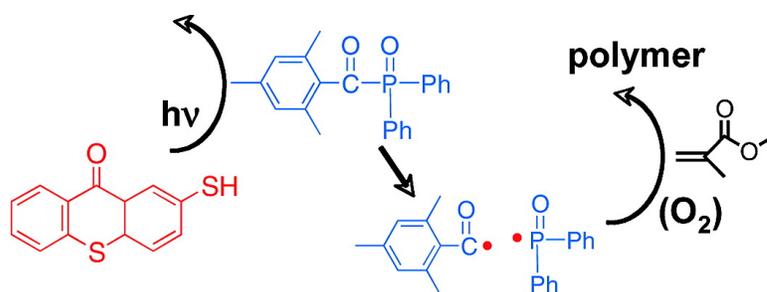


2-Mercaptothioxanthone as Sensitizer and Coinitiator for Acylphosphine Oxide Photoinitiators for Free Radical Polymerization

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Macromolecules, 2008, 41 (13), 4631-4634 • DOI: 10.1021/ma800472u • Publication Date (Web): 03 June 2008

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2-Mercaptothioxanthone as Sensitizer and Coinitiator for Acylphosphine Oxide Photoinitiators for Free Radical Polymerization

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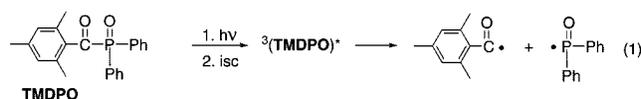
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Received March 3, 2008; Revised Manuscript Received April 11, 2008

ABSTRACT: The initiation efficiencies of photoinitiators for free radical polymerization, 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMDPO) and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (BAPO), are enhanced by addition of mercaptothioxanthone (TX-SH) to the initiator formulation. The additive TX-SH combines the benefits of a triplet sensitizer (enhanced light absorption) and thiol functionality (reduced oxygen inhibition). On the basis of polymerization studies, laser flash photolysis, fluorescence, and phosphorescence, the following mechanism is proposed: most of the light is absorbed by TX-SH to generate $^3(\text{TX-SH})^*$, which transfers its energy to TMDPO and BAPO followed by α -cleavage to produce the initiating radicals. In addition, excellent polymerization yields were observed in air-saturated solutions when TX-SH was added. With the addition of TX-SH to initiation formulations, the inhibition due to oxygen is reduced, probably by the generation of reactive thyl radicals by hydrogen abstraction of inactive peroxy radicals from the thiol functionality.

Introduction

Acyl- and bisacylphosphine oxides are widely used as photoinitiators for free radical polymerization,^{1–8} and their photophysics and photochemistry have been the subject of a number of studies.^{8–18} Upon irradiation, acyl- and bisacylphosphine oxides undergo efficient α -cleavage from the triplet state to generate phosphinoyl and benzoyl radicals (eqs 1 and 2). The high addition rate constants of phosphinoyl radicals to the acrylate double bond was considered to be the main reason for the higher initiation efficiency of these compounds.^{17,18}



Acyl- and bisacylphosphine oxides are widely used in industry where their properties of near-UV/vis absorption, high radical yield, and the bleaching during photocuring (colorless appearance of the cured formulations)² make them attractive photoinitiators.

However, strong oxygen inhibition is observed in the curing of acrylates using acylphosphine oxides. Acylphosphine oxides were found to be much more efficient than benzil dimethyl ketal under nitrogen blanketing (deoxygenation) but less reactive under the usual curing conditions in air.^{2–5} Thiol additives are often used to reduce the oxygen inhibition of polymerization.^{2–5,19}

Another disadvantage of acylphosphine and bisacylphosphine oxide photoinitiators is the relatively low extinction coefficient in the near-UV spectral region ($\sim 600 \text{ M}^{-1} \text{ cm}^{-1}$ at 360 nm;

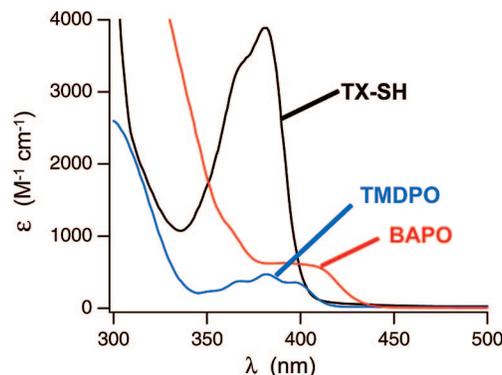


Figure 1. Absorption spectrum (molar absorptivity) of TX-SH, TMDPO, and BAPO in DMF solution [$5 \times 10^{-4} \text{ M}$].

