Original article

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

CrossMark

Ming-Hui He [a], Rui-Xin Xu [a,c], Guang-Xue Chen [a], Zhao-Hua Zeng [b], Jian-Wen Yang [b,*]

[a] State Key Laboratory of Pulp & Paper Engineering, South China University of Technology, Guangzhou 510640, China
[b] Institute of Polymer Science, DSAPM Lab, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China
[c] School of Media and Communication, Shenzhen Polytechnic, Shenzhen 518055, China

A B S T R A C T

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.

© 2014 Jian-Wen Yang. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

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 photo-initiation 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)cyclohexane-carboxylic acid (98%), polyphosphoric acid (85%), acetic anhydride,

* Corresponding author.
  E-mail address: cesyjw@mail.sysu.edu.cn (J.-W. Yang).
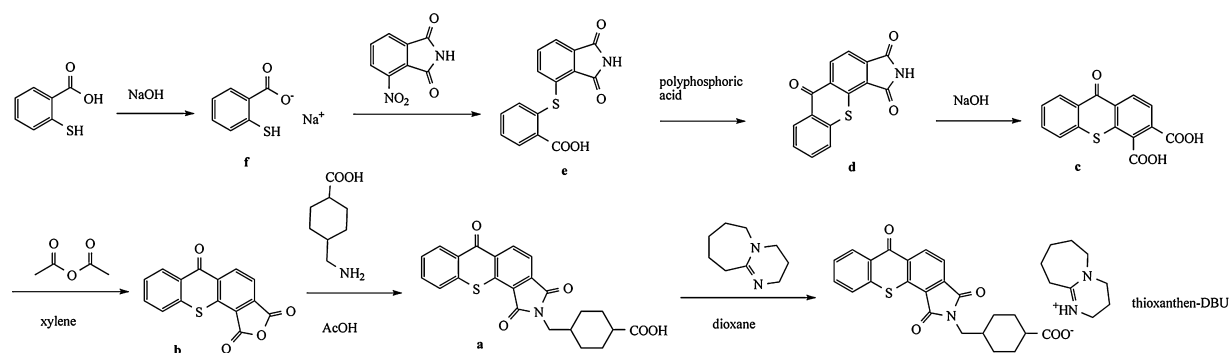
Scheme 1. Synthesis route for thioxanthen-DBU.

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%. ^{1}H 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$_9$NO$_4$S: 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(2H)-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$_2$O, and dried in *vacuo*. Recrystallisation from xylene gave a yellow powder. Yield: 56.2%. ^{1}H 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$_7$NO$_3$S: 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-9H-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%. ^{1}H 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$_8$O$_5$S: C, 60.12; H, 2.75; S, 10.58; Found: C, 64.91; H, 2.81; N, 4.92; S, 11.23.

9-Oxo-9H-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%. ^{1}H 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$_6$O$_4$S: 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(1H,3H,6H)-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). ^{1}H 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$_5$S: 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(1H,3H,6H)-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). ^{1}H 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$_3$O$_5$S: 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 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