

Polymeric Side Chain Thioxanthone Photoinitiator for Free Radical Polymerization

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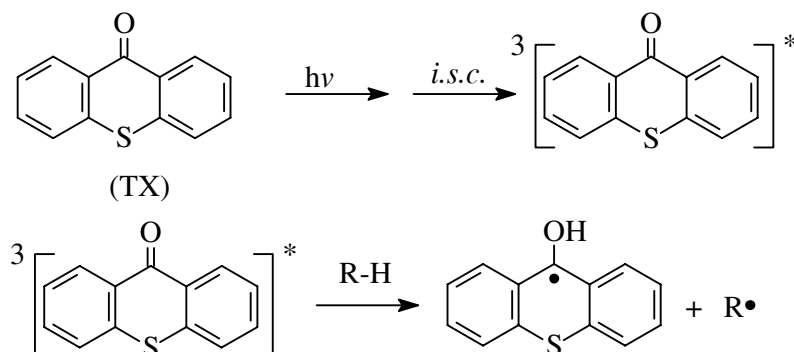
Summary

Side chain thioxanthone-containing polymer (PSt-TX) was synthesized and characterized by modification of polystyrene prepared by Atom Transfer Radical Polymerization. PSt-TX exhibits absorption characteristics similar to that of the unsubstituted thioxanthone. Its capability to act as initiator for the polymerization of methyl methacrylate was also examined.

Introduction

Photoinitiated free radical polymerization is extensively used in numerous applications such as those in coatings, adhesives, inks, printing plates, optical waveguides and microelectronics [1-3]. Almost all of the commercially significant photoinitiators are organic compounds that produce free radicals upon irradiation [4]. The most widely used free radical photoinitiators include benzoin and derivatives, benzyl ketals, acetophenone derivatives, aromatic ketone / amine combinations. Among these initiators thioxanthone (TX) derivatives have recently received a revitalized interest because of their absorption characteristics at near UV range [5-13]. Moreover, their simple synthetic procedure allows various modifications for wavelength tunability or improved solubility by the incorporation appropriate substituents on the thioxanthone structure. Free radical generation process is H-abstraction reaction of thioxanthone triplets from hydrogen donors such as amines and alcohols (Scheme 1). The radical derived from the donor can initiate the polymerization while the radicals stemming from TX are usually not reactive towards vinyl monomers due to bulkiness and/or the delocalization of the unpaired electron. Various structurally different thioxanthone derivatives including dendritic [5-6], polymeric and one-component ones [7-9] possessing both light absorbing chromophoric group and hydrogen donating sites in the same structure have been synthesized and their photochemistry has been studied in detail.

Polymeric photoinitiators have attracted much attention in the past years, for they combine properties of polymers with those of low molecular weight photoinitiators [14-15]. Solubility or miscibility problems, often observed with coatings containing low molecular weight photoinitiators do not occur with the polymeric ones since



Scheme 1. Photoinduced radical generation from thioxanthone

polymers are easily miscible with the resin to be cured as well as with the final, cured film. Moreover, odor and toxicity problems do not occur with macrophotoinitiators owing to the low volatility of large molecules. The low migration tendency of polymeric photoinitiators and of photoproducts brings about a reduced proneness to yellowing of cured coatings.

In this context, we synthesized a novel macrophotoinitiator through introducing thioxanthone moieties onto polystyrene prepared by Atom Transfer Radical Polymerization (ATRP). We also studied the photopolymerization of methyl methacrylate (MMA) by using the obtained photoinitiator.

Experimental Section

Materials

Thiosalicylic acid (98%, Aldrich), *N*-methyldiethanolamine (MDEA; 99%, Aldrich) were used as received. Styrene (99%, Aldrich) and methyl methacrylate (99%, Aldrich) were washed with 5% aqueous NaOH solution, dried over CaCl₂, and distilled over CaH₂ under vacuum just before use. Dimethylformamide (DMF; 99+%, Aldrich) was distilled over CaH₂ under reduced pressure. *N*, *N*, *N*', *N*'', *N*'''-Pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH before use. Tetrahydrofuran (99.8%, J.T. Baker) was dried and distilled over LiAlH₄. All other reagents were purchased from Aldrich and used as received.

Instruments

Gel permeation chromatography (GPC) analyses of the polymers were performed with a set-up consisting of a pump (Waters) and four ultrastyrigel columns of different porosities. Tetrahydrofuran (THF) was used as the eluent (flow rate 3 mL.min⁻¹), and the detection was carried out with the aid of a differential refractometer. The number-average molecular weights were determined using polystyrene standards. ¹H NMR spectra were recorded on a Bruker 250 instrument with *d*-DMSO as solvent and tetramethylsilane (TMS) as the internal standard. UV-visible spectra were taken on an Ati Unicam spectrophotometer.

