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2-Mercaptothioxanthone as a Novel Photoinitiator for Free Radical Polymerization

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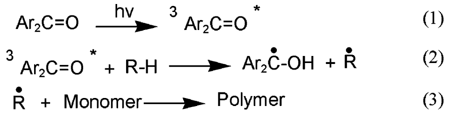
ABSTRACT: 2-Mercaptothioxanthone (TX-SH), a hydrogen abstraction type photoinitiator for free radical polymerization, is synthesized and characterized. Its capability to act as an initiator for the polymerization of methyl methacrylate (MMA), styrene (St), and multifunctional monomers is examined. The relative efficiencies of TX-SH, the parent thioxanthone (TX), and their combination with an amine synergist such as *N*-methyldiethanolamine (MDEA) are compared in the photopolymerization. The postulated mechanism is based on the intermolecular reaction of triplet, ^{3}TX-SH*, with the thiol moiety of ground-state TX-SH. Thus, when TX-SH is irradiated in the presence of a monomer, it can serve as both a triplet photosensitizer and a hydrogen donor. The resulting thiyl radicals initiate the polymerization. Incorporation of TX-S groups into polymers was demonstrated by spectroscopic methods.

Introduction

Photoinitiated free radical polymerization is of enormous commercial importance.[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 both cleavage (type I) and H-abstraction type (type II) initiators.[1] Because the initiation is based on a bimolecular reaction, type II photoinitiators are generally slower than type I photoinitiators, which are based on unimolecular formation of radicals. Photolysis of aromatic ketones, such as benzophenone, thioxanthones, benzil, and quinones, in the presence of hydrogen donors, such as alcohols, amines, or thiols, leads to the formation of a radical produced from the carbonyl compound (ketyl-type radical) and another radical derived from the hydrogen donor.[6−8] The photopolymerization of vinyl monomers is usually initiated by the radical produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. The overall mechanism of the photoinitiation is represented in Scheme 1.

For efficient polymerization, the bimolecular H-abstraction reaction must compete with other side reactions, such as nonreactive quenching (i.e., through energy transfer) of the photoexcited initiator by monomer or oxygen. These systems are therefore more sensitive to oxygen, and polymerization in air may lead to relatively low curing rates. The selection of a co-initiator (H-donor) is undoubtedly of great importance. Tertiary amines are more reactive co-initiators than are alcohols or ethers.[9] Thiols are another class of co-initiators which are particularly used in thiol−ene photopolymerization systems. In this regard it is worth mentioning the pioneering work of Morgan and Ketley,[10] who used benzophenone to absorb light and initiate the polymerization of the radical chain process via a hydrogen abstraction reaction involving the excited benzophenone and a ground state thiol. The thiol−ene photopolymerization system has recently been revitalized[11−13] and used as an effective way to cross-link thermoplastic elastomers.[14,15]

Scheme 1. Photoinitiated Free Radical Polymerization by Aromatic Carbonyl Compound



$$Ar_2C{=}O \xrightarrow{h\nu} {}^3Ar_2C{=}O^* \quad (1)$$

$$ {}^3Ar_2C{=}O^* + R\text{-}H \longrightarrow Ar_2\dot{C}\text{-}OH + \dot{R} \quad (2)$$

$$\dot{R} + \text{Monomer} \longrightarrow \text{Polymer} \quad (3)$$

Among type II photoinitiators, thioxanthone derivatives[16] in conjunction with tertiary amines are efficient photoinitiators with absorption characteristics that compare favorably with benzophenones.

In this study we report the synthesis and the use of a thiol derivative of thioxanthone as a photoinitiator for free radical polymerization. As it will be shown below, a great advantage is that this photoinitiator does not require an additional co-initiator, i.e., a separate molecular hydrogen donor. The photopolymerization initiated by our new mercaptothioxanthone is only slightly inhibited by oxygen.

