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Mechanism of Photoinitiated Free Radical Polymerization by Thioxanthone–Anthracene in the Presence of Air

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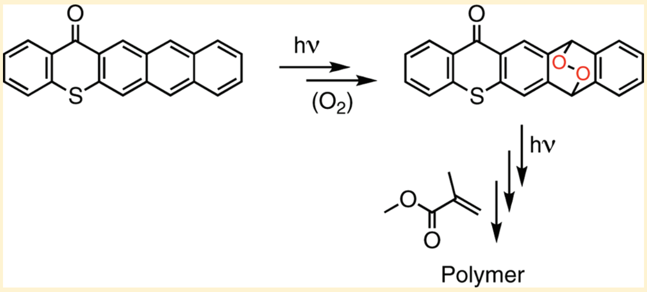
Supporting Information

ABSTRACT: The mechanism of formation of initiating radicals for free radical polymerization by the thioxanthone–anthracene (TX-A) photoinitiator was investigated by laser flash photolysis, fluorescence and phosphorescence spectroscopy, and polymerization studies. The proposed mechanism of photoinitiation involves photoexcitation of TX-A and quenching of triplet excited states of TX-A by molecular oxygen to generate singlet oxygen. Singlet oxygen reacts with the anthracene moiety of TX-A to form an endoperoxide. The endoperoxide intermediate was isolated and characterized by MS and ^{1}H NMR. The endoperoxide undergoes photochemical or thermal decomposition to generate radicals which are able to initiate free radical polymerization. A significant deuterium effect on the polymerization rates using $CDCl_3$ and $CHCl_3$ as solvents confirmed the involvement of singlet oxygen in the initiation process.



INTRODUCTION

Thioxanthone (TX) and derivatives are among the most widely used type II photoinitiators in various UV curing applications because of their excellent light absorption characteristics.[1−3] In most cases, the photoinitiating free radicals are generated by hydrogen abstraction by the triplet excited state of TX from hydrogen donors such as amines or thiols (Scheme 1).[4−6]

However, low-molecular-weight amines, particularly at high concentrations, have several intrinsic disadvantages such as objectionable odor, toxicity,[7] and migration in UV-curing technology and cause a decrease in the pendulum hardness of the cured films.[8] One way to overcome these problems is to chemically incorporate the hydrogen-donating sites into TX chromophores.[9−11] We have previously reported several thiol[12] and acetic acid[13] derivatives of TX as photoinitiators for free radical polymerization. A major advantage of this type of initiator is related to their one-component nature. They can serve as both a triplet photosensitizer and a hydrogen donor.

More recently, we have reported[14] a new photoinitiator shown in Chart 1, thioxanthone–anthracene (TX-A). The latter exhibits completely different photochemical properties compared to conventional TX type photoinitiators. In addition, an interesting application of this photoinitiator in a completely different area has been demonstrated.[15] Achiral molecules of TX-A self-assemble into chiral nanowires by tuning the solvent polarity. Left- and right-handed nanowires with helix structure can be produced from chloroform and acetic ester solution of TX-A, respectively.

Importantly, in contrast to TX type photoinitiators, TX-A is an efficient photoinitiator for free radical polymerization of both acrylic and styrenic type monomers in the presence of oxygen without additional hydrogen donor. For other TX type photoinitiators oxygen inhibits polymerization because of quenching of excited triplet TX with oxygen. Furthermore, in case of TX-A as photoinitiator, molecular oxygen is essential for the initiation process. However, the initiation mechanism is not clear. To resolve this issue, the present paper reports laser flash photolysis, fluorescence, phosphorescence and polymerization studies in order to elucidate and understand the mechanism of free radical polymerization with TX-A as photoinitiator.

RESULTS AND DISCUSSION

Absorption and Fluorescence. As can be seen from Figure 1a, TX-A exhibits a high molecular absorptivity (∼14 000 M^{-1} cm^{-1} at 368 nm) which ensures effective light absorption in the near-UV spectral region, which is attractive for practical applications in photocuring systems. Figure 1 also shows fluorescence excitation (b) and emission (c) spectra of TX-A in acetonitrile. The fluorescence is weak ($\Phi_F = 0.02$), which is typical of ketones. However, the almost identical shape of the excitation spectrum (b) to the

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absorption spectrum of TX-A (a) confirms that the observed fluorescence (c) originated from TX-A and not from impurities. An earlier published spectrum of TX-A has different characteristics and was probably dominated by anthracene impurities,[14] which are expected to have a significantly higher fluorescence quantum yield (0.27).[16] The low fluorescence quantum yield is consistent with efficient intersystem crossing into the triplet state, the state which leads to the production of initiator radicals.

