Photodimerization of thioxanthone–anthracene: formation of monochromophoric Type II initiator

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ABSTRACT
Thioxanthone–anthracene (TX-A) was previously synthesized and used as an initiator for the polymerization of acrylates and methacrylates in air atmosphere. Photodimerization of TX-A was carried out in benzene under light irradiation of >350 nm, and dimer (diTX-A) formation was followed by UV–vis, fluorescence and phosphorescence spectroscopy. The conjugation of anthracene was destroyed after dimerization, and the thioxanthone group was left behind. Therefore, the typical thioxanthone absorption spectrum was seen at 380 nm. TX-A itself does not have phosphorescence emission; however, diTX-A displayed phosphorescence emission spectrum similar to thioxanthone. IR and $^1$H NMR spectrophotometric techniques also helped to determine the structure of diTX-A. Furthermore, photopolymerization of methyl methacrylate (MMA) in the presence of dimer (diTX-A) was another proof of the photodimerization of TX-A. diTX-A initiated polymerization of MMA as good as thioxanthone in the nitrogen atmosphere and displayed typical Type II initiator behaviour.

Introduction
Anthracene and its derivatives are exciting compounds due to their versatile photochemical applications, and they have been used as energy migration probes in polymers and triplet sensitizers. The anthracene ring is capable of acting as a light-induced electron donor or acceptor and it also possesses photochromic properties, which allows them to be used in the design of optical, electronic or magnetic switches. These reversible properties are based on the photodimerization reaction. Anthracene photodimerization is one of the oldest best known photochemical reactions which was reported by Fritzche et al. [1–7].

The first systematic investigation of the photodimerization of substituted anthracene derivatives were reported during the 1960 by Calas and Lalande [8]. The formation of anthracene dimers by excitation at 366 nm through triplet–triplet annihilations were established by Saltiel and co-workers [9].

Calas and Lalande concluded colourless photodimers obtained by the irradiation of solution of most anthracene derivatives and the photodimers were shown to thermally regenerate the monomers.[4,10–12]

A great number of studies were performed on this photoinduced dimerization reaction, revealing a mechanism based on a [4$n$ + 4$n$] cycloaddition of the central ring of the anthracene π-system.[13–22] It is important to know that the photodimerization reaction takes place purely in the absolute absence of oxygen, otherwise the formation of endoperoxides occurs.[23,24]

Thioxanthone–anthracene (TX-A) (Chart 1) was previously synthesized and its photoinitiation efficiency and mechanisms were investigated.[25,26] Importantly, in contrast to TX type photoinitiators, TX-A is an efficient photoinitiator for free-radical polymerization in the presence of oxygen without additional hydrogen donor. The proposed mechanism involves photoexcitation of TX-A, and quenching of triplet excited states of TX-A formed by molecular oxygen to generate singlet oxygen (See Scheme 1). Following addition of singlet oxygen to the anthracene moiety of TX-A leads to TX-A-O2. Photooxidation of TX-A-O2 causes alkoxo or peroxy radicals which are able to initiate free-radical polymerization. For this reason, molecular oxygen is essential for the initiation process of TX-A.[26]

In this study, our aim was to obtain reversible properties based on the photodimerization reaction of TX-A.

Various techniques were used to follow [4 + 4] dimer formation of TX-A, and the results are reported herein.

Experimental
Materials
Anthracene (≥99.0%, Fluka), thiosalicylic acid (98.5%, Fluka), glacial acetic acid (Aldrich), sulphuric acid (H$_2$SO$_4$,
cold finger at 77 K. The $^1$H NMR (250 MHz) spectra were recorded on a Bruker NMR Spectrometer in CDCl$_3$.

**Results and discussion**

The solution of TX-A in benzene was irradiated with long-wave UV light until the typical absorption peaks of the anthracene molecule completely disappeared. The whole photodimerization process was monitored by a UV–vis spectrophotometer, and total irradiation time was around 80 h. For characterization of the filtered product, dimerized TX-A (diTX-A), FTIR, $^1$H NMR, UV–vis, fluorescence and phosphorescence spectroscopy techniques were used. Although the TX-A molecule is a covalent combination of thioxanthone and anthracene molecules as shown in Chart 1, the absorption properties of TX-A are similar to the anthracene molecule (see Figure 1). Even from the absorption spectroscopy, it is easy to follow the photodimerization of TX-A. Dimerization interrupts the conjugation of anthracene since 9, 10 positions are involved for the dimerization and generate thioxanthone. The typical absorption spectrum of thioxanthone appeared after 80 h of irradiation of TX-A as shown in Figure 2 and one can say that the absorption spectrum of diTX-A clearly confirms photodimerization of TX-A.
Another technique, IR spectroscopy, was also used for the confirmation of diTX-A. TX-A itself has an aromatic vibrational band at 3030 cm$^{-1}$, and a carbonyl group appears at 1623 cm$^{-1}$. When diTX-A was isolated from the benzene solution, the carbonyl peak shifted to 1709 cm$^{-1}$ and an aliphatic peak was observed at 2934 cm$^{-1}$ corresponding to C–H bending vibrations (see Figure 3).[27]