Experimental Section

Materials. Thiosalicylic acid (98%, Aldrich), thiophenol (99+%, Aldrich), and *N*-methyldiethanolamine (MDEA, 99%, Aldrich) were used as received. Styrene (St, 99%, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were washed with 5% aqueous NaOH solution, dried over $CaCl_2$, and distilled over CaH_2 under vacuum just before use. Chloroform and dichloromethane (99.9%, HPLC grade, Aldrich) were by distilled over CaH_2. Dimethylformamide (DMF, 99+%, Aldrich) was distilled over CaH_2 under reduced pressure. Trimethylolpropane triacrylate (95%, Aldrich) and Photomer-3038F (Cognis), a mixture of epoxy acrylate (75%)−tri(propylene glycol) diacrylate (TPGDA) (25%), were used as received.

Synthesis of 2-Mercaptothioxanthone (TX-SH). Thiosalycylic acid (1.6 g, 0.010 mol) was slowly added to 15 mL of

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concentrated sulfuric acid, and the mixture was stirred for 5 min to ensure thorough mixing. Thiophenol (6.0 g, 0.055 mol) was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was stirred at room temperature for 1 h and then at 80 °C for 2 h, after which it was left to stand at room temperature overnight. The resulting mixture was poured carefully with stirring into a 10-fold excess of boiling water, and it was boiled further for 5 min. The solution was cooled and filtered. The residue was recrystallized from dioxane−water. Yield: 80%; mp: 149 °C. Anal. Calcd for $C_{13}H_8OS_2$ (244 g mol^{-1}): C, 63.93%; H, 3.27%; S, 26.22%. Found: C, 64.25%; H, 3.81%; S, 26.17%. ^{1}H NMR (250 MHz) in $CDCl_3$: δ 7.58−7.26 (m, 7H, aromatic), 3.38 ppm (b, 1H, SH). ^{13}C NMR (62.86 MHz) in $CDCl_3$: δ 171 (C═O), 137.03−125.01 ppm (m, aromatic). IR(KBr): ν 3055 (C═C), 2497 (S−H), 1651 (C═O), 1600 (C═C), 1089 (C−S), 757 cm^{-1} (Ar−SH).

Photopolymerization. Typical procedure. First, a solution of 1.8 mg (7.4×10^{-3} mmol) of TX-SH 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 equipped with eight Phillips lamps emitting nominally at λ = 350 nm for 60 min in air atmosphere. Poly(methyl methacrylate) formed at the end of irradiation was precipitated in 10-fold excess methanol and dried in vacuo (yield: 16.4%; M_n = 28 000 g/mol). All the other polymerizations using different solvents and concentrations and additives were performed under identical experimental conditions unless otherwise stated. Polymerization rates were calculated for all samples gravimetrically.

Real-Time Infrared Spectroscopy Photopolymerization Studies. Uniform samples of photocurable formulations consisiting of a photoinitiator and bi- or multifunctional monomers in the presence and absence of MDEA were prepared by casting on a KBr pellet. The samples were placed in the compartment of an Fourier transform infrared spectrometer (Mattson 1000 FTIR) and were simultaneously exposed to a UV photolyzing light and an IR analyzing light beam. The photolyzing light was generated by a medium-pressure mercury lamp (Flexicure UV system) and was directed through a flexible fiber optic to the IR compartment. The light intensity (4.37×10^{16} photons s^{-1}) was determined by potassium ferrioxalate actinometry.[17] The spectrometer was operated in the absorbance mode, and the detection wavelength was set at 800 cm^{-1} (C═C−H twist) to monitor the disappearance of double bonds. The degree of conversion, α, can be expressed by the following relation:

$$\alpha = (A_0 - A_t)/A_0$$

where A_0 is the initial absorbance at 800 cm^{-1} and A_t the absorbance value at irradiation time t.

