Journal of Photochemistry and Photobiology A: Chemistry 202 (2009) 63–66

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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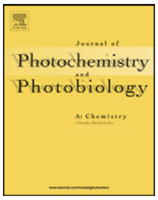

One-pot synthesis of water-soluble polymeric photoinitiator via thioxanthonation and sulfonation process

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ARTICLE INFO

Article history:
Received 21 May 2008
Received in revised form
30 September 2008
Accepted 22 November 2008
Available online 28 November 2008

Keywords:
Free radical polymerization
One-pot synthesis
Polymeric water-soluble photoinitiator
Thioxanthone

ABSTRACT

One-pot synthesis of water-soluble side chain thioxanthone polystyrene (PSt-TX-WS) was achieved, and photoinduced polymerization of acrylamide (AAm) in water was performed with PSt-TX-WS in the presence of a tertiary amine. Since the amine is necessary for photopolymerization to occur, it is likely that PSt-TX-WS initiates polymerization of AAm according to the Norrish Type II reaction. The fluorescence quantum yield of PSt-TX-WS was found to be 0.021, and had a phosphorescence lifetime at 77 K of 95 ms.

1. Introduction

There have been many new developments in synthesis and photochemical studies of novel polymeric photoinitiators. Polymeric photoinitiators have attracted much attention in the past years, for they combine the properties of polymers with those of low molecular weight photoinitiators [1–14]. Solubility and miscibility problems, often observed with coatings containing low molecular weight photoinitiators, do not occur with the polymeric ones since 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 the large molecules. The low migration tendency of polymeric photoinitiators and of photoproducts means that cured coatings are less prone to yellowing [15–19].

In our previous study [14], to overcome some of these problems, we successfully synthesized novel side chain thioxanthone-containing polystyrene (PSt-TX) by ATRP [20] and used it as a polymeric photoinitiator for the free radical polymerization of methyl methacrylate (see Scheme 1).

In this study, an environmental approach was taken to polymeric initiators and synthesis of water-soluble side chain thioxanthone polystyrene (PSt-TX-WS) was achieved. In addition, photoinduced polymerization of acrylamide with PSt-TX-WS in the presence of a tertiary amine was performed.

2. Experimental

2.1. Materials

Thiosalicylic acid (98%, Aldrich) and *N*-methyldiethanolamine (MDEA, 99%, Aldrich) were used as received. Styrene (99%, Aldrich) was washed with 5% aqueous NaOH solution, dried over $CaCl_2$, and distilled over CaH_2 under vacuum just before use. *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH before use. CuBr (99.9%, Aldrich) were used as received. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone–Na. Acrylamide (AAm, 97%, Merck) was used as received. All other reagents were purchased from Aldrich and used as received.

2.2. Instruments

UV–vis spectra were taken on an Agilent 8453. Fluorescence and phosphorescence spectra were recorded on a Jobin Yvon–Horiba Fluoromax-P in cold finger at 77 K. A Perkin–Elmer Spectrum-One FTIR spectrophotometer was used for recording IR spectra. ^1H NMR spectra were recorded on a Bruker 250 instrument with D_2O and $CDCl_3$ as solvents and tetramethylsilane (TMS) as the internal standard. Gel permeation chromatography (GPC) measurements were performed at room temperature with a setup consisting of a pump (HP 1050), a refractive index detector (HP 1047 A), and three high-resolution Waters columns (AQ3.0, AQ4.0 and AQ5.0). The effective molecular weight ranges were 1000–60,000, 10,000–400,000 and 50,000–4,000,000, respectively. Water was used as eluent at a

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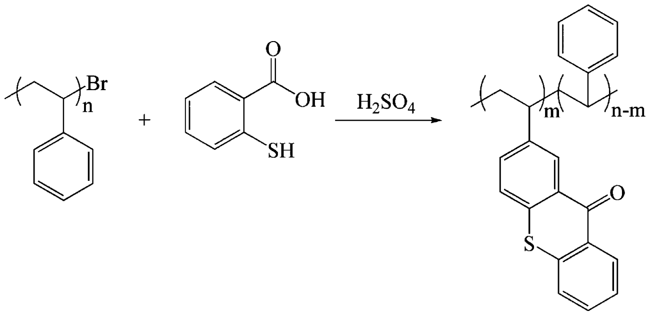
doi:10.1016/j.jphotochem.2008.11.012



Scheme 1. Synthesis of polymeric side chain thioxanthone photoinitiator (PSt-TX).

flow rate of 0.5 mL/min at room temperature. Data analyses were performed with HP Chemstation Software. Calibration with linear polyethylene oxide standards (Polymer Laboratories) was used to estimate the molecular weights. GPC analyses of the low molecular weight polystyrene were performed with a setup consisting of a pump (Waters) and four ultrastyragel columns of different porosities. Tetrahydrofuran (THF) was used as the eluent (flow rate 0.3 mL/min), and detection was carried out with the aid of a differential refractometer. The number-average molecular weights were determined using polystyrene standards.

