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Thioxanthone−Anthracene: A New Photoinitiator for Free Radical Polymerization in the Presence of Oxygen

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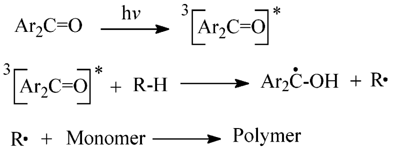
ABSTRACT: A novel thioxanthone−anthracene (TX-A) photoinitiator, namely 5-thia-pentacene-14-one, possessing the respective photochromic groups was synthesized. TX-A is an efficient photoinitiator for free radical polymerization of acrylic and styrenic type monomers in the presence of oxygen. UV−vis, FT-IR, and fluorescence spectroscopic and polymerization studies revealed that photoinitiation occurs through anthracene chromophore. In contrast to thioxanthone-based photoinitiators, TX-A does not require an additional hydrogen donor for the initiation.

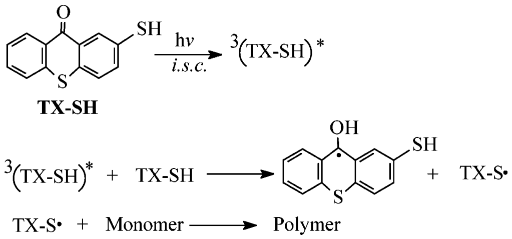
Introduction

Photoinitiated polymerization is a well-accepted technology that finds industrial application in coatings on various materials, adhesives, printing inks, and photoresists.[1−5] Techniques such as curing of coatings on various materials, adhesives, printing inks, and photoresists are based on photoinitiated radical vinyl polymerization. Photoinitiated radical polymerization may be initiated by bond cleavage (type I) and H-abstraction type (type II) initiators.[1] Type II photoinitiators are a second class of photoinitiators based on compounds whose triplet excited states readily react with hydrogen donors, thereby producing initiating radicals[6−8] (Scheme 1). Because of the bimolecular radical generation process, they are generally slower than type I photoinitiators, which form radicals unimolecularly.

Scheme 1. Photoinitiated Free Radical Polymerization by Using Aromatic Carbonyl Compounds

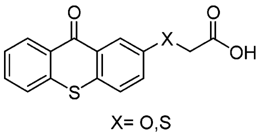


Scheme 2. Photoinitiated Free Radical Polymerization by Using Thioxanthonethiol (TX-SH)



Typical type II photoinitiators include benzophenone and derivatives, thioxanthones, benzil, and quinones, while alcohols, ethers, amines, and thiols are used as hydrogen donors. Among type II photoinitiators, thioxanthone (TX) derivatives in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones.[9] We recently reported[10] the use of a thiol derivative of thioxanthone (TX-SH) as a photoinitiator for free radical polymerization. A major advantage of this initiator is related to its one component nature. It can serve as both a triplet photosensitizer and a hydrogen donor. Thus, this photoinitiator does not require an additional coinitiator, i.e., a separate molecular hydrogen donor. The mechanism of the photoinitiation is based on the intermolecular reaction of triplet, ^{3}TX-SH*, with the thiol moiety of ground state TX-SH. The resulting thiyl radical initiates the polymerization (Scheme 2).

Chart 1. Structure of the Thioxanthone Acetic Acid Derivatives



Recently, we reported[11,12] another photoinitiator belonging to the same class of photoinitiators, an acetic acid derivative of TX, which also exhibits a one-component nature (Chart 1). In both cases, the light-absorbing and hydrogen-donating sites are contained in the photoinitiator molecules. Notably, these one-component photoinitiators initiate the polymerization much more efficiently than two-component systems in which the related functions are composed in independent molecules. As part of our continuing interest in photoinitiating systems, herein we report a new photoinitiator possessing two photochromic groups, anthracene (A) and TX, in the structure. Interestingly, this photoinitiator generates initiator radicals without an added hydrogen donor and thus can be considered also as a one-component photoinitiator.

Experimental Section

Materials. Anthracene (A, 97%, Aldrich), thiosalicylic acid (98.5%, Fluka), glacial acetic acid (99.8%, Aldrich), and *N*-methylethanolamine (MDEA, 99%, Aldrich) were used as received. Methyl methacrylate (MMA, ≥99%, Fluka) and styrene (St, 99%, Aldrich) were washed with 5% aqueous NaOH solution, dried over $CaCl_2$, and distilled from CaH_2 in vacuo. Dichloromethane (DCM,

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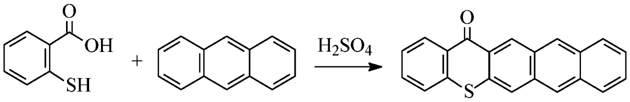
Scheme 3. Synthesis of Thioxanthone−anthracene (TX-A)



99.9%, HPLC grade, Aldrich) was distilled from CaH_2. Dimethylformamide (DMF, +99%, Aldrich) and dimethyl sulfoxide (DMSO, 99.5%, Fluka) were distilled from CaH_2 under reduced pressure. Trimethylolpropane triacrylate (TMPTA, 95%, Aldrich) was used as received.

