An amphipathic thioxanthone-anthracene photoinitiator for free-radical polymerization

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Abstract: A novel thioxanthone-anthracene (TX-A) photoinitiator possessing an octyl group, TX-A-Oct, as amphipathic photoinitiator was synthesized by click chemistry. Its ability to initiate photopolymerization of various monomers, namely methyl methacrylate (MMA), acrylamide (Am), butyl acrylate (BA), styrene (St), and a multifunctional monomer trimethylolpropane triacrylate (TMPTA), was examined in both the presence and absence of air. TX-A-Oct was found to be effective in initiating polymerization also in the absence of a co-initiator. UV, FTIR, and fluorescence spectroscopic analysis and polymerization studies revealed that depending on the conditions photoinitiations occur through both anthracene and thioxanthone chromophoric groups by hydrogen abstraction and endoperoxide formation processes, respectively.

Key words: Photopolymerization, free radical polymerization, photoinitiator, click chemistry, thioxanthone-anthracene

1. Introduction

Click-type reactions, primarily represented by Huisgen 1,3-dipolar azide-alkyne,¹ [3 + 2], or Diels–Alder cycloadditions,² [4 + 2], have received great interest due to their key features, including high yields, high tolerance of functional groups, and selectivity.³ Thiol-ene chemistry⁴ has recently been presented as an alternative click route that can be conducted at moderately low temperatures in the presence and absence of photoinitiators. A Huisgen 1,3-dipolar cycloaddition reaction occurs between an alkyne and an organic azide to give a 1,2,3-triazole ring. By using copper(I) catalyst, the reactions can be performed under mild experimental conditions.⁵,⁶ The development and the application of click chemistry in polymer, bio, and material sciences have been reviewed extensively.⁷

In recent years, photoinitiated polymerization has received renewed interest as it fulfills a wide range of economic and ecological expectations. For over 30 years, photopolymerization has been used as the key technology for numerous conventional applications in coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics.⁸–¹³

Free radical photopolymerization is based on the photochemical generation of initiating species through 2 main processes, namely α-cleavage (Type I) or hydrogen abstraction (Type II) reactions. In Type II systems, initiating radicals are generated by bimolecular interactions of compounds whose triplet excited states readily

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Dedicated to the late distinguished organic chemist, Prof Ayhan Sitki Demir.
react with hydrogen donors (Scheme 1).

\[
\text{Ar}_2\text{C}=\text{O} \xrightarrow{\text{hv}} \text{Ar}_2\text{C}-\dot{\text{O}} \\
\text{Ar}_2\text{C}-\dot{\text{O}} \xrightarrow{\text{R-H}} \text{Ar}_2\text{C}-\text{OH} + \dot{\text{R}} \\
\dot{\text{R}} + \text{Monomer} \rightarrow \text{Polymer}
\]

**Scheme 1.** General mechanism for photoinitiated free radical polymerization using *Type II* photoinitiators.

Benzophenone and derivatives, thioxanthones (TXs), benzil, and quinones are typical *Type II* photoinitiators, while alcohols, ethers, amines, and thiols are employed as hydrogen donors. Compare to benzophenones, TX derivatives exhibit better absorption characteristics and in conjunction with tertiary amines they are efficient photoinitiators. Despite the fact that alkylamines are very efficient hydrogen donors, the high usage of such highly volatile and odorous compounds creates important drawbacks in *Type II* systems. In order to avoid problems associated with the amine hydrogen donors, we have recently reported several new thioxanthone derivatives as photoinitiators for free radical polymerization. Interestingly, these photoinitiators initiate the polymerization without addition of a separate molecular hydrogen donor, since the hydrogen donor is incorporated into the photoinitiator structure. Recently, thiol and carboxylic acid derivatives of TXs containing functional groups with a H-donating nature have been reported. An alternative approach involves the attachment of both chromophoric and hydrogen donating groups to polymer chains. These approaches overcome the odor and toxicity problems perceived with the conventional photoinitiators and amine hydrogen donors. Additionally, we reported on the synthesis and use of 2 new oil and water soluble TX derivatives. These photoinitiators were shown to be photosensitive in the near UV and visible region, also providing environmentally friendly conditions for radical photopolymerizations. Quite recently, a TX derivative with additional carbazole or fluorinone chromophores exhibiting spectral sensitivity at longer wavelengths was reported.