Analysis. GPC analyses of the polymers were performed at room temperature with a setup consisting of a pump (Waters 600E) and four Waters ultrastryragel columns: HR 5E (2000−4 × 10^6 g/mol), HR4 (5000−60 0000 g/mol), HR3 (500−30 000 g/mol), and HR2 (500−20 000 g/mol). THF was used as the eluent (flow rate 1 mL min^{-1}), and the detection was carried out with the aid of a Waters 410 differential refractometer. The number-average molecular weights were determined using Polymer Laboratories polystyrene standards. ^{1}H NMR spectra were recorded on a Bruker 250 instrument with $CDCl_3$ as solvent and tertamethylsilane (TMS) as the internal standard. UV−vis spectra were taken on an Ati Unicam spectrophotometer. IR spectra were recorded on a Jasco FT/IR-3 spectrometer on a KBr disk. Low-temperature phosphorescence spectra were recorded on a Fluorolog 2T2 1680 0.22 m double spectrometer (SPEX) using a liquid nitrogen dewar for measurements at 77 K. Time-resolved phosphorescence measurements were performed by multichannel scaling on a OB900 fluorometer (Edinburgh Analytical Instruments) using a pulsed xenon lamp (μF 900, Edinburgh Analytical Instruments) as excitation source.

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) and a computer-controlled system that has been described elsewhere.[18]

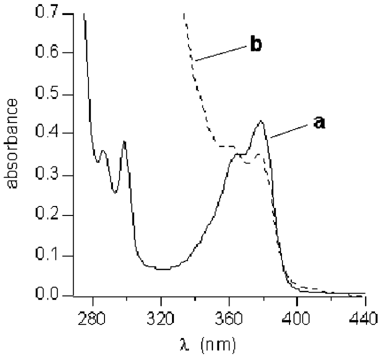
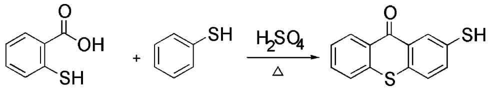


Figure 1. Absorption spectra of 2-mercaptothioxanthone (TX-SH) (a) and poly(methyl methacrylate) obtained by photoinitiated polymerization by using TX-SH (b) in 2-methyltetrahydrofuran in the presence of air.

Scheme 2. Synthesis of 2-Mercaptothioxanthone



(4)

Results and Discussion

2-Mercaptothioxanthone (TX-SH) was synthesized by a modified literature[19] procedure described for the synthesis of 2-hydroxythioxanthone according to Scheme 2.

The structure of the photoinitiator was confirmed by spectral and elemental analysis (see Experimental Section). TX-SH possesses an absorption characteristic similar to the parent thioxanthone with a maximum at 383 nm (ϵ = 3857 L mol^{-1} cm^{-1}) (Figure 1). This high molar absorptivity makes TX-SH attractive as a photoinitiator because of its efficient light absorption. TX-SH was used as a photoinitiator for the polymerization of methyl methacrylate in the presence and absence of air. The results are compiled in Table 1. For comparison, photopolymerizations by using either TX itself or a TX−methyl diethanolamine combination are also included.

As can be seen, TX is not an efficient photointiator in the absence of a co-initiator. The presence of an amine such as *N*-methyldiethanolamine (MDEA) is important for effective photoreduction and photopolymerization. MDEA plays a dual action in the polymerization. Besides hydrogen donation (eq 2), MDEA can react with oxygen, thereby reducing the retarding effect of oxygen on the polymerization.[20,21] Another common technique of oxygen depletion consists of the addition of thiol compounds[22] (Scheme 3). Peroxy radicals formed by the oxygen scavenging of carbon-centered radicals (eq 5) are also capable of abstracting hydrogen atoms from thiol (eq 6).