$^1$H NMR spectroscopy is a very useful tool for characterization of the obtained photodimer of TX-A. Figure 4 clearly demonstrates the occurrence of the photodimerization of TX-A.

The $^1$H NMR chemical shifts of the tertiary bridgehead protons are characteristic of the 9,10; 9',10' types of structure. The bridgehead protons of diTX-A were observed at $\delta$ 4.00 ppm in CDCl$_3$. In the literature, based on the different substituents attached to anthracene, dimer proton is observed between 3.7 and 6.5.[28–30] While dimerization procedure was carried out under nitrogen atmosphere, $\delta$ 6.15–6.5 ppm protons belonging to endoperoxide formation were not observed. However, $\delta$ 4.00 ppm protons belong to bridgehead protons of photodimer product was seen as shown in Figure 4.

Fluorescence and phosphorescence spectroscopy are two very useful and important techniques for confirmation of the obtained photodimer from irradiation of TX-A in benzene. First, the fluorescence emission spectrum of the adduct, diTX-A, was taken in ethanol and compared with the fluorescence emission spectrum of TX-A, and a clear shift to a lower wavelength was observed. Furthermore, the fluorescence excitation and emission spectra of TX-A was compared with the excitation and emission spectra of diTX-A and TX (see Figure 5). The similar excitation spectrum of di-TXA and TX is another good proof for the formation of photodimer.

The emission spectrum of diTX-A clearly demonstrates the thioxanthone structure as a result of the degeneration of the anthracene structure.

TX-A does not phosphorescence emission in contrast to the thioxanthone molecule. Therefore, phosphorescence spectroscopy was used to see the formation of diTX-A. As expected, diTX-A presented a nice phosphorescence emission spectrum similar to thioxanthone at 475 nm in ethanol glass at 77 K since the conjugation of anthracene was destroyed after dimerization (excitation wavelength was 380 nm, see Figure 6).

Beside all of the spectroscopic investigations to determine the formation of the photodimer of TX-A, photopolymerization experiments were also used to see the behaviour of the obtained dimer diTX-A.

TX-A undergoes 4 + 4 dimerization reaction by irradiation around 350 nm, as seen from Table 1, TX-A, thioxanthone (TX) and the obtained photodimer, diTX-A, were used as initiators for the polymerization of MMA in the
as we know from our previous studies, TX-A needs oxygen to form endoperoxide and undergoes decomposition to generate radicals that are able to initiate the polymerization of MMA.

4.5% of the polymer formation was observed with TX-A in air and no polymer resulted in N₂ atmosphere, in contrary to thioxanthone and the photodimer diTX-A. TX and diTX-A both initiate the polymerization reaction under inert atmosphere, and the polymer yield in the presence of TX was slightly higher than diTX-A.

Furthermore, to test the reversible dimerization of diTX-A, the dimer was exposed to a UVC light source for 6 h of irradiation to follow the transformation of diTX-A to TX-A. This reaction was recorded by UV–vis spectroscopy. Figure 7 demonstrates this reversible process; after 6 h of irradiation, the shape of absorbance started to change and the maximum absorption of diTX-A was at 380 nm similar to thioxanthone itself.

In conclusion, photodimerization of the photoinitiator thioxanthone–anthracene was successfully achieved by irradiation with 350 nm light, and the structure of the photodimer, diTX-A, was characterized by several spectroscopic methods.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

| Table 1. Photoinitiated polymerization of methyl methacrylate in DMF with a medium pressure mercury lamp. |
| --- |
| **Photoinitiator** | **N₂** | **Conversion (%)** |
| TX-A | + | – |
| TX-A | – | 4.5 |
| TX | + | 7.2 |
| TX | – | – |
| di TX-A | + | 5.9 |
| di TX-A | – | 0.3 |

**Note:**

aPl = 5.0 × 10⁻³ M, MMA: 4.68 M.
bIr : 15 min.
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