Among these TX derivatives, thioxanthone-anthracene (TX-A) deserves a special discussion. TX-A initiates the polymerization of acrylate and styrene monomers in the presence of air, which cannot be accomplished by all conventional photoinitiators. Although TX-A is an efficient photoinitiator for free radical polymerization even in the presence of oxygen, it suffers from low solubility in neat monomers and nonpolar solvents, which limits its use in practical applications.

In the present work, we report on the synthesis of a new TX-A possessing a long alkoxy group via copper catalyzed azide-alkyne click chemistry. Such functionalization has brought about improved solubility. As will be shown below, such modification methodology does not destroy the photochemical behavior of the chromophores and both anthracene and thioxanthone functionalities are preserved. TX-A is highly soluble in a range of solvents with different polarity and initiates the polymerization of both hydrophobic and hydrophilic vinyl monomers in the presence of air without the necessity for an additional hydrogen donor.

### 2. Experimental section

#### 2.1. Materials

Anthracene (99%, Acros), thiosalysilic acid (97%, Sigma-Aldrich), sodium hydroxide (NaOH, Riedel-de Haën), n-butyl lithium (n-BuLi, Acros), triethylamine (Acros), trimethylol propane triacylate (TMPTA, 99%, Sigma-Aldrich), sulfuric acid (H\(_2\)SO\(_4\), 95–97%, Fluka), hydrogen bromide (HBr, ≥99%, Aldrich), sodium borohydride (NaBH\(_4\), Aldrich), pentyanoic acid (99%, Aldrich), poly(ethylene glycol) monomethylether (Me-PEG,
Mₙ: 500, Fluka), azidotrimethylsilane (TMS-N₃, Fluka), tert-butyl nitrite (t-BuONO, Aldrich), L-ascorbic acid sodium salt (99%, Acros), acryl amide (Am, Fluka), dichloromethane (J.T. Baker), n-hexane (95%, Aldrich), tetrahydrofuran (THF, 99.8%, J.T. Baker), toluene (99.9%, Sigma-Aldrich), ethanol (Riedel-de Haën), and diethyl ether (J.T. Baker) were used as received. Styrene (St, 99%, Aldrich), butyl acrylate (BA, 99%, Aldrich), and methyl methacrylate (MMA, 99%, Aldrich) were passed through a basic alumina column to remove the inhibitor before use. Methanol (technical) was used for the precipitation of polymers without further purification.

2.2. Synthesis of thioxanthone-anthracene (5-thiapentacene-14-one) (TX-A)
Thioxanthone-anthracene (TX-A) (5-thiapentacene-14-one) was synthesized according to the literature procedure.¹⁶ ¹H NMR (250 MHz) in CDCl₃: δ 8.86 (s, 1H), 8.61–8.64 (d, 1H), 8.42–8.45 (t, 1H), 8.35 (s, 1H), 7.96–8.1 (m, 2H), 7.82–7.91 (d, 1H), 7.44–7.72 (m, 5H). FTIR % T(cm⁻¹): 3050, 1672, 1622, 1593, 1339, 1147, 956, 883, 725.

2.3. Synthesis of TX-A-NO₂
TX-A (50 mg, 0.16 mmol) was dissolved in 0.50 mL of glacial acetic acid at room temperature over 10 min. Then 70% HNO₃ (0.01 mL, 0.16 mmol) was slowly added to this mixture, which was stirred for 30 min (until clear solution) in an ice-bath and then the reaction mixture was filtered and the NO₂-TX-NO₂ obtained was precipitated in a mixture of HCl (37%, 0.07 mL) and equal mole of glacial acetic acid. Then yellow TX-A-NO₂ precipitate was obtained. This precipitate was washed with glacial acetic acid twice and with water until a neutral substance was obtained. This substance was dissolved in hot 10% NaOH (0.16 mmol, 0.09 mL) at 60–70 °C and washed with warm 10% NaOH and then water. Finally, it was dried and recrystallized from glacial acetic acid to give an orange-yellow product with 90% yield.