Figure 1). Addition of a triplet sensitizer with high extinction coefficient can improve the light absorption. It was reported that the reactivity of α -aminoacetophenone photoinitiators was enhanced by addition of thioxanthone as sensitizer.^{20,21} 2-Mercaptothioxanthone (TX-SH) as shown in eq 3 is an additive that combines the triplet sensitizer functionality (enhanced light absorption) and thiol functionality (reduced oxygen inhibition). TX-SH possesses a significantly higher molar absorptivity than the acylphosphine and bisacylphosphine oxides in the industrial attractive spectral region of 340–400 nm (Figure 1). Previously, we have shown that TX-SH itself is a one-component initiator for initiation of free radical polymerization that does not require an additional coinitiator.²² In this study, we report the beneficial effects of TX-SH as additive for acyl- and bisacylphosphine oxide photoinitiator formulations on polymerization of methacrylates.

Experimental Section

Materials. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TMDPO) and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (BAPO) were obtained from Ciba Specialty Chemicals and used as received. Trimethylol propanetriacrylate (TMPTA), *N*-methyldiethanolamine (MDEA), and dimethylformamide (DMF) were obtained from Aldrich and used as received. Methyl methacrylate (MMA) was washed with NaOH (5%), dried

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with sodium sulfate (Na_2SO_4), and distilled under vacuum. 2-Mercaptothioxanthone was synthesized as reported in the literature.²²

Photoinitiated Polymerization. Appropriate solutions of monomer, TMDPO, and BAPO in the presence and in the absence of *N*-methyl-diethanolamine and 2-mercaptothioxanthone were irradiated in a photoreactor equipped with 12 Philips lamps emitting nominally at $\lambda = 350$ nm for 60 min in an air atmosphere. The light intensity was measured with a radiometer (Macam UV203 ultraviolet radiometer) and was found as $I = 9.4$ mW/cm². The polymer was obtained after precipitation in methanol and drying in vacuum. Conversions (%) were calculated for all samples gravimetrically.

Laser Flash Photolysis. 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.²³ Solutions of BAPO in acetonitrile were prepared at concentrations such that the absorbance was 0.3 at the excitation wavelength (355 nm).

Analysis. GPC analyses of the polymers were performed with a setup consisting of a pump (Agilent 1100), three columns (Zorbax PSM), and an Agilent 1100s differential refractometer. THF was used as the eluent (flow rate 0.3 mL/min). The number-average molecular weight was determined using Polymer Laboratories polystyrene standards. UV-vis spectra were taken on an Agilent 8453 spectrometer. Fluorescence spectra were recorded on a Jobin Yvon-Horiba Fluoromax-P-3 fluorometer.

Photodifferential Scanning Calorimetry (Photo-DSC). The photoinitiated polymerization of TMPTA was performed in a Photo-DSC setup (DSC Q100, TA Instruments). UV light was applied from a medium-pressure mercury lamp with a light intensity of 20 mW/cm² at the level of the surface of the cured samples. The mass of the TMPTA samples was 2 ± 0.1 mg, and the measurements were carried out in an isothermal mode at room temperature under a nitrogen flow of 50 mL/min. The reaction heat liberated in the polymerization is directly proportional to the number of acrylate reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (*C*) or the extent of the reaction was determined according to eq 3:

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \quad (3)$$

where ΔH_t is the reaction heat evolved at time *t* and $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion. A reaction heat for an acrylate double-bond polymerization of $\Delta H_0^{\text{theory}} = 86$ kJ/mol was used.²⁴ The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by eq 4:

$$R_p = (dC/dt)(dH/dt) / \Delta H_0 \quad (4)$$

Results and Discussion

Photopolymerization experiments in air-saturated DMF solutions of MMA were performed using TMDPO or BAPO as photoinitiator in the absence and presence of TX-SH. The gravimetrically determined conversions of monomer (MMA) into polymer for these experiments are shown in Table 1 (entries 1, 2, and 5–10). Photopolymerization using BAPO as initiator in the absence of TX-SH yielded in a low conversion (5.5%; Table 1, entry 2). A significant increase of the conversion was achieved by addition of TX-SH (entries 6, 8, and 10). The highest conversion was achieved at a concentration of 1 mM TX-SH (19.5%; entry 8). An even more significant improvement of the photopolymerization efficiency was observed in case of TMDPO. The conversion increased 1 order of magnitude after addition of TX-SH (compare entries 1 and 7). The lower conversion (17.5%, entry 6) at higher TX-SH concentration (10 mM) is probably caused by the poor penetration depth of the light due to total light absorption at the surface layer of the 1 cm sample tube.

