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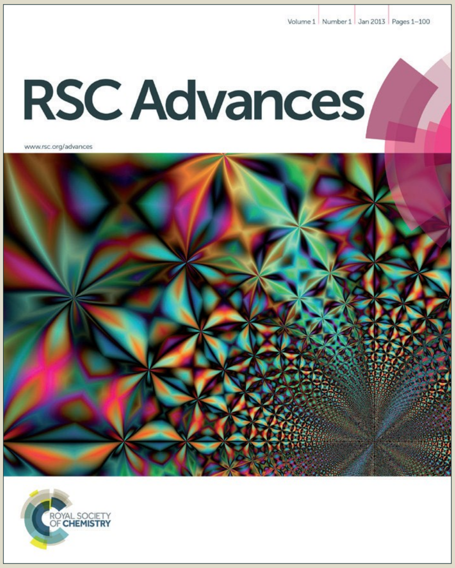

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Thioxanthone Dicarboxamide Derivatives as One-Component Photoinitiators for Near-UV and Visible LED (365-405nm) Induced Photopolymerizations[†]

Guangxue Chen,[a, ‡] Xiaoyuan Guan,[a, ‡] Ruixin Xu,[c] Junfei Tian, [a] Fachuang Lu, [a] Minghui He [*a] and Jianwen Yang[b]

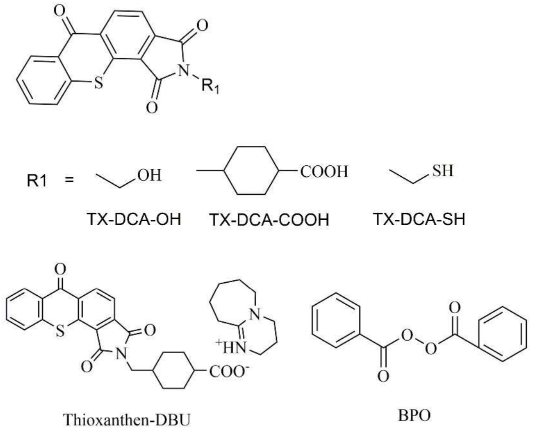
A series of thioxanthone dicarboxamide derivatives (TX-DCAs) containing hydrogen donors as one-component photoinitiators (PIs) have been prepared. In particular, the photoreactivity of these PIs was remarkably improved due to the covalent binding of *N*-phthalimido derivative and type II chromophore thioxanthone. These derivatives exhibit interesting shifted absorption so that they can be utilized as versatile PIs upon exposure to various violet and visible LEDs (365 nm, 385 nm, 395 nm and 405 nm), and can efficiently actuate the free radical photopolymerization of acrylates.

Introduction

Photopolymerizations upon light-emitting diodes (LEDs) are receiving a great deal of attention, and demonstrating an enormous potential as substitutes of traditional Hg lamp induced photopolymerizations due to their advantages including lower cost, better environment-friendliness and larger application fields.[1] However, the classical/commercial photoinitiators (PIs) usually suffer from poor light absorption properties for λ > 365 nm due to their initial development for UV lamps and their good matching with the emission spectra of Hg lamps.[2, 3] Hence, to successfully use LEDs in photopolymerization reactions, the design and development of high-performance PIs with adapted absorption wavelengths and excellent photochemical properties is one of the most important points.

Among these recently developed PIs with novel structures,[2, 4-9] a lot of aromatic ketones are renowned for their excellent optical characteristics. Of particular interest is thioxanthone (TX) due to its adaptability for bearing different functionalities and its applications in various modes of photopolymerization, in which it accomplishes photoinitiation in conjunction with other co-initiator compounds; a behavior that is referred to as bi-molecular photoinitiation.[10-13] Interestingly, if there is a hydrogen-donating site on these introduced groups, a one-component initiating system can be achieved by the intramolecular or intermolecular hydrogen donating reaction.[14-20] It is worth noting that these one-component initiating systems usually have a higher initiating efficiency than those two-component initiating systems.[21]

Very recently, we have reported a thioxanthone-based *N*-phthalimidoamino acid ammonium salt (Thioxanthen-DBU, Scheme 1) used as the highly effective photocaged superbase.[22] 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. Furthermore, the amine-mediated redox photopolymerization of acrylate was able to rapidly actuate by Thioxanthen-DBU in combination with a benzoyl peroxide (BPO) initiator.