2.4. Reduction of TX-A-NO₂
TX-A-NO₂ (45 mg, 0.126 mmol), HCl (9.95 μL, 0.126 mmol), distilled water (494 μL, 0.126 mmol), and Fe⁰ (302.4 mg, 0.126 mmol) were mixed in 3 mL of ethanol at 90 °C over 90 min. After this, the solution was filtered while it was hot. After drying, TX-A-NH₂ was obtained in 80% yield and characterized by ¹H NMR and IR.

2.5. Synthesis of TX-A-N₃
TX-A-NH₂ (36 mg, 0.109 mmol) and t-BuONO (19.32 μL, 0.109 mmol) were dissolved in dried THF, TMS-N₃ (17.3 μL, 0.109 mmol) was added dropwise over 1 h, and the mixture was stirred for an additional 2 h in an ice-bath under nitrogen. Then the reaction mixture was concentrated under vacuum, washed with THF, and dried. The final product was obtained in 88% yield and characterized by ¹H NMR and IR.

2.6. Synthesis of propargyl octane (Pr-Oct)
Propargyl alcohol (2.107 mL, 0.035 mol) and NaH (0.93 g, 39.16 mmol) were mixed with 10–20 mL of dried THF under nitrogen in an ice-bath for 2 h and then bromooctane (6.81 mL, 4.6 mmol) was added, followed by stirring for 24 h at room temperature. The solution was refluxed at room temperature for 3 h. Finally, the product obtained was characterized by ¹H NMR and IR.
2.7. Synthesis of octyl functional thioxanthone-anthracene (TX-A-Oct)

TX-A-N₃ (30 mg, 0.09 mmol) and Pr-Oct (8.72 mg, 0.09 mmol) were mixed in dried THF under nitrogen atmosphere. After mixing, CuBr (12.23 mg, 0.09 mmol) and PMDETA (18.85 μL, 0.09 mmol) were added, followed by stirring for 40 min in an ice-bath under nitrogen atmosphere. Then the solution was stirred at room temperature overnight. The formed product (TX-A-Oct) was filtered over Al₂O₃ and washed with THF, concentrated, dried, and characterized by ¹H NMR and IR. Yield was 87%.

2.8. General procedure for photopolymerization

Appropriate solutions of photoinitiator and different monomers (MMA, Am, BA, St) were irradiated in a photoreactor equipped with 12 Philips lamps emitting nominally at λ > 350 nm for 90 min in the presence and absence of triethylamine (TEA) in either air or N₂ atmosphere. The polymer formed at the end of irradiation was precipitated in 10-fold excess methanol and dried in vacuo. The conversion % was calculated gravimetrically for all samples.

2.9. Instrumentation

¹H NMR measurements were recorded in CDCl₃ with Si(CH₃)₄ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FTIR spectra were recorded on a PerkinElmer FTIR Spectrum One-B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, 3 ViscogEL GPC columns (G2000H₉R, G3000H₉R, and G4000H₉R), a Viscotek UV detector, and a Viscotek differential refractive index (RI) detector with a THF flow rate of 1.0 mL min⁻¹ at 30 °C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Diamond differential scanning calorimeter.

2.10. Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified PerkinElmer Diamond differential scanning calorimeter equipped with a high pressure mercury arc lamp (320–500 nm). A uniform UV light intensity was delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 53 mW cm⁻² by a UV radiometer capable of broad UV range coverage. The mass of the sample was 3 mg, and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min⁻¹. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate groups reacted in the system. The conversion of the acrylate groups (C) or the extent of the reaction was determined according to Eq. (1) by integrating the area under the exothermic peak:

\[ C = \frac{\Delta H_t}{\Delta H_0^{\text{theory}}}, \quad (1) \]

where \( \Delta H_t \) is the reaction heat evolved at time \( t \) and \( \Delta H_0^{\text{theory}} \) is the theoretical heat for complete conversion. \( \Delta H_0^{\text{theory}} = 86 \text{ kJ mol}^{-1} \) for an acrylic double bond.⁴⁸ The rate of polymerization \( (R_p) \) is directly related to the heat flow \( (dH/dt) \) as given by Eq (2):

\[ R_p = \frac{dC}{dt} = \frac{(dH/dt)}{\Delta H_0^{\text{theory}}}. \quad (2) \]
3. Results and discussion
3.1. Synthesis and characterization of the photoinitiator

In order to apply click chemistry for modification, it was essential to synthesize the click component of the photoinitiator, namely azide functionalized thioxanthone-anthracene (TX-A-N₃). For this purpose, the precursor TX-A-NO₂ was synthesized. The nitro compound obtained is easily transformed to TX-A-NH₂ by hydrogen-transfer reduction in the presence of Fe/HCl with quantitative conversion. Here it should be pointed out that the conventional azidation process either requires excessive chemicals or is explosive. In order to overcome such problems, we employed a method utilizing stable and nonexplosive reagents, tert-butyl nitrite (t-BuONO) and azidotrimethylsilane (TMSN₃). The desired azido compound was obtained in quantitative yield. The overall synthesis protocol is summarized in Scheme 2.