Laser Flash Photolysis. Laser flash photolysis experiments were performed to investigate the properties of the triplet state (T_1) of TX-A. Figure 2 shows the transient absorption spectrum of argon saturated acetonitrile solution containing TX-A recorded 0.3−2 μs after irradiation with laser pulses of 427 nm from a dye laser. The spectrum shows transient absorption between 400 and 550 nm with a lifetime of 28 μs. The transient was quenched by molecular oxygen with a rate constant of 2.8×10^9 M^{-1} s^{-1} (Figure S1, Supporting Information) and was tentatively assigned to the triplet state of TX-A. It is known that most of the triplet excited states of photosensitizers, including TX and A triplets, are quenched by oxygen with a similar rate constant.[17]

Photopolymerization. Polymerization experiments in the presence and absence of oxygen clearly confirm the crucial role of oxygen for a successful polymerization (Table 1). Solutions of MMA and TX-A were irradiated in air or nitrogen atmosphere. Surprisingly, polymer formation was observed in air-saturated solutions, but not in the absence of oxygen. Furthermore, if pure TX was used as photoinitiator, no polymer was generated in the presence or absence of oxygen. In addition, under similar experimental conditions, only small amount of polymer was observed, if pure anthracene was used as photoinitiator (Table 1). These experiments demonstrate that oxygen is involved in generation of initiator radicals from TX-A.

Scheme 1. Photoinitiated Free Radical Polymerization Using TX as Photoinitiator

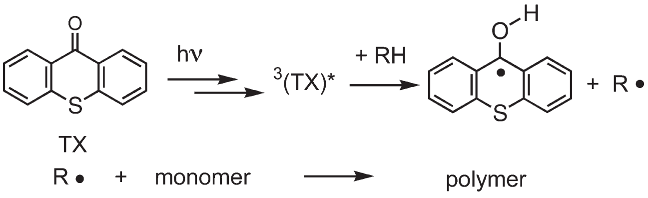
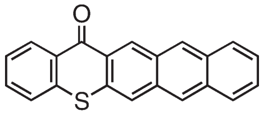


Chart 1. Structure of TX-A



TX-A

Singlet Oxygen Phosphorescence. When oxygen is quenched by triplet states, singlet oxygen, a reactive oxygen species, is commonly formed by energy transfer. To test if singlet oxygen is formed as a result of quenching of the triplet excited state of TX-A by triplet oxygen (ground state molecular oxygen), NIR phosphorescence spectroscopy was performed. Singlet oxygen is known to show a characteristic phosphorescence at 1270 nm.[18] Figure 3 (right) shows the NIR luminescence spectrum of an air-saturated $CDCl_3$ solution of TX-A (λ_{ex} = 426 nm) which is consistent with singlet oxygen phosphorescence. The excitation spectrum (Figure 3, left) of this luminescence spectrum (λ_{em} = 1270) resembles the absorption spectrum of TX-A (Figure 1a), which confirms that singlet oxygen is generated by photoexcitation of TX-A.

Singlet oxygen is known to react efficiently with polyaromatics, such as anthracene, by 2 + 4 cycloaddition to form endoperoxides.[19] Thus, singlet oxygen is expected to react with the anthracene moiety of TX-A. To determine the rate constant for this reaction with TX-A, singlet oxygen was generated independently by sensitization with Rose Bengal (λ_{ex} = 532 nm), and the phosphorescence decay kinetics was followed at varying TX-A concentrations. The slope of the plot of the pseudo-first-order decay rate constant of the singlet oxygen phosphorescence vs the TX-A concentration yields directly the bimolecular quenching rate constant of singlet oxygen by TX-A ($k_{^1O_2} = 8.5 \times 10^5$ M^{-1} s^{-1}) as shown in Figure S2. This rate constant is similar to the reported value for anthracene itself ($k_{^1O_2} = 5.4 \times 10^5$ M^{-1} s^{-1}).[20]