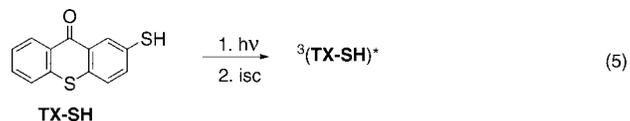
It is reported that the curing efficiency of acylphosphine oxides in air can be improved by addition of amines.^{25–27} Under

Table 1. Photoinitiated Polymerization of Methyl Methacrylate (MMA) in Dimethylformamide (DMF) in the Absence or Presence of TMDPO, BAPO, TX-SH, TX, and MDEA in Air Atmosphere

entry	PI ^a	[MDEA] (mM)	[TX-SH] (mM)	[TX] (mM)	conv ^b (%)	<i>M_n</i> (g/mol)	<i>M_w/M_n</i>
1	TMDPO				1.5	79 140	2.67
2	BAPO				5.5	74 400	2.59
3	TMDPO	10			2.7	66 050	2.83
4	BAPO	10			6.1	78 040	2.38
5	TMDPO		10		15.0	32 700	2.47
6	BAPO		10		17.5	38 900	2.26
7	TMDPO		1		15.0	26 620	2.63
8	BAPO		1		19.5	24 510	1.70
9	TMDPO		0.1		9.1	29 360	2.09
10	BAPO		0.1		9.1	29 950	2.56
11	TMDPO			1	12.2	31 830	1.85
12	BAPO			1	10.8	27 440	1.87
13			10		10.0	48 640	2.61
14			1		6.2	49 940	2.11

^a 1 mM. ^b Conversion of monomer into polymer measured gravimetrically; [MMA] = 4.7 mM.

our polymerization condition, only a minor improvement of conversion was observed after addition of *N*-methyl-diethanolamine (Table 1, entries 3 and 4) compared to the large increased conversion in the presence of TX-SH (entries 5–10). Previously, we reported that TX-SH initiates the polymerization of MMA upon irradiation.²² Polymerization experiments were performed with TX-SH in the absence of BAPO or TMDPO (Table 1, entries 13 and 14). Only low conversions ($\leq 10\%$) were observed. Furthermore, the sum of the conversions of the processes, where BAPO (entry 2) or TX-SH (entry 14) is used without additives, is smaller than the conversion in the combined initiator mixture (BAPO + TX-SH). Therefore, the mechanism of conversion enhancement is cooperative and synergistic, not additive. A possible mechanism for a cooperative conversion enhancement is sensitization of BAPO (or TMDPO) by TX-SH, where TX-SH predominantly absorbs the light to generate singlet excited states of TX-SH, which rapidly convert into the triplet state (eq 5). Because the triplet energy of TX-SH (272 kJ/mol)²² is higher than the triplet energies of TMDPO or BAPO (263 and 255 kJ/mol, respectively),¹⁶ energy transfer from ³(TX-SH)* to generate triplet states of TMDPO or BAPO is expected to be efficient (eqs 6 and 7).



To determine the rate constant of triplet energy transfer, laser flash photolysis experiments were performed. Deoxygenated acetonitrile solutions of TX-SH were irradiated with laser pulses (355 nm, 5 ns) to generate triplet states of TX-SH, which show triplet-triplet absorption at 625 nm.²² Decay traces were recorded at different concentrations of BAPO, which were fitted to a pseudo-first-order kinetic model. The quenching rate constant was determined from the slope of the plot of the pseudo-first-order rate constants vs the BAPO concentration ($k_q = 4.4 \times 10^9 \text{ s}^{-1} \text{ M}^{-1}$) (Figure 2). This high rate constant shows that sensitization of BAPO (eq 7) is efficient under our polymerization conditions.