![Scheme 2. Synthesis of TX-A-N₃.](image)

The structures of the intermediates and final product were confirmed by ¹H NMR spectra (CDCl₃) (Figure 1). The aromatic protons of phenyl groups emerge at around 8 ppm, due to the electron withdrawing effect of the –NO₂. The reduction process led to 2 changes in the spectra. While N–H protons appeared at 5.30 as new peaks, the aromatic peaks resonated at higher magnetic fields in the range of 8.1–6.8 ppm. The integration ratio of N–H protons to aromatic C–H protons (2:11) confirms a quantitative reduction process. The efficient transformation of TX-A-NH₂ to TX-A-N₃ was also evidenced from ¹H NMR analysis wherein the resonance due to N–H protons disappeared completely.

Additionally, FTIR spectra of the related compounds confirm the expected structures. TX-A-NO₂ exhibits strong symmetric and asymmetric νN–O peaks at 1348 and 1527 cm⁻¹ (Figure 2). These peaks disappear completely after reduction and new broad symmetric and asymmetric νN–H peaks appear at 3368 cm⁻¹ and 3456 cm⁻¹. After the transformation of amine groups to azide groups, a strong and new vibration centered at 2104 cm⁻¹ appeared in the spectrum.
Figure 1. $^1$H NMR spectra of TX-A, TX-A-NO$_2$, TX-A-NH$_2$, and TX-A-N$_3$.

Figure 2. IR spectra of TX-A, TX-A-NO$_2$, TX-A-NH$_2$, and TX-A-N$_3$. 
Propargyloctane (Pr-Oct), deliberately selected as the other click component in order to introduce both solubility and hydrogen donating capability to the TX-A photoinitiator, was synthesized by a simple etherification procedure (Scheme 3).

Scheme 3. The synthesis of Pr-Oct.

Then a standard click protocol was established. TX-A-N\textsubscript{3} was dissolved in THF and reacted with Pr-Oct in the presence of copper sulfate/sodium ascorbate in aqueous solution at room temperature to give the desired photoinitiator (Scheme 4).


The modification drastically changes the solubility behavior of bare TX-A. As can be seen from Table 1, TX-A-Oct is soluble in highly polar solvents such as water and DMF as well as in the less polar solvents such as THF, confirming that amphipathic nature.

Evidence for the occurrence of click reactions was obtained from \textsuperscript{1}H NMR spectra. As can be seen from Figure 3, where \textsuperscript{1}H NMR spectra of TX-A-N\textsubscript{3}, Pr-Oct, and TX-A-Oct were recorded, alkyne end functionality of Pr-Oct observed at 3.4 ppm disappeared completely. Furthermore, the successful transformation of azide moieties into the triazole ring was confirmed. Typically, in the case of TX-A-Oct, the new methylene protons adjacent to the triazole ring (triazole–CH\textsubscript{2}O) and triazole proton appear at 4.3 ppm at 8.1 ppm, respectively (Figure 3).

Table 1. Solubility of TX-A-Oct in solvents ranked according to dielectric constants.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant\textsuperscript{a}</th>
<th>TX-A</th>
<th>TX-A-Oct</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>80</td>
<td>NS</td>
<td>S</td>
</tr>
<tr>
<td>DMF</td>
<td>38</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>9.1</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>THF</td>
<td>7.5</td>
<td>SS</td>
<td>S</td>
</tr>
<tr>
<td>CHCl\textsubscript{3}</td>
<td>4.81</td>
<td>SS</td>
<td>S</td>
</tr>
</tbody>
</table>

\textsuperscript{a} At 25 °C.

S, soluble; SS, slightly soluble; NS, nonsoluble.