However, the practical application of thiols suffers from their strong unpleasant odor. TX-SH has no odor and initiates the polymerization without additional co-intiator, and oxygen does not significantly inhibit the polymerization. Although the TX-MDEA system is still the most efficient photoiniator, it is clear that TX-SH photoiniator avoids the use of large amounts of amines in the system. This is particularly important for curing applications, since formulations containing amine at high concentrations causes a decrease in the pendulum hardness of the cured films due to the plasticizing effect of amines.[23,24] Among the several solvents tested in our

Table 1. Photoinitiated Polymerization[a] of Methyl Methacrylate in Various Solvents in Air

photoinitiator (PI)	[PI] (mol L^{-1})	solvent	[MMA] (mol L^{-1})	[MDEA] (mol L^{-1})	$R_p \times 10^5$ (mol^{-1} L s^{-1})	$M_n{}^c \times 10^{-4}$ (g mol^{-1})	M_w/M_n
TX	8.49×10^{-3}	CH_2CI_2	4.68				
TX-SH	7.40×10^{-3}	CH_2CI_2	4.68		10.2	2.0	1.99
TX	5.66×10^{-3}	CH_2CI_2	3.12	2.91	43.0	1.8	1.91
TX-SH	4.92×10^{-3}	CH_2CI_2	3.12	2.91	25.4	1.9	1.59
TX-SH	7.40×10^{-3}	THF	4.68		5.8	1.7	1.73
TX-SH	7.40×10^{-3}	CH_2CI_2	4.68		14.3[b]	2.5	1.89
TX-SH	7.40×10^{-3}	DMF	4.68		21.4	2.8	1.60

[a] $\lambda = 350$ nm; irradiation time = 60 min. TX = thioxanthone, TX-SH = 2-mercaptothioxanthone, and MDEA = *N*-methyldiethanolamine. [b] Carried out under nitrogen. [c] Determined by GPC.

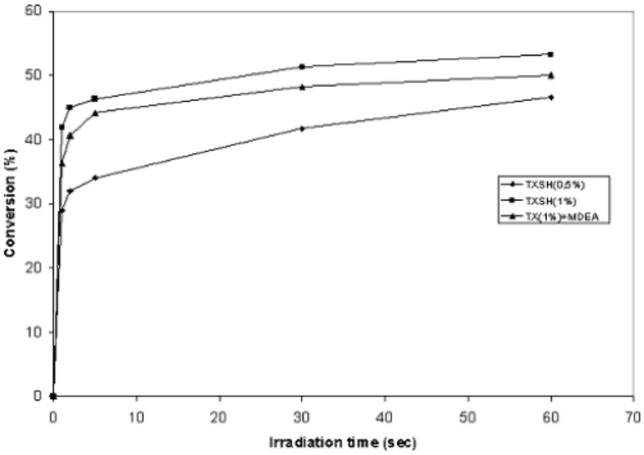


Figure 2. Real-time FTIR kinetic profiles demonstrating the photopolymerization of epoxy acrylate/tri(propylene glycol) diacrylate mixture (3/1, v/v) containing different photoinitiators with polychromatic light (unfiltered light from a medium-pressure lamp). Photoinitiator: (♦) 2-mercaptothioxanthone (TX-SH) (0.5%), (■) TX-SH (1%), and (▲) thioxanthone (TX) (1% + *N*-methyldiethanolamine (MDEA)).

Scheme 3. Oxygen Depletion by Thiol Compounds

$$P\bullet + O_2 \longrightarrow POO\bullet \qquad (5)$$

$$POO\bullet + RSH \longrightarrow POOH + RS\bullet \qquad (6)$$

experiments, dimethylformamide (DMF) seemed to be the most suitable solvent for the photopolymerization initiated by TX-SH. Obviously, the situation is complex, and two effects are combined. First, TX-SH dissolves in DMF better than the other solvents. Second, although radical polymerizations are not sensitive to the polarity of the solvent,[25] triplet-state lifetime of photoinitiators involving electron transfer such as thioxanthone derivatives may depend on some polarity effects.[26]

The efficiency of the TX-SH in the photocuring of formulations containing multifunctional monomers was also studied. The disappearance of double bonds during the photocuring of the formulations was followed by Fourier transform real-time infrared spectroscopy (RT-FTIR).[27,28] By monitoring changes in the characteristic monomer IR absorption bands, it allows the direct monitoring of fast polymerization process continuously. In Figure 2, kinetic profiles referring to the polymerization of the mixture epoxy acrylate and tri(propylene glycol) diacrylate under polychromatic light are shown. TX-SH and TX/MDEA served as photoinitiators. The curves were obtained by monitoring the absorption decrease of the band at 800 cm^{-1}. The shape of the curves indicates the existence of two stages—a rapid first stage followed by a slow stage. It can be seen that at sufficiently high concentrations polymerization takes place more rapidly with TX-SH than with TX/MDEA.