To investigate the effect of molecular oxygen on the polymerization mechanism, photopolymerization experiments were performed in the absence of oxygen. Table 2 shows the

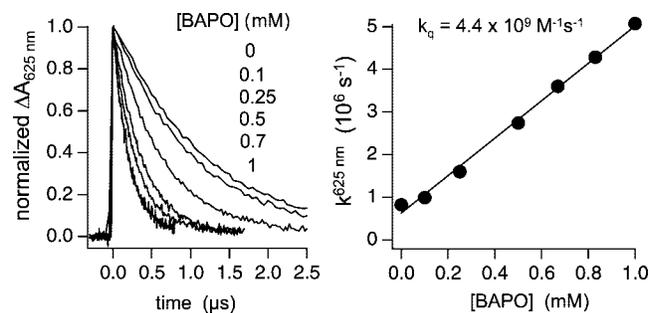


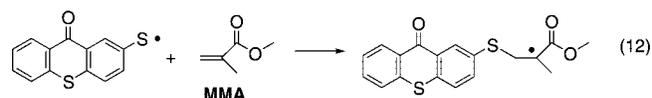
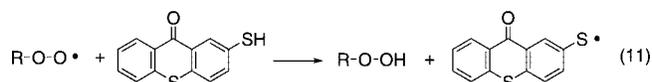
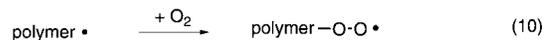
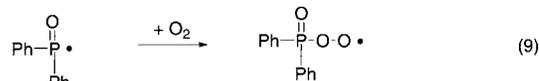
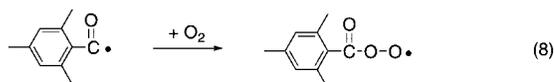
Figure 2. Quenching of TX-SH triplets by BAPO in acetonitrile at 23 °C. Left: decay traces of the absorbance of $^3(\text{TX-SH})^*$ at 625 nm in the absence and presence of BAPO. The decay traces were generated by laser excitation (355 nm) of argon-saturated acetonitrile solutions of TX-SH. Right: dependence of the pseudo-first-order rate constant of the decay at 625 nm on the concentration of BAPO.

Table 2. Photoinitiated Polymerization of Methyl Methacrylate (MMA) in Dimethylformamide (DMF) in the Absence or Presence of TMDPO, BAPO, TX-SH, and TX under Nitrogen Atmosphere

entry	PI ^a	[TX-SH] (mM)	[TX] (mM)	conv ^b (%)	M_n (g/mol)	M_w/M_n
1	TMDPO			5.4	23 700	4.53
2	BAPO			7.3	28 770	4.50
3	TMDPO	10		12.9	30 310	2.14
4	BAPO	10		12.2	34 810	2.11
5	TMDPO	1		10.9	47 650	2.15
6	BAPO	1		11.4	45 630	1.91
7		10		9.1	48 640	2.61
8		1		6.2	49 940	2.11
9	TMDPO		1	10.1	32 190	1.89
10	BAPO		1	8.5	28 260	1.73

^a 1 mM. ^b Conversion of monomer into polymer measured gravimetrically; [MMA] = 4.7 mM.

conversions of monomer (MMA) to polymer using TMDPO, BAPO, TX-SH, and/or TX as photoinitiators. As expected, without additives higher conversions were observed in the absence of oxygen using TMDPO (5.4%) or BAPO (7.3%) as initiator (Table 2, entries 1 and 2) compared to air-saturated conditions (1.5% and 5.5%, respectively; Table 1, entries 1 and 2) due to oxygen scavenging of initiator (eqs 8 and 9) and polymer (eq 10) radicals. Remarkably, the opposite trend was observed in the presence of TX-SH. Higher conversions were observed in the presence of oxygen (Table 1, entries 5–8) compared to deoxygenated samples (Table 2, entries 3–6).



Polymerization experiments were performed using TX instead of TX-SH as sensitizer to study the effect of the SH group on

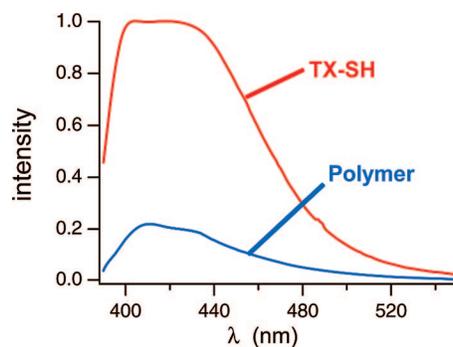


Figure 3. Fluorescence emission spectra of TX-SH and polymer (PMMA) obtained by photoinitiated polymerization by using BAPO and TX-SH. Benzene solutions; $\lambda_{\text{ex}} = 360$ nm.