Scheme 1. Chemical structures of the studied thioxanthone dicarboxamide derivatives (TX-DCAs) and previously investigated Thioxanthen-DBU and BPO

These encouraging results prompted us to explore further the possibility to prepare novel thioxanthone dicarboxamide derivatives (TX-DCAs) use as LED PIs with adapted absorption wavelengths and excellent photochemical properties. In the present paper, we synthesized three new TX-DCAs in conjunction with hydrogen donors such as carboxyl, thiol and hydroxyl groups (Scheme 1), which had taken the following points into consideration. First, TX with maxima at 383 nm possesses good absorption characteristics and high photoinitiation efficiency in the near-UV and visible regions. Second, the interactions between *N*-substituted maleimides and type II PIs will lead to enhanced photoefficiency. Finally, one-component molecular structures were designed by introducing the hydrogen bond donors such as carboxyl, thiol and hydroxyl groups. The photophysical and photochemical properties were investigated. Especially, in order to demonstrate the potential of TX-DCAs as LED PIs, the free radical polymerization (FRP) of acrylates were monitored (by RT-FTIR) in the ultraviolet-to-visible wavelength range using selected LEDs at 365 nm, 385 nm, 395 nm and 405nm.

Experiments

Materials

1*H*-thioxantheno[4,3-c]furan-1,3,6-trione was synthesized according to the literature procedure.[22] *trans*-4-(Aminomethyl)cyclohexanecarboxylic acid (98%), 2-isopropylthioxanthone (ITX, Tianjin Jiuri Chemical) and 2-aminoethanol (99%) were purchased from Aladdin-reagent (China). Mercapto-ethylamine (95%, Xiya Reagent) and tripropylene glycol diacrylate (TPGDA, Sartomer Company) were used as received. All other chemicals used were analytical grade and used without further purification.

Characterization

The NMR spectra were obtained on a Varian 300 MHz spectrometer with DMSO-d_6 and TMS as the solvent and internal standard, respectively. FTIR spectra were obtained on a Bruker/Tensor 27 spectrophotometer and recorded from 32 scans with a resolution of 4 cm^{-1}. Elemental analysis was obtained on an Elementar Vario EL analyzer. Thermogravimetric (TG) tests were performed in the 40-750 ^{o}C range, using a TG-209 Netzsch thermogravimetric analyzer at a heating speed of 20 ^{o}C/min under N_2 atmosphere. 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. Photopolymerizations 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 acrylate polymerization kinetics.

2-(2-Hydroxyethyl)thiochromeno[2,3-e]isoindole-1,3,6(2*H*)-trione (TX-DCA-OH).

A solution of 1*H*-thioxantheno[4,3-c]furan-1,3,6-trione (1.410 g, 5 mmol) and 2-aminoethanol (0.305 g, 5 mmol) in 1,4-dioxane (70 mL) was refluxed for 3 h. The reaction mixture was cooled to room temperature, dried in vacuo, and then washed with ether to give a yellow product. Yield**:** 94.0%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.79 (1H, d), 8.44(1H, d), 7.95(2H, t), 7.82(1H, t), 7.62(1H, t), 3.66(4H, m). IR (KBr, cm^{-1}): 735(υ C-S) , 1589($\upsilon_{C=C}$) , 1640, 1765 ($\upsilon_{C=O}$), 1463($\upsilon_{O=H}$). Anal. Found: C, 62.59; H, 3.49; N, 4.33; O, 19.68; S, 9.91. Calcd for $C_{17}H_{11}NO_4S$: C, 62.76; H, 3.41; N, 4.31; O, 19.67; S, 9.85%.

4-((1,3,6-Trioxothiochromeno[2,3-e]isoindol-2(1*H*,3*H*,6*H*)-yl)methyl)cyclohexanecarboxylic acid (TX-DCA-COOH).

A solution of 1*H*-thioxantheno[4,3-c]furan-1,3,6-trione (1.410 g, 5 mmol) and *trans*-4-(aminomethyl)-cyclohexanecarboxylic acid (0.785 g, 5 mmol) in acetic acid (500 mL) was refluxed for 3 h. The reaction mixture was cooled to room temperature and stood overnight. The obtained yellow crystalline product was filtered, washed with dimethylbenzene, and then dried in vacuo. Yield**:** 66.1%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.80 (1H, d), 8.44(1H, d), 7.95(2H, t), 7.83(1H, t), 7.63(1H, t), 3.44 (2H, d), 2.14 (1H, m), 1.90 (2H, m), 1.72 (3H, m), 1.22 (2H, m), 1.05 (2H, m). IR (KBr, cm^{-1}): 734(υ C-S) , 927, 1400($\upsilon_{O=H}$), 1590($\upsilon_{C=C}$) , 1640, 1773 ($\upsilon_{C=O}$). Anal. Found: C, 65.29; H, 4.56; N, 3.24; O, 19.21; S, 7.70. Calcd for $C_{23}H_{19}NO_5S$: C, 65.54; H, 4.54; N, 3.32; O, 18.98; S, 7.61%.