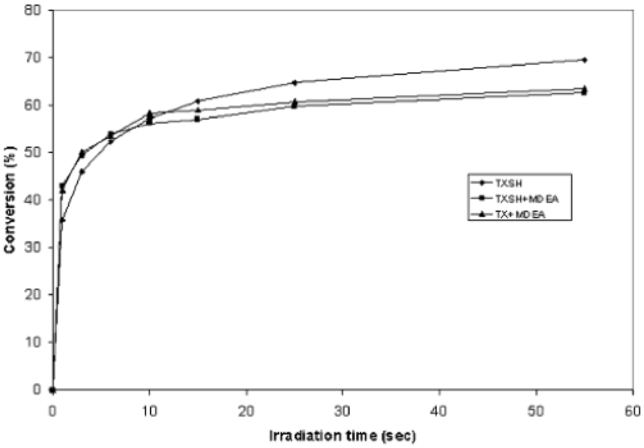


Figure 3. Real-time FTIR kinetic profiles demonstrating the photopolymerization of trimethylolpropane triacrylate containing different photoinitiators with polychromatic light (unfiltered light from a medium-pressure lamp). Photoinitiator (1%): (♦) 2-mercaptothioxanthone (TX-SH), (■) TX-SH and *N*-methyldiethanolamine (MDEA), and (▲) thioxanthone (TX) and MDEA.

Scheme 4. Photoinitiated Radical Polymerization by 2-Mercaptothioxanthone

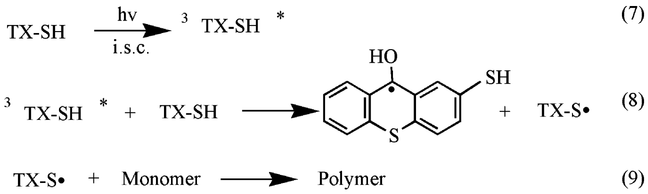


Figure 3 depicts the response of the polymerization of trimethylolpropane triacrylate to photoinitiation by TX-SH in the absence and presence of MDEA. A curve for the polymerization with the TX/MDEA system is also provided for comparison. Again, slightly higher conversion is observed using the TX-SH photoinitiator.

The overall polymerization process can be represented by Scheme 4.

As thiol compounds exhibit a strong hydrogen donor character, the triplet TX-SH is expected to abstract hydrogen from another ground state TX-SH molecule to generate the initiating thiyl radicals (eq 8). Intramolecular hydrogen abstraction was excluded by laser flash photolysis experiments. Flash photolysis (355 nm excitation) of a highly diluted solution of TX-SH affords a readily detectable transient absorption spectrum, which decayed in a first-order kinetic with a lifetime of 20 μs (Figure 4).

Transient absorption and lifetime are similar to the triplet−triplet absorption of the parent TX.[29] Therefore, we concluded that the transient absorption corresponds to the triplet−triplet absorption of TX-SH. If intramo-