Deuterium Effect in Polymerization. The lifetime of singlet oxygen is known to have a strong H/D isotope effect. The lifetime of singlet oxygen in a deuterated solvent, such as $CDCl_3$ (8.9 ms), is significantly longer than in the protonated equivalent ($CHCl_3$; 0.23 ms).[18] Thus, comparative photopolymerization studies using TX-A as initiator in air-saturated solutions in $CDCl_3$ and $CHCl_3$ were performed. In these experiments, highly diluted monomer solutions were subjected to irradiation to minimize the contribution of singlet oxygen quenching by the protonated monomer. The polymer yields are shown in Table 2. Because of low monomer concentrations, quite low conversions were attained. However, the critical observation is that the conversions of polymerizations initiated in $CDCl_3$ were considerably higher than those initiated in $CHCl_3$. These results show that the initiation occurs more effectively when the singlet oxygen has a longer lifetime, being consistent with the fact that singlet oxygen is involved in the initiation mechanism.

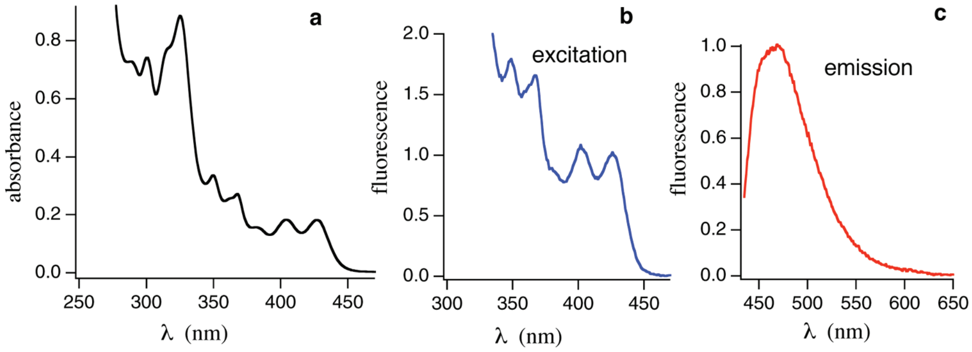


Figure 1. Absorbance (a), fluorescence excitation (b), and emission (c) spectra of TX-A in acetonitrile solutions.

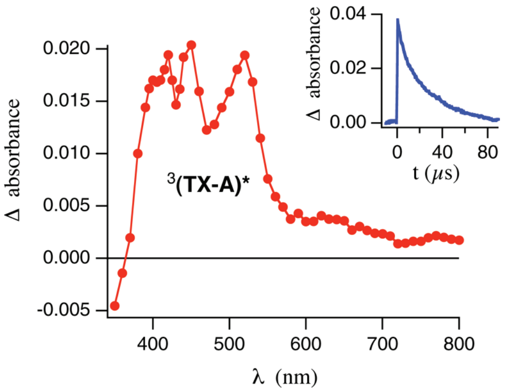


Figure 2. Transient absorption spectrum of TX-A recorded 0.3−2 μs after the laser pulse (427 nm, ∼2 mJ/pulse). Inset: decay trace at 520 nm.

Table 1. Photoinitiated Polymerization of Methyl Methacrylate (4.7 M) in DMF for 15 min

initiator (5 mM)		conversion[a] (%)
TX-A	N_2	0.0
TX-A	air	4.5
TX	air	0.0
TX + anthracene	air	0.0
anthracene	air	0.7

[a] Determined gravimetrically.

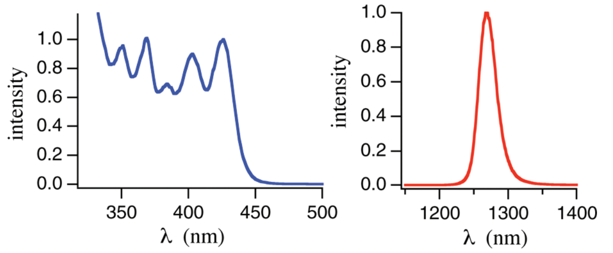


Figure 3. Singlet oxygen phosphorescence (right) generated by photoexcitation of TX-A in air-saturated $CDCl_3$ (λ_{ex} = 426 nm). Singlet oxygen phosphorescence excitation spectrum (left) monitored at 1270 nm.

Table 2. Photoinitiated Polymerization of Methyl Methacrylate in Dilute Air-Saturated Solutions Containing TX-A (0.64 mM)

solvent	[MMA] (M)	irradiation time (min)	conversion[a] (%)
$CHCl_3$	0.94	30	0.5
$CDCl_3$	0.94	30	1.1
$CHCl_3$	1.9	15	0.3
$CDCl_3$	1.9	15	0.8

[a] Determined gravimetrically.