2-(2-Mercaptoethyl)thiochromeno[2,3-e]isoindole-1,3,6(2*H*)-trione (TX-DCA-SH).

A solution of 1*H*-thioxantheno[4,3-c]furan-1,3,6-trione (1.410 g, 5 mmol) and mercapto-ethylamine (0.385 g, 5 mmol) in acetic acid (20 mL) was refluxed for 3 h. The reaction mixture was cooled to room temperature and stood overnight. The obtained yellow crystalline product was filtered, washed with dimethylbenzene, and then dried in vacuo. Yield**:** 76.2%. ^{1}H NMR (300 MHz, DMSO-d_6, δ, ppm): 8.85 (1H, d), 8.48(1H, d), 7.99(2H, t), 7.85(1H, t), 7.66(1H, t), 3.79(2H, m), 2.78(2H, m). IR (KBr, cm^{-1}): 736(υ C-S) , 1583($\upsilon_{C=C}$) , 1640, 1767($\upsilon_{C=O}$), 2537(υ_{S-H}). Anal. Found: C, 59.72; H, 3.26; N, 4.01; O, 14.61; S, 18.40. Calcd for $C_{17}H_{11}NO_3S_2$: C, 59.81; H, 3.25; N, 4.10; O, 14.06; S, 18.78%.

Photopolymerization procedure

Typical procedure used as follows: photoinitiator TX-DCAs (1×10^{-5} mol) was dissolved in 1,4-dioxane (0.5 mL) under ultrasonication, and then monomer TPGDA (0.5 g) was added to this solution. At last, the mixture was injected into a mold. The photopolymerization was initiated by optical cable-directed LED light source (UVEC-4II, Lamplic Technology. China) possessing 365 nm, 385 nm, 395 nm and 405nm were as used as the irradiation source. The light intensity at the surface level of the cured samples was measured to be 20 mW/cm^{2}.

Results and Discussions

1 Synthesis and characterization of TX-DCAs

In this paper, we synthesize three new and one-component TX-DCAs in conjunction with hydrogen donors such as carboxyl, thiol and hydroxyl groups. First, type II TX-based PIs have become a preferable class of PIs over other similar structures such as benzophenones, primarily because of their spectral characteristics. Their absorption maxima appear in the range of 380-420 nm, laying in the near UV and visible ranges, which reduces the required energy for photoexcitations and subsequent formation of initiating radicals. Next, chemical incorporation of various co-initiators into the structure of PIs makes one-component PIs exhibit double functionality. One-component Type II PIs form initiating species through intramolecular and/or intermolecular interactions between the triplet state chromophore core and co-initiator part of the PI, and overcome the drawbacks such as odor, toxicity and migration resulted from the use of low molecular-weight coinitiators for most of the conventional hydrogen abstraction PIs.[9, 17] In this regard, carboxyl-, thiol- and hydroxyl-like hydrogen donors have been incorporated into PI structures to make one-component photoinitiating systems. Finally, there are significant interactions between *N*-substituted maleimides and type II PIs, which lead to enhanced photoefficiency. Thus, we would design the new thioxanthone dicarboxamide derivatives (TX-DCAs) in conjunction with hydrogen donors. The obtained TX-DCA-COOH, TX-DCA-OH and TX-DCA-SH were characterized by ^{1}HNMR (**Figure S1-S3**), IR spectra (**Figure S4-S6**) and elemental analysis.

Thermal stability is one of the important parameters of PIs. As shown in **Figure 1** and **Table 1**, both *TG₀* (the initial decomposition temperature) and *TG5%* (the decomposition temperature at the point of 5% weight loss) were above 125 °C and 210 °C, respectively, exhibiting good thermal stability.

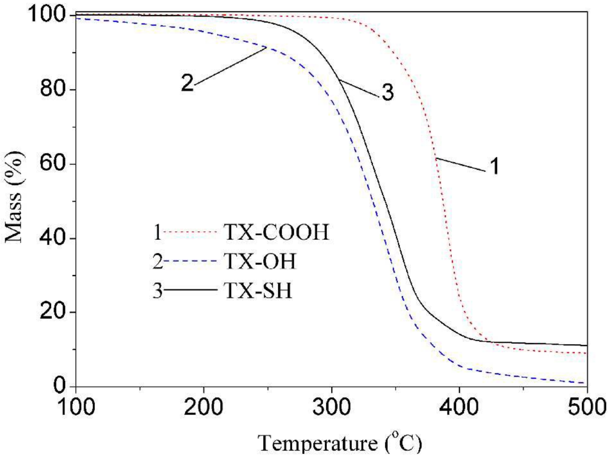


Figure 1. Thermogravimetric profiles of TX-DCAs PIs with heating rate at 20 °C/min under N^2.