Synthesis of Thioxanthone−Anthracene (5-Thia-pentacene-14-one) (TX-A). A heated solution of anthracene (0.50 g, 6×10^{-3} mol) in glacial acetic acid (20 mL) was added slowly to thiosalicylic acid (0.15 g, 2×10^{-3} mol) under stirring followed by the addition of 4 mL of concentrated sulfuric acid. After the addition, the reaction mixture was refluxed at 118 °C for 4 h, after which it was left standing at room temperature overnight. The resulting mixture was poured carefully under stirring into a 10-fold excess of boiling water. The mixture was stirred under boiling for an additional 5 min. The solution was cooled and filtered. The residue was recrystallized from dioxane−water. Yield: 0.49 g, 80%; mp: 230 °C. Anal. Calcd for $C_{21}H_{12}OS$ (312 g mol^{-1}): C, 80.76%; H, 3.85%; S, 10.26% Found, C, 79.84%; H, 4.00%; S, 9.57%. ^1H NMR (250 MHz) in $CDCl_3$: δ 7.42−7.72 (m, 5H, aromatic), 7.86−7.90 (d, J = 9.27 Hz, 1H, aromatic), 7.96−8.08 (m, 2H, aromatic), 8.35 (s, 1H, aromatic), 8.40−8.46 (t, J = 16.11; 7.32 Hz, 1H, aromatic), 8.60−8.64 (d, J = 7.81 Hz, 1H, aromatic), 8.86 (s, 1H, aromatic).

Photopolymerization. *Typical Procedure*: First, a solution of 0.2 mg (6.4×10^{-7} mmol) of TX-A in 0.5 mL of DMF was added to 0.5 mL (4.68 mmol) of 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: 15.3 ± 0.2%; M_n = 22 000 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. Polymerization rates were calculated for all samples gravimetrically.

Analysis. Gel permeation chromatography (GPC) measurements were performed at room temperature with a setup consisting of a pump (Agilent 1100), a refractive index detector (Agilent 1100s), and three high-resolution Zorbax PSM columns (60S, 300S, and 1000S). The effective molecular weight ranges were 500−10 000, 3000−300 000, and 10 000−1 000 000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at room temperature. Data analyses were performed with Polymer Laboratories Caliber Software Calibration with linear polystyrene standards (Polymer Laboratories) used to estimate the molecular weights.

UV−vis spectra were taken on an Agilent 8453. Fluorescence spectra were recorded on a Jobin Yvon-Horiba Fluoromax-P. A Perkin-Elmer Spectrum-One FTIR spectrophotometer was used for recording IR spectra and for real time FTIR studies. Elemental analysis was performed on a CHNS-932 LECO instrument.

Results and Discussion

Synthesis and Spectral Characterization. The thioxanthone−anthracene (TX-A) photoinitiator, 5-thia-pentacene-14-one, was synthesized by a modified literature[12] procedure described for the synthesis of 2-hydroxythioxanthone according to Scheme 3.

The structure of the photoinitiator was confirmed by ^1H NMR spectroscopy and elemental analysis (see Experimental Section). TX-A possesses absorption characteristics similar to the parent TX and A which absorb light at 300−450 nm range (Figure 1).

Figure 2 shows that a nearly mirror-image-like relation exists between absorption and emission of TX-A. The emission spectrum represents the characteristics of the A moiety rather than TX, indicating the dominant photoexcited state of the photoinitiator.

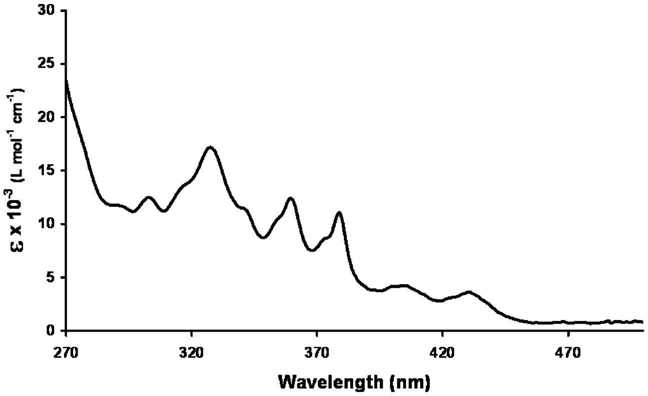


Figure 1. Absorption spectrum of thioxanthone−anthracene (TX-A) (4.45×10^{-5} mol L^{-1}) in dimethylformamide (DMF).