The FTIR spectra of TX-A-Oct also confirmed the quantitative reaction, as the azide stretching band at around 2104 cm\textsuperscript{-1} disappears completely while a strong ether band at 1100 cm\textsuperscript{-1} is detectable (Figure 4).
Figure 3. $^1$H NMR spectra of TX-A-N$_3$, Pr-Oct, and TX-A-Oct.

Figure 4. IR spectra of TX-A-N$_3$, and TX-A-Oct.

Figure 5. Absorption spectra of TX, TX-A, TX-N$_3$, and TX-A-Oct in DMF (the concentration is $1.0 \times 10^{-5}$ M).
Photophysical characteristics of the obtained thioxanthone compounds were investigated by UV and fluorescence spectroscopy. As can be seen from Figure 5, TX-A displays characteristic 5-finger absorbance in the 300–400 nm range. TX-A-Oct exhibits an absorption spectrum similar to that of bare TX-A, except for a tail absorption in the visible wavelength region probably due to the extended conjugation arising from the aromatic triazole ring.

The mirror-image-like relation between absorption and emission of TX-A-Oct is presented in Figure 6a and b, respectively. The emission spectrum represents the characteristics of the anthracene (A) moiety rather than TX, indicating the dominant photoexcited state of photoinitiator as bare TX-A at this excitation wavelength.

### Table 2. Photoinitiated polymerizations\(^a\) of vinyl monomers in bulk.

<table>
<thead>
<tr>
<th>M</th>
<th>TEA (mol L(^{-1}))</th>
<th>(N_2)</th>
<th>Conversion(^b) (%)</th>
<th>(M_w/M_c) (\times 10^{-4}) (g mol(^{-1}))</th>
<th>(M_w/M_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>10.1</td>
<td>2.2</td>
</tr>
<tr>
<td>MMA</td>
<td>-</td>
<td>+</td>
<td>2.4</td>
<td>8.9</td>
<td>2.1</td>
</tr>
<tr>
<td>MMA</td>
<td>(5 \times 10^{-2})</td>
<td>-</td>
<td>7</td>
<td>2.4</td>
<td>1.7</td>
</tr>
<tr>
<td>BA</td>
<td>-</td>
<td>-</td>
<td>29</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td>BA</td>
<td>-</td>
<td>+</td>
<td>20</td>
<td>3.5</td>
<td>2.1</td>
</tr>
<tr>
<td>BA</td>
<td>(5 \times 10^{-2})</td>
<td>-</td>
<td>56</td>
<td>13.7</td>
<td>2.7</td>
</tr>
<tr>
<td>BA</td>
<td>(5 \times 10^{-2})</td>
<td>+</td>
<td>30</td>
<td>18.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Am(^a)</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>(\infty^c)</td>
<td>-</td>
</tr>
<tr>
<td>Am(^a)</td>
<td>-</td>
<td>+</td>
<td>12.2</td>
<td>(\infty^e)</td>
<td>-</td>
</tr>
<tr>
<td>Am(^a)</td>
<td>(5 \times 10^{-2})</td>
<td>-</td>
<td>53.1</td>
<td>(\infty^e)</td>
<td>-</td>
</tr>
<tr>
<td>St</td>
<td>(5 \times 10^{-2})</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)[TX-A-Oct] = \(5 \times 10^{-3}\) mol L\(^{-1}\); irradiation time = 90 min, \(^b\)Determined gravimetrically, \(^c\)Determined by GPC using polystyrene standards, \(^d\)In water, [Am] = 3.6 mol L\(^{-1}\), \(^e\)Insoluble polymer.

Figure 6. Fluorescence excitation (a) and emission (b) spectra of TX-A-Oct in DMF; \(\lambda_{exc} = 350\) nm. [TX-A-Oct] = \(1.4 \times 10^{-4}\) mol L\(^{-1}\).