Table 1. Thermal stability of TX-DCAs

PIs	TG_0 (°C) ^{a}	$TG_{5\%}$ (°C) ^{b}
TX- DCA-COOH	309.8	335.5
TX-DCA-OH	128.3	214.1
TX- DCA-SH	170.0	278.3

[a] The initial decomposition temperature; [b]The decomposition temperature at the point of 5% weight loss.

2 Light absorption of the studied photoinitiators

The light absorption spectra of TX-DCA-COOH, TX-DCA-OH and TX-DCA-SH in dimethyl sulfoxide are depicted in **Figure 2** and **Table 2**. All TX-DCAs exhibit similar absorption characteristics with maxima at 280 nm and 410 nm, and a tail over 460 nm, exhibiting a red shift compared with 2-isopropylthioxanthone (ITX), due to the presence of the carboxamide structures on the TX skeleton. In particular, for TX-DCA-COOH and TX-DCA-SH, the maxima are located in the UV light range (i.e., λ_{max} = 284 nm, $\varepsilon_{284\ nm}$ ~132250 $M^{-1}cm^{-1}$ and λ_{max} = 283 nm, $\varepsilon_{283\ nm}$ ~134800 $M^{-1}cm^{-1}$ for TX-DCA-COOH and TX-DCA-SH, respectively) and visible light region (i.e., λ_{max} = 414 nm, $\varepsilon_{414\ nm}$ ~29080 $M^{-1}cm^{-1}$ and λ_{max} = 417 nm, $\varepsilon_{417\ nm}$ ~27940 $M^{-1}cm^{-1}$ for TX-DCA-COOH and TX-DCA-SH, espectively). As to the spectrum of TX-DCA-OH, it presents a much better light absorption (λ_{max} = 280 nm, $\varepsilon_{280\ nm}$ ~141340 $M^{-1}cm^{-1}$ and λ_{max} = 404 nm, $\varepsilon_{404\ nm}$ ~41020 $M^{-1}cm^{-1}$). However, ITX with the shortest maximum absorption wavelength has the poorest light absorption (λ_{max} = 280 nm, $\varepsilon_{280\ nm}$ ~124338 $M^{-1}cm^{-1}$ and λ_{max} = 404 nm, $\varepsilon_{404\ nm}$ ~16096 $M^{-1}cm^{-1}$).

The extended light absorption range of these three compounds makes them adapted to a wider range of LED devices (i.e.from near UV to visible LED light sources with a dominant emission wavelength range between 365 nm and 405 nm). For TX-DCAs under different LED (365 nm, 385 nm, 395 nm and 405 nm), the observed order of extinction coefficients is $\varepsilon_{405\ nm} > \varepsilon_{395\ nm} > \varepsilon_{385\ nm} > \varepsilon_{365\ nm}$. TX-DCA-OH presents a much better light absorption than other TX-DCAs and ITX. ITX with the shortest maximum absorption wavelength has the poorest light absorption in the near-UV and visible regions.

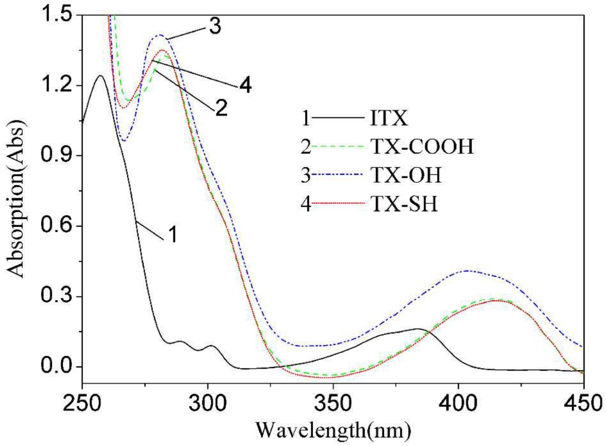


Figure 2. UV-vis absorption spectra of TX-DCAs (1×10^{-5} M) in DMSO.

Table 2. Light absorption properties of the studied ITX and TX-DCAs: maximum absorption wavelengths λ_{max} and extinction coefficients at λ_{max} and at the maximum emission wavelengths of the different irradiation devices.

PIs	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)^a	$\varepsilon_{365\ nm}$ ($M^{-1}cm^{-1}$)^b	$\varepsilon_{385\ nm}$ ($M^{-1}cm^{-1}$)^b	$\varepsilon_{395\ nm}$ ($M^{-1}cm^{-1}$)^b	$\varepsilon_{405\ nm}$ ($M^{-1}cm^{-1}$)^b
ITX	257, 383	124338, 16096	11804	16006	8098	234
TX-DCA-COOH	284, 414	132250, 29080	185	12640	21000	26800
TX-DCA-OH	280, 404	141340, 41020	15560	30490	38160	40890
TX-DCA-SH	283, 417	134800, 27940	711	11690	19960	25690

[a] Maximum absorption wavelength in the near visible range. [b] for different UV or visible LEDs.