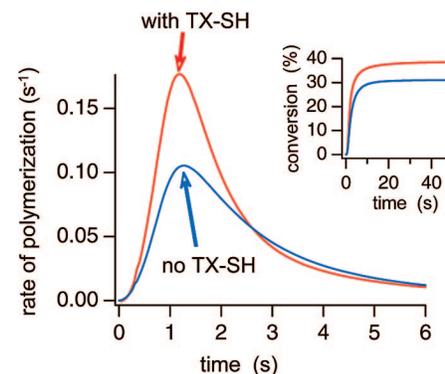


Figure 4. Photo-DSC profile for polymerization of TMPTA using BAPO (0.2 wt %) as photoinitiator in the absence (blue) and presence (red) of TX-SH (0.02 wt %). Inset: conversion of acrylate monomers vs time.

the polymerization. Generally, higher polymer yields were observed using TX-SH as sensitizer for TMDPO and BAPO compared to TX (Tables 1 and 2). For example, in air-saturated conditions, using TX-SH as sensitizer for BAPO, a conversion of 19.5% was observed (Table 1, entry 8), whereas using TX as sensitizer, only 10.8% conversion was observed (Table 1, entry 12). This demonstrates the beneficial effect of the SH group on the polymerization, which operates cooperatively with the energy transfer effect.

The proposed mechanism involves radical scavenging by oxygen to form peroxy radicals (eqs 8–10) and hydrogen abstraction of the peroxy radicals from TX-SH to form TX-S[•] radicals (eq 11). Thiyl radicals are known to be resistant against oxygen scavenging and add to monomer double bonds to initiate polymerization (eq 12).

A consequence of this mechanism is that the TX-chromophore is incorporated into the polymer chain. Fluorescence experiments were performed of solutions containing PMMA polymer, which was obtained by photopolymerization of methyl methacrylate in the presence of BAPO and TX-SH. The fluorescence spectra of the polymer solution showed similar features compared to TX-SH solutions (Figure 3), which is consistent with the incorporation of the TX-chromophore into the polymer chain (eq 12).

Photo-DSC has been widely used to elucidate photopolymerization parameters, such as the rate of polymerization and the consumption of monomers.^{24,28} The technique is based on the interpretation of heat generated by the polymerization reaction. For these studies, a triacrylate, TMPTA, was selected as monomer because it forms films, which are suitable for DSC measurements. Figure 4 shows a representative example of the photo-DSC profiles generated under our experimental conditions.

A formulation of TMPTA containing BAPO and TX-SH was irradiated inside the DSC setup, and the heat generated by acrylate polymerization was recorded. After ~10 s irradiation, the maximum conversion was reached (38%). A quantitative conversion is not expected due to the hindered diffusion in cross-linked TMPTA polymer films. In the absence of TX-SH, the polymerization was significantly slower and lower conversions were observed (Figure 4). These photo-DSC experiments confirm the beneficial effect of the additive TX-SH.

Conclusions

The initiation efficiency of free radical polymerization using acyl- and bisacylphosphine oxides (TMDPO and BAPO) as photoinitiators is improved by addition of TX-SH. In the proposed mechanism, most of the light is absorbed by TX-SH to generate $^3(\text{TX-SH})^*$, which transfers its energy to TMDPO and BAPO followed by α -cleavage to produce the initiating radicals. This triplet sensitization improves the efficiency of light absorption by the initiator formulation. In addition, excellent polymerization yields were observed in air-saturated solutions when TX-SH was added. The inhibition due to oxygen is reduced, probably by the generation of reactive thiyl radicals by hydrogen abstraction of inactive peroxy radicals from the thiol functionality. The combination of the sensitizer and thiol functionality should make TX-SH attractive as additive in photoinitiator formulations.

Acknowledgment. S.K. and N.A. thank TUBITAK (Project No. TBAG/1820, TBAG-AY/257) and Yildiz Technical University Research Foundation (20-01-02-02) for their valuable support. S.J. and N.J.T. thank the National Science Foundation (Grants NSF-CHE-04-15516 and NSF-CHE-07-17518) for financial support.

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