the absorption spectrum of thioxanthen-DBU. It exhibits good absorption characteristics with a maximum at 285 nm and 418 nm and surprisingly a tail over 480 nm. A clear red shift was observed compared with TX due to the amide substituents on the TX skeleton. The $n \to \pi^*$ absorption band appears in the visible region and high molar absorptivity may allow this photocaged base to be used in day light polymerization applications (instead of medium pressure mercury lamps). Furthermore, photogenerated protonated DBU (*m*/*z* 153.4) can be detected by ESI-MS spectra after 30 min of irradiation (Fig. 2), which was the direct evidence for the generation of DBU from irradiated thioxanthen-DBU.

The catalytic behaviors of the photocaged redox initiator combination (thioxanthen-DBU&BPO), and its parent compounds, thioxanthen-DBU and BPO, were compared using real-time FTIR spectroscopy at room temperature (Fig. 3). As depicted in Table 1, control experiments (entries 1 and 2) indicate that both the photocaged base and photoirradiation are essential to trigger this redox photopolymerization. The photopolymerization of TMPTA in the presence of thioxanthen-DBU was fast (Fig. 3, curve b), 80% final conversion was achieved in 1 min. As described in the previous work [20,24], planar *N*-aromatic maleimides do not generate radicals and initiate photopolymerization. Hence, the photopolymerization initiated by thioxanthen-DBU alone should be attributed to the structure of TX. On the other hand, BPO alone

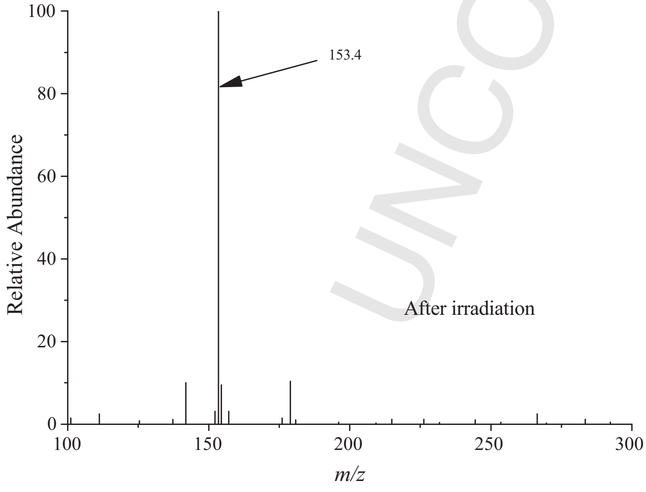

Fig. 2. Positive ion ESI-MS spectra of irradiated thioxanthen-DBU in DMSO (0.01 mol/L).

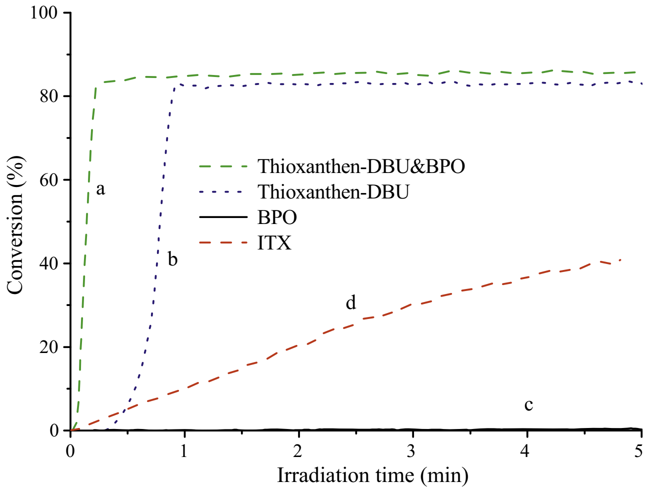

Fig. 3. Conversion *vs* time for the photopolymerization of TMPTA in the presence of: (a) thioxanthen-DBU&BPO, (b) thioxanthen-DBU, (c) BPO, and (d) ITX.

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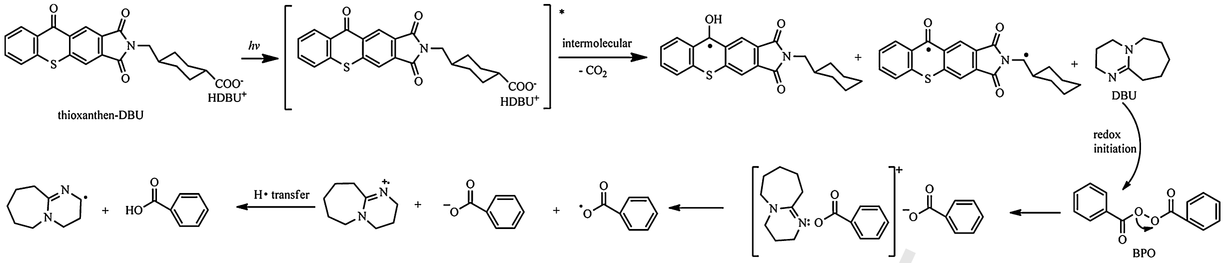

Scheme 2. Proposed mechanism of photoinduced radical generation.

cannot initiate a clear polymerization (Fig. 3, curve c). Interestingly, the thioxanthen-DBU&BPO combination can invoke the newborn amine-mediated redox radical polymerization (Fig. 3, curve a), and 82.5% yield was obtained in 0.22 min. Compared to thioxanthen-DBU, the induction period (T_{start}) of the two-component redox system was obviously shortened from 0.3 min to 0.03 min and the maximum initiation rate (R_{pmax}) dramatically increased from 378 min^{-1} to 580 min^{-1}, indicating this two-component catalytic system proceeded rapidly and efficiently. Due to the one-component structure of the thioxanthen-DBU, both the photosensitizer and the hydrogen bond donor are combined together therefore this type of PI does not require an additional co-initiator. Hence, compared to the conventional PI ITX (Fig. 3, curve d), the superiority of thioxanthen-DBU can be clearly observed.

The involvement of a decarboxylation process during the photolysis of *N*-phthalimidoamino acid derivative was described in the literature [24,25]. Furthermore, as proposed in the literatures [26–28], this kind of acetic acid-based thioxanthone derivative that self-quenching from the triplet state could lead to the formation of the initiating radicals during the decarboxylation process. After extrusion of CO_2, the corresponding methyl radical is possibly responsible for the initiation of the polymerization of TMPTA. Moreover, photogenerated DBU can transiently activate the oxidation-reduction polymerization in conjunction with the oxidant BPO. Taking the foregoing points into consideration, the principal photoreaction pathways of thioxanthen-DBU and BPO are laid out in Scheme 2.

4. Conclusion

In the paper, a photocaged base (thioxanthen-DBU) using Thioxanthen as the peripheral chromophore of *N*-phthaloyltranexamic acid ammonium salt is proposed. In combination with a benzoyl peroxide initiator, its ability to initiate free radical photopolymerization of TMPTA was demonstrated and compared with that of the parent thioxanthen-DBU, BPO, and conventional PI ITX. It is found that thioxanthen-DBU&BPO is a highly effective photoinitiator combination. The mechanism of the radical formation to initiate the redox photopolymerization is proposed. This photodecarboxylation reaction is of particular interest as it is can facilitate the design of new photocaged bases with very promising properties.

Acknowledgments

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