3 Photoinitiating ability of the investigated PIs.

Initially the catalytic behavior of TX-DCAs and commercial PI ITX, were compared upon the near-UV and visible LED (365 nm, 385 nm, 395 nm and 405 nm) at room temperature by real-time Fourier transform infrared (FTIR) spectroscopy. As depicted in **Figure 3**, these photopolymerizations without obvious induction periods could be rapidly actuated under photo-irradiation. Almost 100% final conversions of double bonds were achieved, and all PIs exhibited the fastest photopolymerization rates under the LED 365 nm. The maximum initiation rate (R_{pmax}) and reaction time at 90% conversion ($T_{C90\%}$) are two more meaningful parameters for assessing photopolymerization efficiency of PIs. As listed in **Table 3,** TX-DCA-COOH had a relatively low efficiency under the LED 385 nm and 405 nm, 90% conversions were obtained in 1.4 min, while the highest efficiency (R_{pmax} = 328.1 min^{-1}, $T_{C90\%}$ = 0.63 min) was reached when the FRP was carried out under the LED 365 nm (**Figure 3a**, **Table 3**). After LED 365 nm, the next fastest polymerization was observed under the LED 395 nm (R_{pmax} = 149.2 min^{-1}, $T_{C90\%}$ = 1.06 min). TX-DCA-OH also exhibited an excellent efficiency (**Figure 3b**, **Table 3**), the observed order of polymerization rate was 365 nm (R_{pmax} = 148.4 min^{-1}, $T_{C90\%}$ = 1.46 min) > 405 nm (R_{pmax} = 133.4 min^{-1}, $T_{C90\%}$ = 1.70 min) > 395 nm (R_{pmax} = 109.1 min^{-1}, $T_{C90\%}$ = 2.03 min) > 385 nm (R_{pmax} = 65.9 min^{-1}, $T_{C90\%}$ = 2.36 min). As to the photopolymerizations of TX-DCA-OH and ITX (**Figure 3c-d**, **Table 3**), the LED 365 nm and 395 nm exhibited similar order of polymerization rate, and the order of polymerization rate was 365 nm ≈ 395 nm > 405 nm > 385 nm.