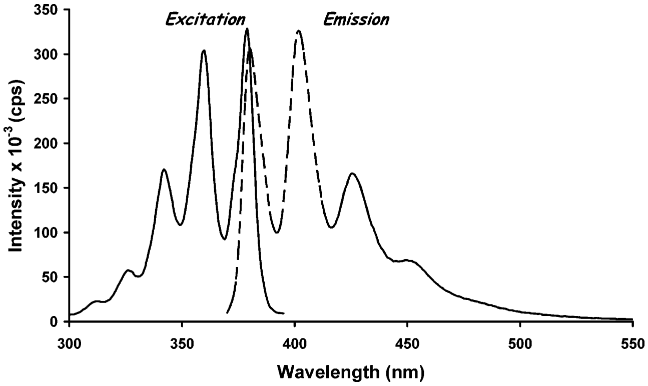


Figure 2. Fluorescence excitation (—) and emission (---) spectra of thioxanthone−anthracene (TX-A) in benzene; λ_{exc} = 360 nm.

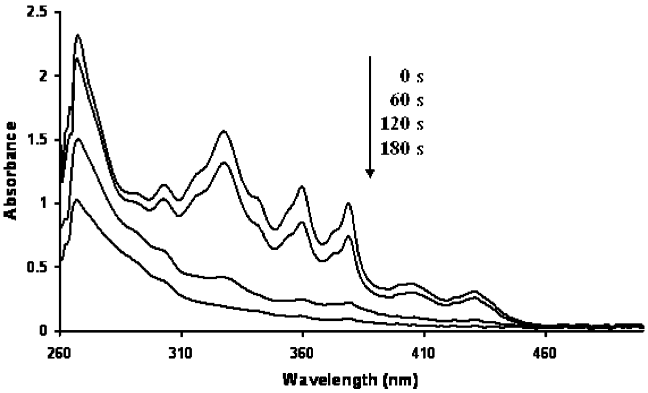


Figure 3. Absorption spectra of thioxanthone−anthracene (TX-A) (2.5×10^{-6} mol L^{-1}) in air saturated dimethylformamide (DMF) solutions after irradiation at 366 nm for 0, 60, 120, and 180 s.

The photodecomposition of TX-A was followed by detecting UV spectral changes upon photolysis. The UV spectra of TX-A in acetonitrile were recorded after the solution had been exposed to the light of a UV lamp at the intervals of 60, 120, and 180 s (Figure 3). As the photolysis proceeds, the photoinitiator is consumed and the absorption spectra change. At the end of the irradiation, while the absorption bands of the A moiety completely disappeared, the weak absorption of the TX group at 380 nm was still detectable.

Photopolymerization. TX-A was used as a photoinitiator for the polymerization of MMA in the presence and absence of air. The results are compiled in Table 1. As can be seen, TX-A

Table 1. Photoinitiated Polymerization[a] of Methyl Methacrylate (MMA) with Thioxanthone−Anthracene (TX-A) in Dimethylformamide (DMF)

[TX-A] (mol L^{-1})	[MDEA] (mol L^{-1})	conv (%)	M_n[b] $\times 10^{-4}$ (g mol^{-1})	M_w/M_x[b]
6.4×10^{-4}		15.3	2.20	2.10
6.4×10^{-4}	5.0×10^{-2}	11.2	1.47	1.23
1.0×10^{-3}		11.7	2.86	1.68
1.0×10^{-3}	5.0×10^{-2}	8.4	1.61	1.47
2.5×10^{-3}		10.6	2.25	2.30
2.5×10^{-3}	5.0×10^{-2}	5.8	1.69	1.81
5.0×10^{-3}		4.5	2.07	3.31
5.0×10^{-3}	5.0×10^{-2}	3.8	2.37	2.32
1.0×10^{-2}		6.3	3.24	1.96
1.0×10^{-2}	5.0×10^{-2}	4.0	4.83	1.92
6.4×10^{-4}[c]		0.0		

[a] [MMA] = 4.7 mol L^{-1}; irradiation time = 15 min. [b] Determined by GPC using polystyrene standards. [c] Carried out under a nitrogen atmosphere.