On the basis of above results, a plausible and feasible mechanism for the initiation process involves the formation of an endoperoxide (TX-A-O_2) by the reaction TX-A with singlet oxygen generated from the triplet excited state of TX-A in the presence of oxygen as illustrated in Scheme 2. Photoexcitation of TX-A-O_2 leads to the formation of peroxy and/or alkoxy radicals[19] capable of initiating free radical polymerization.

Isolation of Endoperoxide Intermediate. The involvement of the thioxanthone−endoperoxide (TX-A-O_2) in the initiation process was confirmed by its formation under monomer-free conditions. Irradiation of TX-A in $CDCl_3$ solution containing 50 μM methylene blue as the singlet oxygen sensitizer at $\lambda >$ 470 nm at −5 °C under oxygen bubbling for 30 min resulted in more than 50% reduction of the TX-A absorbance. HPLC-MS analysis of the reaction mixture confirmed the formation of TX-A-O_2 by its MS spectrum (Figure S3e; Supporting Information). In addition, the UV absorption spectrum of this HPLC fraction (Figure S3c) is blue-shifted compared to TX-A and similar to thioxanthone due to the loss of the anthracene moiety. ^{1}H NMR analysis (Figure S4; Supporting Information) of the main photoproduct, which was isolated by HPLC, is consistent with an endoperoxide structure (TX-A-O_2) shown in Scheme 2.

A consequence of the proposed polymerization mechanism is that the thioxanthone chromophore is incorporated into the polymer chain with the anthracene π-conjugation interrupted (Scheme 2). To test if the resulting polymer contains thioxanthone end groups, phosphorescence spectroscopy was performed on purified polymer, which was generated by photopolymerization of MMA with TX-A. A phosphorescence spectrum (λ_{max} = 450 nm) consistent with alkyl-substituted thioxanthones[21] was observed with a phosphorescence lifetime of 105 ms at 77 K (Figure S5, Supporting Information). TX-A does not show detectable phosphorescence at 77 K similar to most anthracene derivatives. Therefore, we conclude that the thioxanthone chromophore was incorporated into the polymer chain with interruption of the anthracene π-system, which is consistent with the proposed mechanism (Scheme 2).

CONCLUSION

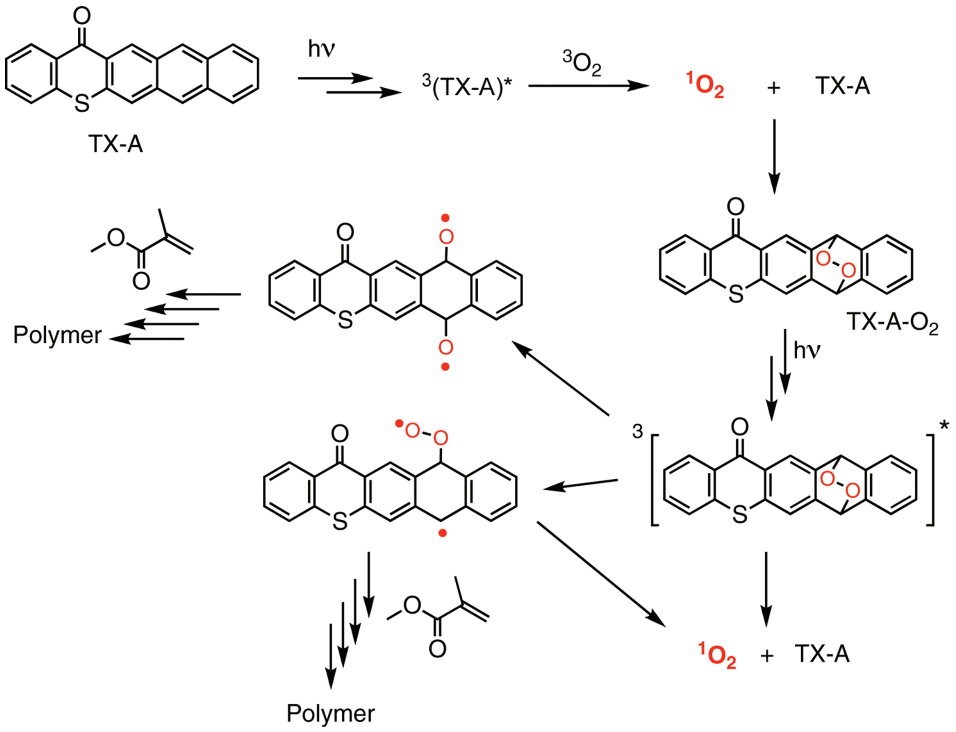
Laser flash photolysis, fluorescence and phosphorescence spectroscopy, and polymerization studies demonstrate that TX-A exhibits good optical properties. Photoinitiated free radical polymerization by TX-A without a co-initiator (hydrogen donor) proceeds only in the presence of oxygen. The initiation mechanism (Scheme 2) involves the formation of singlet oxygen by energy transfer from triplet TX-A. Subsequent addition of singlet oxygen to the anthracene moiety of TX-A leads to TX-A-O_2. Photoexcitaion of TX-A-O_2 probably leads to alkoxy or peroxy radicals which are able to initiate free radical polymerization. The peculiar photoinitiating behavior of TX-A in air makes this photoinitiator particularly important for thin film applications where the oxygen inhibition is one of the most challenging problems.