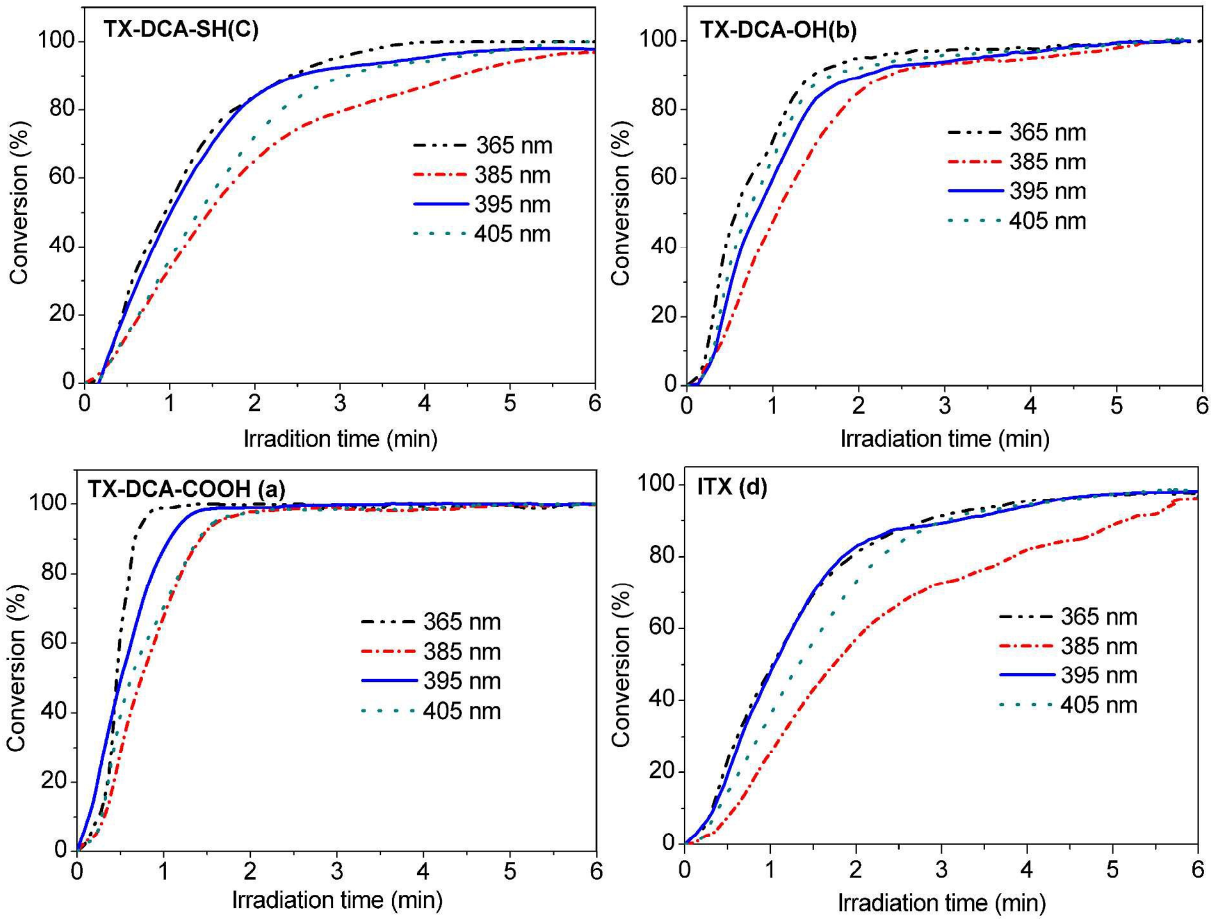


Figure 3. Photopolymerization profiles of TPGDA upon the near-UV and visible LED (365 nm, 385 nm, 395 nm and 405 nm) in the presence of (a) TX-DCA-COOH, (b) TX-DCA-OH, (c) TX-DCA-SH and (c) ITX. Experimental conditions: [TX-DCAs] = 1×10^{-5} mol, dioxane = 0.5 g, TPGDA = 0.5 g.

Table 3. Photopolymerization properties of the studied PIs: maximum initiation rate R_{pmax} and reaction time at 90% conversion $T_{C90\%}$.

	365 nm		385 nm		395 nm		405 nm	
PIs	R_{pmax} (min^{-1})[a]	$T_{C90\%}$ (min)[b]	R_{pmax} (min^{-1})	$T_{C90\%}$ (min)	R_{pmax} (min^{-1})	$T_{C90\%}$ (min)	R_{pmax} (min^{-1})	$T_{C90\%}$ (min)
TX-COOH	328.1	0.63	112.1	1.40	149.2	1.06	145.5	1.40
TX-OH	148.4	1.46	65.9	2.36	109.1	2.03	133.4	1.70
TX-SH	88.1	2.40	40.9	4.38	69	2.50	44.9	3.07
ITX	73.7	2.80	34.0	5.06	66.7	3.15	45.9	3.12

[a] The maximum initiation rate. [b] $T_{C90\%}$ can be expressed by the reaction time at 90% conversion.

For the purpose of obtaining highly effective photopolymerization, the effect of the PI structures on the rate profiles of photopolymerization initiated by the same LED light source were investigated (**Figure 4**). Generally, compared to TX-DCA-OH initiated photopolymerization, TX-DCA-COOH remarkably accelerated the photopolymerization, showing enhanced polymerization rate R_{pmax} and $T_{C90\%}$. After TX-DCA-OH, the next faster polymerization was observed with TX-DCA-SH, followed by ITX. Indeed, under the same LED light source, the observed order of polymerization rate was TX-

DCA-COOH > TX-DCA-OH > TX-DCA-SH > ITX. This can be explained by the fact that these one-component PIs were designed by chemical incorporation of various co-initiators into the structure of PIs, and significant interactions between *N*-substituted maleimides and type II PIs enhanced the photoefficiency.