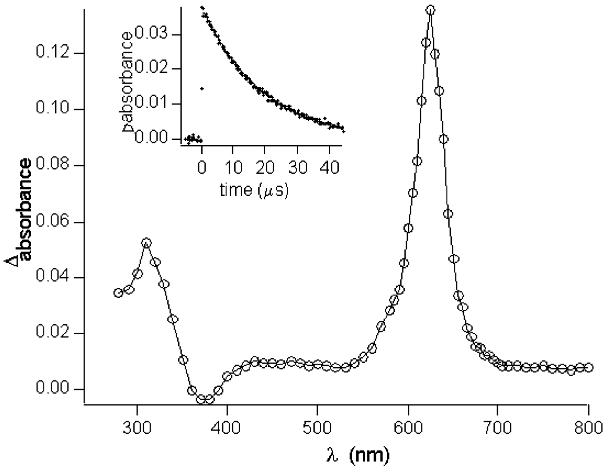
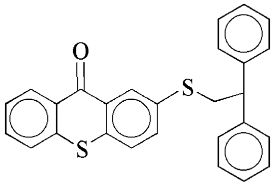


Figure 4. Transient optical absorption spectrum recorded 1−5 μs following laser excitation (355 nm, 5 ns) of 2-mercaptothioxanthone (TX-SH) (1×10^{-4} M) in argon-saturated acetonitrile solution at 23 °C. Inset: transient absorption kinetic observed at 625 nm.

Scheme 5. Structure of 2-Mercaptothioxanthone/Diphenylethylene Adduct



lecular hydrogen abstraction would dominate, than the transient decay kinetic should be significantly faster. This is consistent with an unfavorable interaction of the excited carbonyl group with the thiol moiety caused by the rigidity of the linked aromatic groups. Similar limitations were accounted for Michler's ketone[30] as a photoinitiator which also possesses both chromophoric and hydrogen-donating sites. The ketyl radical of TX-SH formed concomitantly is expected not to react effectively with olefinic monomers. The low reactivity of aromatic ketyl radicals was previously reported.[31] The ketyl radical is expected to combine with other radicals, such as TX-S$^\bullet$, propagating polymer radicals, and other ketyl radicals. In addition, the ketyl radical can trap oxygen to form peroxy radicals. In all these termination reactions the thiol moiety remains unaffected, which is a potential hydrogen-donating site for the triplet TX-SH. The initiating radicals were determined in experiments using an excess of 1,1-diphenylethylene as a nonpolymerizable model. The thioxanthone thiyl radical addition product of the following structure (424 Da of molar masses in FAB-MS) was found to be one of the main products in addition to a series of side products occurring from different radical reactions.One of the consequences of the above mechanism is that thioxanthone moiety should be incorporated into the polymer chain. Indeed, the UV−vis spectra of the resulting poly(methyl methacrylate) (PMMA) purified by several reprecipitation presents an absorption with a maximum at 383 nm (Figure 1b) similar to that of the low molecular weight precursor, TX-SH (Figure 1a). H NMR spectra of the polymer present weak resonances of the aromatic protons indicative of the presence of the thioxanthone moiety. Phosphorescence spectra of TX covalently attached polymers may also provide further evidence for the initiation mechanism. As can be seen from Figure 5, phosphorescence spectra in 2-methyltetrahydrofuran at 77 K of TX-SH (spectrum a) and PMMA obtained from photopolymerization initiated by TX-SH (spectrum b) are very similar. The excitation spectra for the emission signal are in good agreement with the absorption spectra of TX-SH (see also Figure 1). The phosphorescence lifetimes at 77 K are also very similar; 147 and 145 ms. Thus, various spectroscopic investigations reveal that thioxanthone groups are incorporated into the polymers.

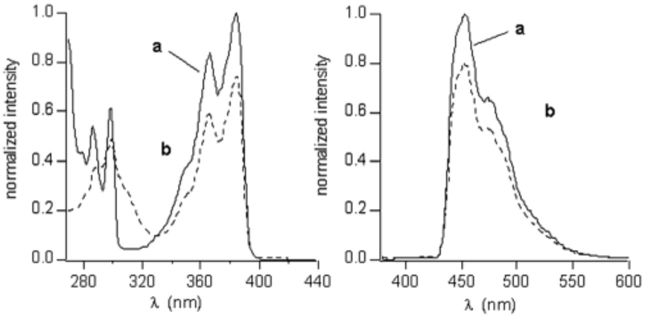


Figure 5. Phosphorescence excitation (left) and emission (right) spectra of 2-mercaptothioxanthone (TX-SH) (a) and poly(methyl methacrylate) obtained by photoinitiated polymerization by using TX-SH (b) in 2-methyltetrahydrofuran at 77 K. $\lambda_{exc} = 375$ nm.