Table 2. Effect of Solvent on the Photoinitiated Polymerization[a] of Methyl Methacrylate (MMA) with Thioxanthone−Anthracene (TX-A)

[TX-A] (mol L^{-1})	[MDEA][b] (mol L^{-1})	conv[c] (%)	conv[d] (%)	conv[e] (%)
6.4×10^{-4}		15.3	6.20	4.00
6.4×10^{-4}	5.0×10^{-2}	11.2	8.40	5.50

[a] [MMA] = 4.7 mol L^{-1}; irradiation time = 15 min. [b] *N*-Methylethanolamine. [c] In dimethylformamide (DMF). [d] In dimethyl sulfoxide (DMSO). [e] In dichloromethane (DCM).

Table 3. Photoinitiated Polymerization[a] of Methyl Methacrylate (MMA) in Dimethylformamide (DMF) in the Presence of Thioanthone (TX) and Anthracene (A)

[TX] (mol L^{-1})	[A] (mol L^{-1})	MDEA[b] (mol L^{-1})	conv (%)
5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-2}	2.0
5.0×10^{-3}		5.0×10^{-2}	2.7
	5.0×10^{-3}	5.0×10^{-2}	3.8
5.0×10^{-3}	5.0×10^{-3}		0.0
5.0×10^{-3}			0.0
	5.0×10^{-3}		0.7

[a] [MMA] = 4.7 mol L^{-1}; irradiation time = 15 min. [b] *N*-Methylethanolamine.

Table 4. Photoinitiated Polymerization[a] of Styrene (St) in Dimethylformamide (DMF) in the Presence of Thioxanthone−Anthracene (TX-A)

[TX-A] (mol L^{-1})	[MDEA][b] (mol L^{-1})	conv (%)
1.0×10^{-2}		4.3
1.0×10^{-2}	5.0×10^{-2}	8.6
5.0×10^{-3}		3.6
5.0×10^{-3}	5.0×10^{-2}	9.4
2.5×10^{-3}		3.7
2.5×10^{-3}	5.0×10^{-2}	7.5
1.0×10^{-3}		3.7
1.0×10^{-3}	5.0×10^{-2}	7.0
6.4×10^{-4}		3.8
6.4×10^{-4}	5.0×10^{-2}	4.4

[a] [St] = 4.5 mol L^{-1}; irradiation time = 15 min. [b] *N*-Methylethanolamine.

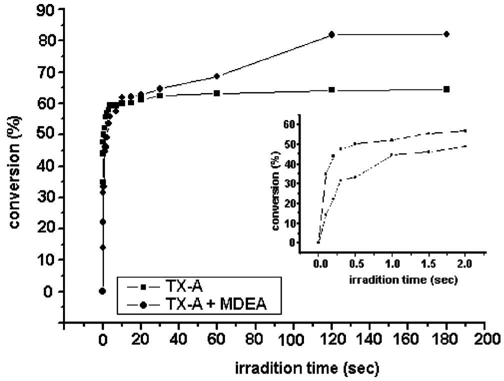


Figure 4. Polymerization kinetics of trimethylpropane triacrylate (TMPTA) in bulk with thioxanthone−anthracene (TX-A) (1 mol %) in the presence and absence of *N*-methyldiethanolamine (MDEA) (5.0×10^{-2} mol L^{-1}) with polychromatic light (unfiltered light from a medium-pressure lamp) in an air atmosphere The polymerization kinetics was measured as percent loss of olefinic double bonds at 810 cm^{-1} by IR spectroscopy. The inset shows the polymerization kinetics in the initial phase.

is not an efficient photoinitiator in the presence of a coinitiator such as *N*-methylethanolamine (MDEA). Polymerization also did not proceed under nitrogen, indicating the crucial role of oxygen. It also appears that as the concentration of TX-A is increased, the extent of the polymerization decreases. This behavior is due to the total complete absorption of irradiation by the photoinitiator and self-quenching of the excited photoinitiator at high concentrations.[13]

Polymerization experiments were performed in various solvents to investigate the effect of solvent on the rate of polymerization (see Table 2). Among the several solvents tested in our experiments, dimethylformamide (DMF) seemed to be the most suitable solvent for the photopolymerization initiated by TX-A. Obviously, the situation is complex and two effects are combined. First, TX-A dissolves in DMF better than the other solvents. Second, although radical polymerizations are generally not sensitive to the polarity of the solvent, triplet-state lifetimes of photoinitiators particularly those possessing TX chromophoric groups may depend on some polarity effects.[14]