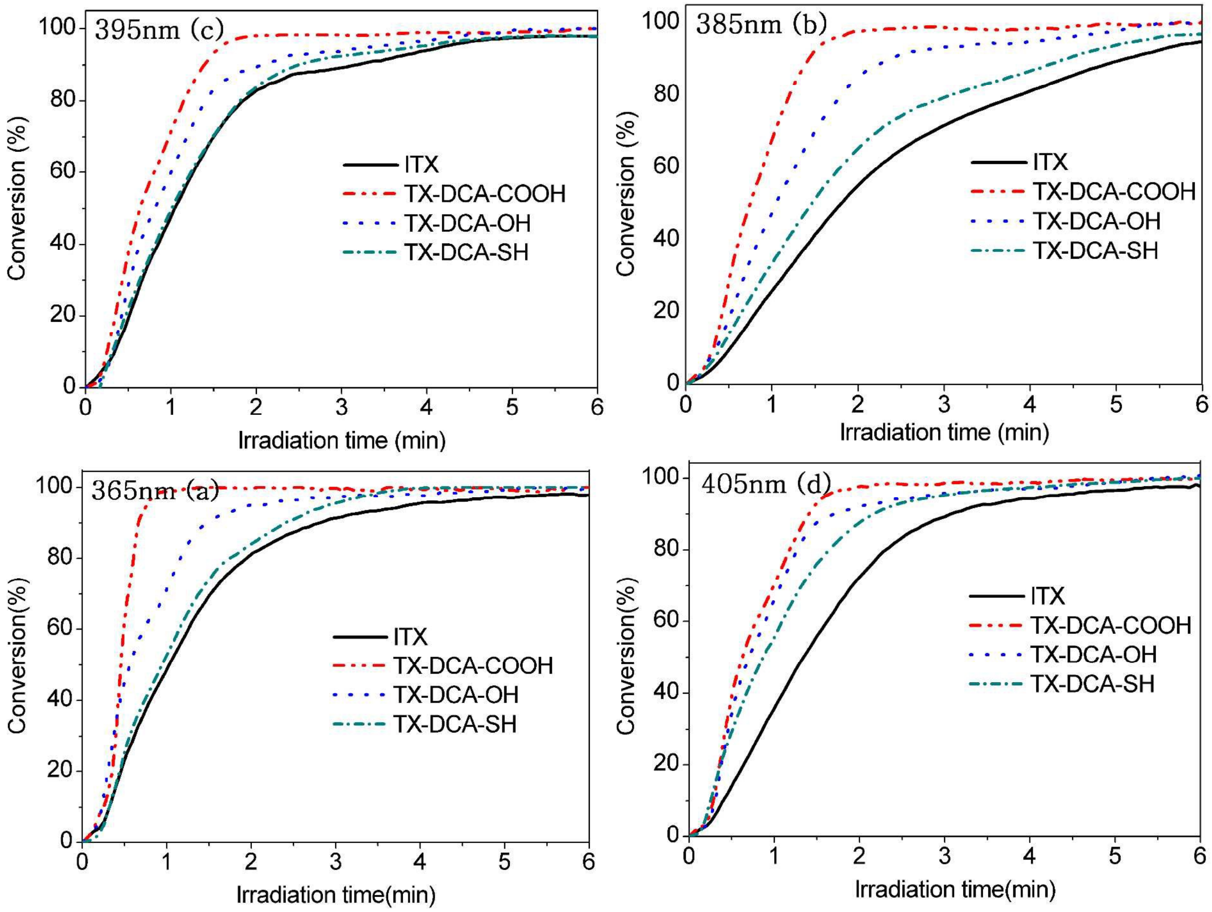


Figure 4. Photopolymerization profiles of TPGDA in the presence of different PIs (TX-DCA-COOH, TX-DCA-OH, TX-DCA-SH and ITX) upon the near-UV and visible LED (a) 365 nm, (b) 385 nm, (c) 395 nm and (c) 405 nm. Experimental conditions: [TX-DCAs] = 1×10^{-5} mol, dioxane = 0.5 g, TPGDA = 0.5 g.

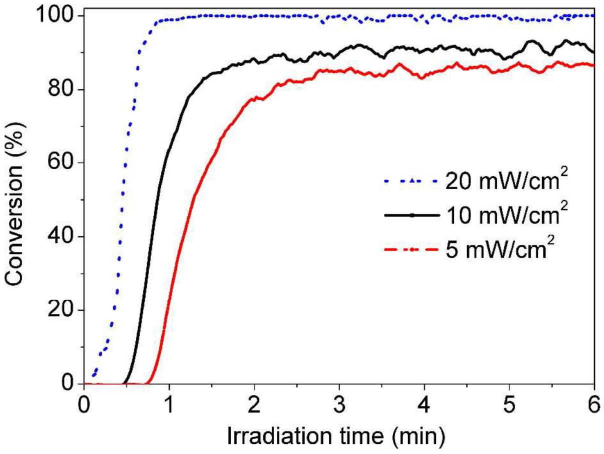
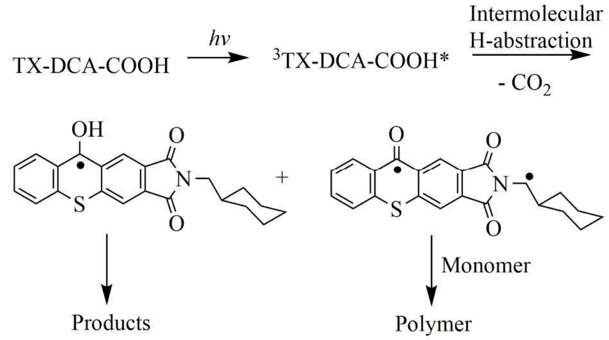


Figure 5. Photopolymerization profiles of TPGDA upon the 365nm LED with a variation of power intensity (5, 10 and 20 mW/cm^2)

The effect of a variation of power intensity (5, 10 and 20 mW/cm^2) on the initiation capability was investigated, as exemplified by TX-DCA-COOH upon the 365 nm LED. TX-DCA-COOH possessing the fastest photosensitive rate was chosen for more in-depth study. As shown in **Figure 5**, the polymerization rate and final conversion showed a consistent dependence on the power intensity, which also could be used to further shorten the polymerization duration.