Table 2. Photoinitiated Polymerization[a] of Methyl Methacrylate in CH_2Cl_2 in the Presence of Thioxanthone (TX) and Thiophenol

[thiophenol] (mol L^{-1})	$R_p \times 10^5$ (mol^{-1} L s^{-1})
8.1×10^{-3}	2.2
1.8×10^{-2}	3.5
4.5×10^{-2}	1.9
6.7×10^{-2}	0.9
9.1×10^{-2}	*b*

[a] [MMA] = 4.65 mol L^{-1}, [TX] = 8.45×10^{-3} mol L^{-1}, $\lambda = 350$ nm, and irradiation time = 60 min. [b] No polymer observed.

Moreover, phosphorescence measurements are useful to gain information on the triplet configuration of TX-SH. Phosphorescence spectra of ketones with n−π* nature of the lowest triplet state are usually structured due to the vibrational progression of the C=O vibration, and π−π* triplets are mostly unstructured.[32,33] In addition, the phosphorescence lifetime for n−π* triplets are significantly shorter (on the order of several milliseconds) compared to π−π* triplets (more than 100 ms).[29,32] Thus, the broad structureless phosphorescence of TX-SH, together with the long phosphorescence lifetime in a matrix at 77 K, indicates a π−π* nature of the lowest triplet state. This is in agreement with the π−π* nature of the lowest triplet state of unsubstituted TX.[34]

It is interesting to note that when the light-absorbing and hydrogen-donating sites are composed in independent molecules, i.e., when photoinitiated polymerization is performed by using a combination of TX and thiophenol (Table 2), the rate of polymerization is much lower than that of the one-component system, TX-SH. The higher activity of the TX-SH is mainly due to the double functionality of the initiator. Triplet TX-SH reacts with ground-state TX-SH by hydrogen abstraction to produce TX-S$^\bullet$ (eq 8), which initiates the polymerization and gets incorporated into the polymer (TX-S polymer) (eq 9). The TX-S polymer can be photoexcited again during the course of the polymerization to generate the triplet TX-S polymer, which can abstract hydrogen from TX-SH to

Table 3. Photoinitiated Polymerization[a] of Styrene in Bulk

photoinitiator (PI)	[PI] (mol L^{-1})	$R_p \times 10^5$ (mol^{-1} L s^{-1})	$M_n{}^c \times 10^{-4}$ (g mol^{-1})
TX-SH	7.43×10^{-3}	9.6	0.56
TX[b]	8.48×10^{-3}	5.0	18.1

[a] $\lambda = 350$ nm, irradiation time = 60 min, TX-SH = 2-mercaptothioxanthone, and TX = thioxanthone. [b] Also contains 4.36 mol L^{-1} *N*-methyldiethanolamine. [c] Determined by GPC.

produce the initiating TX-S$^\bullet$. This possibility does not exist for the two-component system.

Another striking advantage of the TX-SH 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 of the monomer and the low reactivity of α-amino radicals with styrene.[35] As shown in Table 3, TX-SH initiates the polymerization of styrene much more efficiently than does the TX/MDEA combination. The higher initiation efficiency observed with TX-SH may be due to the higher reactivity of thiyl radicals. The lower number-average molecular weight values (M_n) noted with TX-SH also indicates the generation of higher numbers of initiating radicals and possible chain transfer reactions usually observed with mercapto compounds.

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

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Supporting Information Available: Table of FAB-MS data of ions formed in the photolysis of TX-SH in the presence of DPE and ^{1}H NMR spectrum of PMMA. This material is available free of charge via the Internet at http://pubs.acs.org.

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