### 3.2. Photopolymerization using TX-A-Oct

TX-A-Oct is used as photoinitiator for the polymerizations of various monomers including methylmethacrylate (MMA), butylacrylate (BA), acrylamide (Am), and styrene (St) in the presence and absence of air with either co-initiator or not. The results are compiled in Table 2.
As can be seen, TX-A-Oct is an efficient photoinitiator in the absence of a co-initiator. Notably, the addition of a hydrogen donor such as TEA accelerates the polymerization. The presence of an amine such as TEA is important for effective photoreduction of the TX moiety. Polymerization experiments in the presence and absence of oxygen clearly confirm the crucial role of oxygen in confirming the particular mechanism involved in the initiation of the polymerization. An increase in the extent of polymerization was observed in air-saturated solutions compared to nitrogen-saturated solutions. In this case, anthracene moiety is the dominant chromophore and oxygen is involved in the generation of initiating radicals from TX-A-Oct through endoperoxide intermediate formation. The endoperoxide undergoes photochemical or thermal decomposition to generate radicals that are able to initiate free radical polymerization.\textsuperscript{29,47}

Among the several monomers tested, BA seemed to be the most suitable for photopolymerization initiated by TX-A-Oct. The observed high conversion of BA can be explained in terms of its chemical structure similarity with photoinitiators due to the long alkoxy group, which leads to improved solubility of TX-A-Oct. It is evident from Table 2 that Am monomer, which is more prone to hydrogen bonding, exhibits a relatively high extent of polymerization. In this way, monomers behave partly like difunctional species and the termination rate constant is dramatically reduced.\textsuperscript{50} It is also likely that hydrogen bonding facilitates preorganization, thereby forcing the double bonds of the monomers in close proximity to each other. As a consequence, the propagation reaction rate constant ($k_p$) is enhanced, resulting in a higher rate of polymerization.

We have also tested the polymerizability of S monomer with TX-A-Oct. In complete contrast to TX-A, polymerization of S with this macrophotoinitiator in the presence of TEA did not proceed. Although aromatic carbonyl/amine combinations represent an effective photoinitiator system for the polymerization of (meth)acrylates, they appear to be less reactive toward styrene monomers due to the high quenching rate of the monomer and the low reactivity of R-amino radicals with S.\textsuperscript{51,52}

The above results clearly confirm that, albeit at different rates, TX-A-Oct is an efficient photoinitiator for the polymerization of all the monomers studied. It is also evident that either or both thioxanthone and anthracene moieties are photosensitive to generate initiating radicals. The overall mechanisms involving hydrogen abstraction and endoperoxide formation are presented in Scheme 5.

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**Figure 7.** Heat flow versus time for the photopolymerization of TMPTA initiated by TX-A-Oct ($5 \times 10^{-3}$ mol L$^{-1}$) in the presence and absence of TEA at 30 °C by UV light with an intensity of 53 mW cm$^{-2}$.

**Figure 8.** Conversion versus time for the photopolymerization of TMPTA initiated by TX-A-Oct ($5 \times 10^{-3}$ mol L$^{-1}$) in the presence and absence of TEA at 30 °C by UV light with an intensity of 53 mW cm$^{-2}$.
It was of interest to evaluate the efficiency of TX-A-Oct in the photocuring of formulations containing multifunctional monomers. In Figure 7, a photo-DSC exotherm referring to the polymerization of 1,1,1-tris(hydroxymethyl)propane triacrylate (TPTA) containing TX-A-Oct in the presence or absence of TEA under polychromatic light is shown. It is evident from Figure 8 that TX-A-Oct in the presence of additional hydrogen donor exhibits a higher rate of polymerization. Figure 8 displays a plot of the conversion vs. irradiation time derived from Figure 7. The “conversion-time” kinetics curves represent 2 distinct stages: a rapid first stage followed by a slow stage. It is quite likely that, in the second stage, gelation and vitrification of the polymerizing trifunctional acrylate reduce the diffusion of the components in the formulation.

4. Conclusion
A novel amphipathic thioxanthone-anthracene–based photoinitiator possessing an octyloxy group, TX-A-Oct, as oil-/water-soluble was synthesized via copper-catalyzed azide-alkyne click chemistry. This photoinitiator initiates the polymerization of both hydrophobic and hydrophilic vinyl monomers in the presence and absence of hydrogen donor and under air or nitrogen atmosphere. Depending on the experimental conditions, either hydrogen abstraction or endoperoxide formation mechanisms may be operative in generating initiating radicals through thioxanthone or anthracene photoexcitations, respectively. Moreover, the water solubility of TX-A-Oct enables its use as an initiating system in water-borne formulations. Such wide flexibility offered by this photoinitiator suggests that it may find use in a variety of practical applications.

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