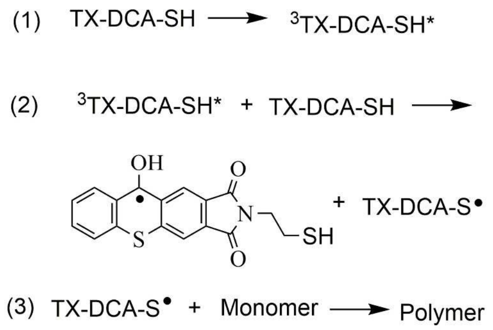
4 Photopolymerization mechanism of TX-DCAs.

Early mechanistic studies on one-component systems of thioxanthone acetic acid derivative suggested an aromatic carbonyl sensitized decarboxylation mechanism.[15, 23, 24] The decarboxylation process during the photolysis of *N*-phthalimidoamino acid derivative was also described in the literatures.[25, 26] Excited aromatic carbonyl compounds can undergo the abstraction of the acidic hydrogen by the triplet excited state TX core. Subsequent decarboxylation process evolves carbon dioxide, and yields initiating alkyl radicals. Taking the foregoing points into consideration, the principal photopolymerization mechanism of TX-DCA-COOH can be laid out in **Scheme 2**.



Scheme 2. Photopolymerization mechanism of TX-DCA-COOH through intramolecular hydrogen abstraction.

Thiol or hydroxyl substituted TXs, as one-component TX PIs, has been extensively utilized in preliminary works.[27-29] As revealed by the above laser flash photolysis studies, an intermolecular interaction between triplet ^{3}TX-SH* and ground state TX-SH molecules results in the formation of thiyl radicals through consecutive electron transfer and hydrogen atom abstraction processes. Intramolecular interaction is unlikely to happen due to the rigidity of the spacer group between the carbonyl and thiol functionalities and therefore the dominant reaction is through an intermolecular hydrogen abstraction process. As the example of TX-DCA-SH, photopolymerization mechanism of TX-DCA-SH through hydrogen abstraction can be described in **Scheme 3**.



Scheme 3. Photoinitiated radical polymerization of TX-DCA-SH.

Conclusions

In this paper, three novel photoinitiators TX-DCA-COOH, TX-DCA-OH and TX-DCA-SH are proposed for the radical polymerization of acrylates upon exposure to near UV or visible LED lights. These one-component and odourless new photoiniators are very attractive, since these do not require additional hydrogen donors. The interactions between *N*-substituted maleimides and type II PIs led to enhanced photoefficiency. For TX-DCA-based PIs, the excellent efficiency was found for the initiation of the polymerization of acrylates. The present paper opens a new direction for the design of new scaffolds and further novel derivatives usable as high-performance PIs under various UV or visible LEDs.

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Notes

[a] State Key Laboratory of Pulp & Paper Engineering, South China University of Technology, Guangzhou 510640, China

[b] DSAPM Lab, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou, 510275, China

[c] School of Media and Communication, Shenzhen Polytechnic, Shenzhen, 518055, China

‡ These authors contributed equally to this work.

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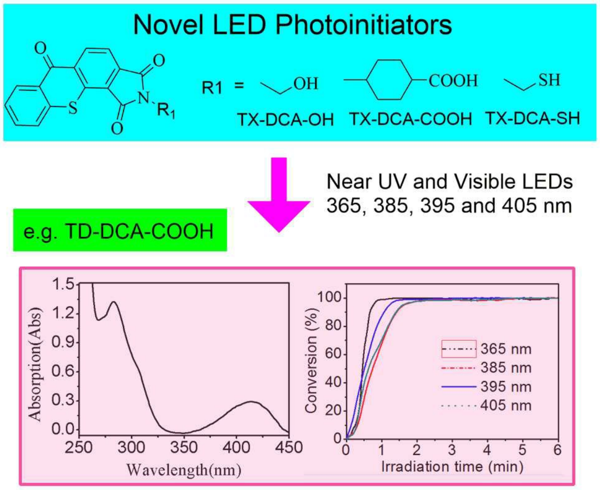

A series of thioxanthone dicarboxamide derivatives containing hydrogen donors as one-component LED photoinitiators have been prepared.