EXPERIMENTAL SECTION

Materials. Thioxanthone−anthracene (5-thia-pentacene-14-one) (TX-A) was synthesized as described previously.[14,22] Anthracene (97%, Aldrich), thioxanthone (TX, 98%, EGA Chemie), and acetonitrile were used as received. Methyl methacrylate (MMA) (≥99%, Fluka) was washed with 5% aqueous NaOH solution, dried over $CaCl_2$, and distilled over CaH_2 in vacuo. Dimethylformamide (DMF) (Fluka) was purified by conventional drying and distillation procedure. Chloroform ($CHCl_3$) and deuterated chloroform ($CDCl_3$) were obtained from Fisher Scientific and dried with K_2CO_3.

Photopolymerization. Typical Procedure: First, a solution of 1.56 mg (5 μmol) of TX-A in 0.5 mL of DMF was added to 0.5 mL (4.7 mmol) of

Scheme 2. **Proposed Mechanism of Photoinitiated Free Radical Polymerization of Methyl Methacrylate Using TX-A as Photoinitiator in the Presence of Oxygen**



MMA. The solution was put into a Pyrex tube (i.d. = 9 mm) and irradiated in a photoreactor consisting of a 400 W medium-pressure mercury lamp and a water cooling system for 15 min in an air atmosphere. Poly(methyl methacrylate) formed at the end of irradiation was precipitated in 10-fold excess methanol and dried in vacuo (yield: 4.5%; M_n = 20 000 g/mol). All the other polymerizations using different solvents and concentrations and additives were performed under identical experimental conditions unless otherwise stated. For the experiments under nitrogen, the same solutions were put into a Pyrex tube that was heated in vacuo with a heat gun and flushed with dry nitrogen prior irradiation. Polymerization rates were calculated for all samples gravimetrically.

Measurements. UV–vis spectra were recorded on an Agilent 8453 spectrometer. Steady-state luminescence spectra were recorded on a Fluorolog-3 fluorometer (HORIBA Jobin Yvon). Phosphorescence experiments at 77 K were performed on a Fluoromax-3P fluorometer (HORIBA Jobin Yvon). Laser flash photolysis experiments employed the pulses from a Spectra Physics GCR-150-30 Nd:YAG laser (355 nm, ca. 5 mJ/pulse, 5 ns) or a Lambda Physik dye laser (FL3002) which was pumped with an Lambda Physik Excimer laser (Lextra 50) and a computer-controlled system that has been described elsewhere.[23] Solutions of the thioxanthone derivatives were prepared at concentrations such that the absorbance was ∼0.3 at the exciton wavelength (355 nm). Singlet oxygen phosphorescence measurements were performed on a modified Fluorolog-2 spectrometer (HORIBA Jobin Yvon) in conjunction with a NIR-sensitive photomultiplier tube (H9170-45, Hamamatsu).[24] A 450 W Xe was use for steady-state excitation to record singlet oxygen phosphorescence spectra and a Spectra-Physics GCR-150-30 Nd:YAG laser (355 nm, ca. 5 mJ/pulse, 5 ns) was used for pulsed excitation to collect phosphorescence decay kinetics at 1270 nm.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Determination of the quenching rate constants, photoproduct studies by HPLC-MS, ^{1}H NMR spectrum of TX-A-O$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ ACKNOWLEDGMENT

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