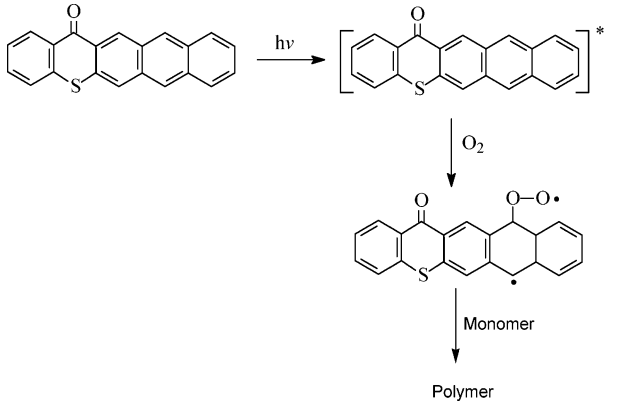
For comparison, photopolymerization experiments using either TX or A themselves or their combinations in the presence and absence of the hydrogen donor MDEA were performed (Table 3).

In all cases, the conversions were lower than those obtained with TX-A. When MDEA was omitted from the formulations, either no polymer or a negligible amount of polymer was formed after the same irradiation time. These results indicate that, in contrast to TX-A, the hydrogen donor component of the initiating system is indispensable for the polymerization to occur for either or both photoinitiators (TX and A).

Another striking advantage of the TX-A photoinitiator concerns its applicability to styrene-based monomer formulations. Although aromatic carbonyl/amine combinations represent an effective photoinitiator system for the polymerization of acrylates, they appear to be less reactive toward styrene monomers due to the high quenching rate constants shown in Table 4; TX-A initiates the polymerization of styrene efficiently. A higher initiation efficiency with TX-A was observed in the presence of MDEA.

For the possibility of using the described photoinitiator in practical applications, the efficiency of TX-A in the photocuring of formulations containing multifunctional monomers was also studied. To investigate the polymerization kinetics,[15,16] the disappearance of the monomer double bonds (810 cm^{-1}) during the photocuring of the formulations was followed by Fourier transform real-time spectroscopy (RT-FTIR). By monitoring changes, it allows to follow fast polymerization process continuously. Figure 4 shows profiles referring to the polymerization of trimethylolpropanetriacrylate (TMPTA) under polychromatic light. TX-A and TX-A/MDEA served as photoinitiators. The curves were obtained by monitoring the absorption decrease of the band at 810 cm^{-1}, corresponding to the frequency of the twisting vibration of the double bonds.

Scheme 4. Photoinitiated Free Radical Polymerization by Using Thioxanthone−Anthracene (TX-A)



The shape of the curves indicates the existence of two stages: a rapid first stage followed by a slow stage. At the second stage, gelation and vitrification of the polymerizing trifunctional acrylate most likely render the diffusion of the components more difficult. At early irradiation times, polymerization takes place more rapidly in the absence of MDEA, whereas after certain irradiation times (20 s of irradiation) higher conversions were observed in the presence of MDEA.

On the basis of the above results, the following important statements can be drawn: (i) Although TX-A exhibits the absorption characteristics of both groups, the A moiety is the dominant part in the formation of initiating radicals. This was inferred from the fact that photoinitiation and photobleaching occur even in the absence of a hydrogen donor. Moreover, the precipitated polymer and photoinitiator still contain weak TX absorption. (ii) Photoinitiation by TX-A does not need a hydrogen donor in the system and presumably does not proceed via a type II hydrogen abstraction mechanism. (iii) Polymerization occurs in the presence of air. In fact, in contrast to the thioxanthone-based systems, oxygen is required for a successful polymerization. (iv) TX-A is a more efficient photoinitiator than both TX and A even if they are used in conjunction with a hydrogen donor. (v) TX-A is also an efficient photoinitiator for the polymerization of styrenic monomers.

Considering the above observations, a nontraditional initiation mechanism is expected. Because the presence of oxygen is essential for the polymerization to proceed, peroxides are probably involved (Scheme 4). Anthracene derivatives are known to form instable endoperoxides upon irradiation.[17] These endoperoxides decompose (thermally and photochemically) through radical intermediates,[18−20] which could initiate the polymerization of the monomers. A thorough mechanistic study by using laser flash photolysis technique is in progress, and the results will be subject to an upcoming publication.

Conclusion

TX-A is an efficient photoinitiator for free radical polymerization. This novel photoinitiator does not require an additional hydrogen donor for radical formation and initiates the polymerization of both acrylate and styrene monomers in the presence of air. In addition, TX-A possesses excellent optical absorption properties in the near-UV spectral region, ensuring efficient light absorption from most UV-curing tools. These properties suggest that TX-A may find use in a variety of practical applications.

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