Synthesis of polystyrene (PSt) by ATRP

In a typical bulk polymerization, a Schlenk tube was charged with 3 mL (26.2 mmol) of styrene, 0.045 g (0.26 mmol) of PMDETA, 0.037 g (0.26 mmol) of CuBr. 0.051 g (0.26 mmol) Ethyl-2-bromo- isobutyrate was added and the system was degassed three times. The tube was immersed in a preheated oil bath (110 °C) for 16 minutes. The crude product was dissolved with THF, filtered with neutral alumina. Excess of THF was removed by rotary evaporater, and polymer solution was precipitated in 10-fold excess methanol. The polymers were dried in vacuum at room temperature. The yields were determined gravimetrically.

Preparation of polystyrene photoinitiator with thioxanthone (PSt-TX) moieties

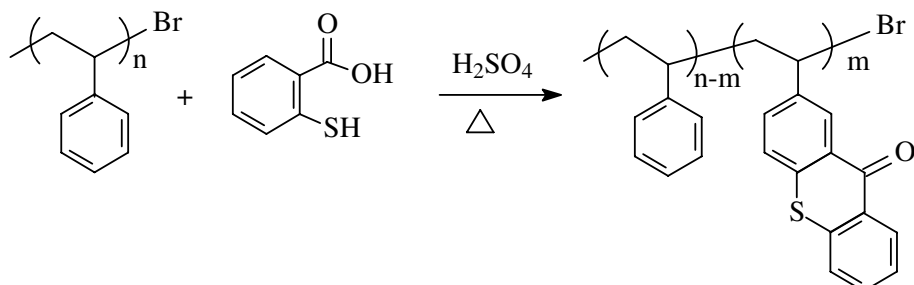
Thiosalicylic acid 1.7 g (11 mmol) was slowly added to 15 mL of concentrated sulfuric acid, and the mixture was stirred for 10 min. PSt, 0.2 g (0.1 mmol), was added slowly to the stirred mixture over a period of 30 min. After the addition, the reaction mixture was further stirred at room temperature for 1 h and then at 80 °C for 3 h. At the end of this period, it was left to stand at room temperature overnight. The resulting mixture was poured with stirring into a 10-fold excess of boiling water, and it was boiled further for 5 min. The solution was cooled and filtered. Yield: 70%. $M_n = 4580 \text{ g mol}^{-1}$ as determined by NMR and elemental analysis.

Photopolymerization

Typical procedure: Appropriate solutions of the monomer, MMA, and PSt-TX were irradiated in a photoreactor consisting of a 400 W medium pressure mercury lamp and a water cooling system, in an air atmosphere. Polymers were obtained after precipitation in methanol and drying under vacuum. Polymers were then purified by dissolving in THF and unreacted PSt-TX was readily separated as insoluble part. Dissolved PMMA was precipitated into methanol. Conversions were calculated gravimetrically.

Results and Discussion

Macrophotoinitiator containing side-chain TX moieties was synthesized by the modified literature procedure according to Scheme 2.



Scheme 2. Synthesis of polymeric thioxanthone photoinitiator

ATRP is an established method to obtain various polymer architectures with predetermined molecular weights and narrow polydispersity [16]. ATRP involves reversible homolytic cleavage of a carbon-halogen bond by a redox reaction between an organic halide (R-X) and a transition metal, such as copper (I) salts. Polystyrene with low polydispersity ($M_w/M_n = 1.04$) was obtained by ATRP of styrene using ethyl-2-bromo-isobutyrate as initiator in the presence of the CuBr/PMDETA complex. The polymerization condition and results are given in Table 1.

Table 1. ATRP of styrene at 110 °C initiated by ethyl-2-bromo-isobutyrate

Sample	Time (min)	Conversion (%)	M_n (g mol ⁻¹)	M_w/M_n
PSt-Br	16	12	1900	1.04

^a[M]₀: [I]₀[CuBr]:[PMDETA] = 100:1:1:1

The aromatic groups of the resulting polymer were then used as linkage units with which to form thioxanthone structures (Scheme 2). The structure was confirmed by FT-IR, ¹H-NMR spectra and elemental analysis. The signal of carbonyl groups of PSt-TX is observed at 1629 cm⁻¹ in FT-IR spectra. Moreover, compared with the precursor PSt, the appearance of the new signals related to the aromatic protons of the thioxanthone moiety in the ¹H-NMR spectrum was considered as evidence of completion of the addition reaction (Figure 1).

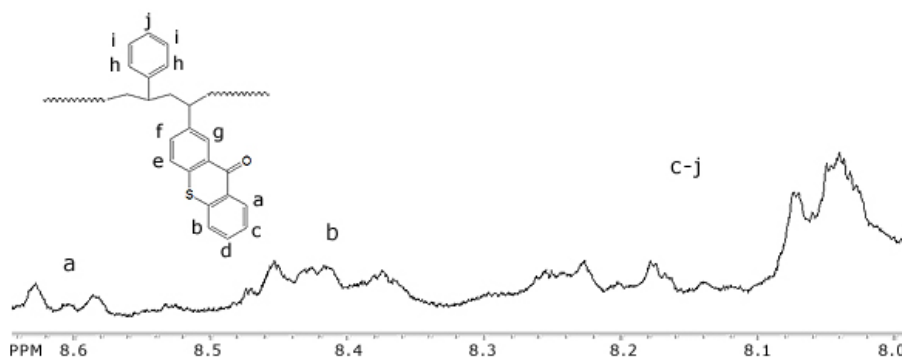


Figure 1. ¹H-NMR spectra of PSt-TX in d-DMSO

The composition of PSt-TX was determined with the elemental analysis data (carbon content/sulfur content). The analysis results showed that about 80 % aromatic groups of PSt reacted with thiosilylic acid. UV-vis absorption spectra of PSt-TX is shown in Figure 2a. It exhibits the usual characteristics absorption of thioxanthone with $\lambda_{max} = 389$ nm. Compared with the maximum of absorption of bare TX (Figure 2b), the observed slight shift may be attributed to the macromolecular structure of PSt-TX [12].

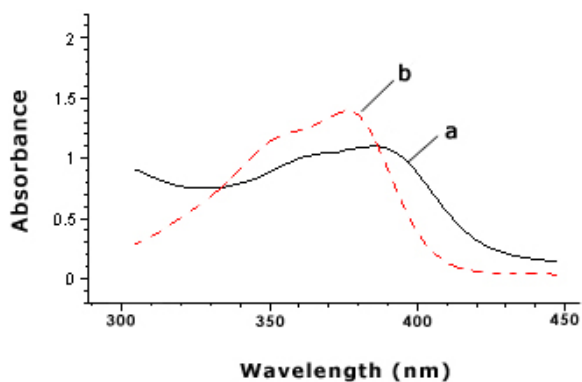


Figure 2. Optical absorption spectrum of PSt-TX a) and thioxanthone b) in presence of air in DMF

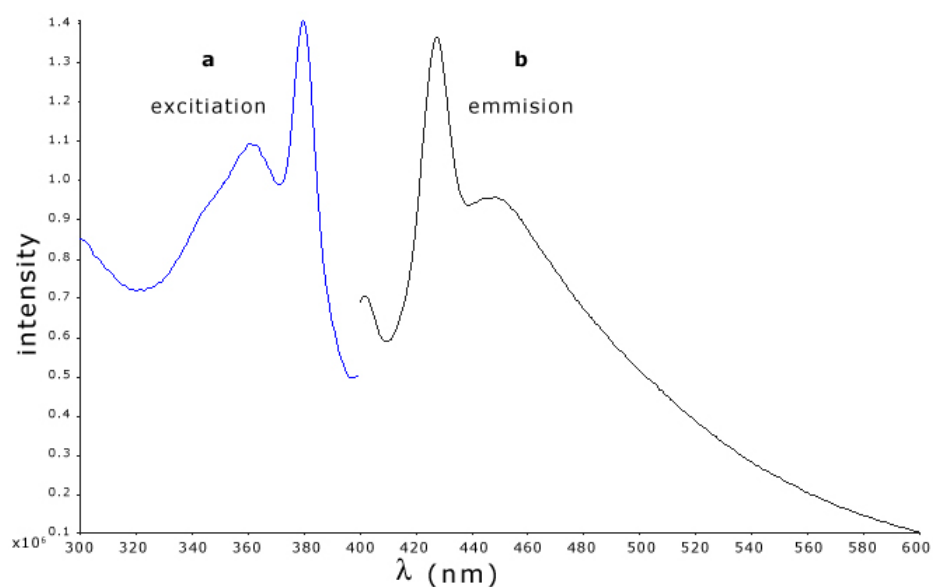


Figure 3. Fluorescence excitation (a) and emission spectrum (b) of PSt-TX in DMF at 25 °C

Figure 3 shows that a nearly mirror-image-like relation exists between absorption and emission of PSt-TX again indicating successful incorporation of thioxanthone moieties. PSt-TX was used as a photoinitiator for the polymerization of MMA. The results are compiled in Table 2. The presence of an amine such as N-methyldiethanolamine is important for effective photoreduction and photopolymerization (see Scheme 1, R-H = MDEA). It is also seen that the conversion is increased with increasing concentration of PSt-TX indicating that the rate of initiation is proportional to the absorbed light and consequently the amount of initiator.

Table 2. Photoinitiated polymerization^a of methyl methacrylate in DMF by using PSt-TX at room temp.

[PSt-TX] (mol L ⁻¹)	Conversion (%)	$M_n^b \times 10^{-4}$ (g mol ⁻¹)	M_w/M_n^b
5,1 x 10 ⁻⁴	5,3	2,5	1,39
9,5 x 10 ⁻⁴	8,8	3,1	1,50
1,9 x 10 ⁻³	12,1	2,3	1,39
3,8 x 10 ⁻³	14,1	2,0	1,45

^a[MMA] = 4,68 mol L⁻¹, [MDEA] = 10⁻² mol.L⁻¹, Time = 15 min.

^bDetermined by GPC according to PSt standards

Conclusions

In conclusion, although these results are preliminary in nature, they serve to indicate that polymeric side-chain thioxanthone photoinitiator can readily be synthesized by using polystyrene in the conventional synthetic procedure of thioxanthenes and used as an efficient photoinitiator for free radical polymerization. Studies on the photophysical and photochemical properties of the photoinitiator, together with the efforts to prepare polymeric photoinitiators possessing both thioxanthone and the hydrogen donating sites in the chain, are now in progress.

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