2.3. Synthesis of polystyrene (PSt) by ATRP

In a typical bulk polymerization, an Schlenk tube was charged with (3 mL, 26.2 mmol) of styrene and (0.045 g, 0.26 mmol) of PMDETA, (0.037 g, 0.26 mmol) of CuBr and (0.051 g, 0.26 mmol) of 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 17 min. The crude product was dissolved with THF and filtered with neutral alumina. Excess THF was removed by rotary evaporator, and the polymer solution was precipitated in 10-fold excess methanol. The polymers were dried in vacuum at room temperature. Yield: 20%, $Mn = 2050\,\mathrm{g\,mol^{-1}}$, PDI = 1.08.

2.4. Synthesis of water soluble thioxanthonated polystyrene macrophotoinitiator (PSt-TX-WS)

Thiosalicylic acid (0.15 g, 1 mmol) was slowly added to 5 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 65 °C for 3 h. At the end of this period, it was left to stand at room temperature overnight. The resulting mixture was precipitated in a large excess amount of diethylether with stirring. After precipitation, the polymer was filtered. Yield: 70%. $Mn_{(\mathrm{GPC})} = 4500\,\mathrm{g\,mol^{-1}}$. UV (water), $\lambda = 396$ nm, $\varepsilon = 9600\,\mathrm{L\,mol^{-1}\,cm^{-1}}$. IR (KBr): 3430, 2928, 1636, 1180, and 1038 $\mathrm{cm^{-1}}$.

2.5. Sulfonation level determination

The sulfonation level of PSt-TX-WS was determined by titration with a standard 0.01N NaOH solution in water. All titrations were carried out by dissolving 10 mg of PSt-TX-WS in 30 ml of water. The sulfonation degree is expressed as mole percent of the sulfonated styrene units.

2.6. General procedure for photopolymerization

Appropriate aqueous solutions of the monomer (AAm) and PSt-TX-WS in the presence of MDEA were irradiated in a photoreactor consisting of a 400 W medium pressure mercury lamp and a water-cooling system. Polymers were obtained after precipitation in methanol and drying under vacuum. Conversions were calculated gravimetrically.

3. Results and discussion

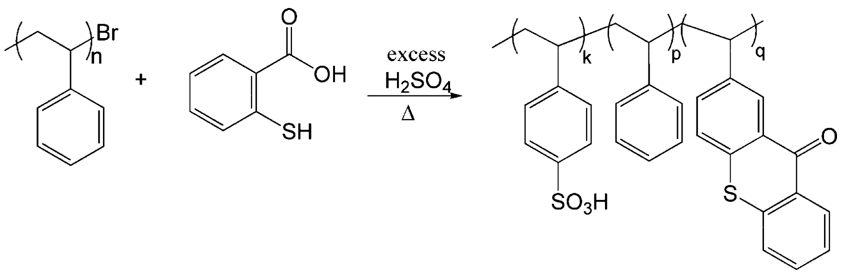
Polystyrene with low polydispersity ($Mw/Mn = 1.08$) was obtained by ATRP of styrene using ethyl-2-bromo-isobutyrate as initiator in the presence of the CuBr/PMDETA complex (see Section 2). ATRP is an established method to obtain various polymer architectures with predetermined molecular weights and narrow polydispersity [20]. Synthesis of water-soluble thioxanthonated polystyrene macrophotoinitiator was achieved via thioxanthonation and sulfonation of PSt. Excess amount of sulfuric acid was used for sulfonation process (see Section 2) (Scheme 2).

The content of TX moieties in the PSt-TX-WS was measured from UV absorption spectra of isopropylthioxanthone (ITX) and PSt-TX-WS in ethanol by use of the extinction coefficient of pure ITX ($\lambda_{\max} = 385$ nm, $\varepsilon_{385} = 6700\,\mathrm{L\,mol^{-1}\,cm^{-1}}$). The ratio of thioxanthonated styrene moieties was 10 in 20. The sulfonation degree of PSt-TX-WS was determined as 38 mole% according to NaOH titration results.

The sulfonic group vibration bands of the macrophotoinitiator were seen at approximately 1040 and 1180 $\mathrm{cm^{-1}}$ [21]. The symmetric stretching vibration of SO_3H groups was observed at 1038 $\mathrm{cm^{-1}}$. It was verified that the ν_{as} (S–O) vibration at 1180 $\mathrm{cm^{-1}}$ appeared as a broad band at approximately 1100–1350 $\mathrm{cm^{-1}}$. In addition, the signal of the carbonyl groups appeared at 1636 $\mathrm{cm^{-1}}$ due to the attaching of thioxanthone molecules on to phenyl groups. Moreover, compared with the precursor PSt, the appearance of the shifted signals related to the aromatic protons of the thioxanthone moiety in the ^{1}H NMR spectrum and was considered as evidence of completion of the addition reaction (Fig. 1).

The absorption spectrum of PSt-TX-WS is given in Fig. 2. Although water was used as solvent, it exhibits the typical absorption characteristics of thioxanthone with $\lambda_{\max} = 396$ nm. The absorption wavelength maxima of the initiator shifted to the visible region of the electromagnetic spectrum (see Fig. 2).

The fluorescence and phosphorescence properties of this novel water-soluble photoinitiator are given in Figs. 3 and 4. The phos-



Scheme 2. One-pot synthesis of water-soluble polymeric photoinitiator (PSt-TX-WS).

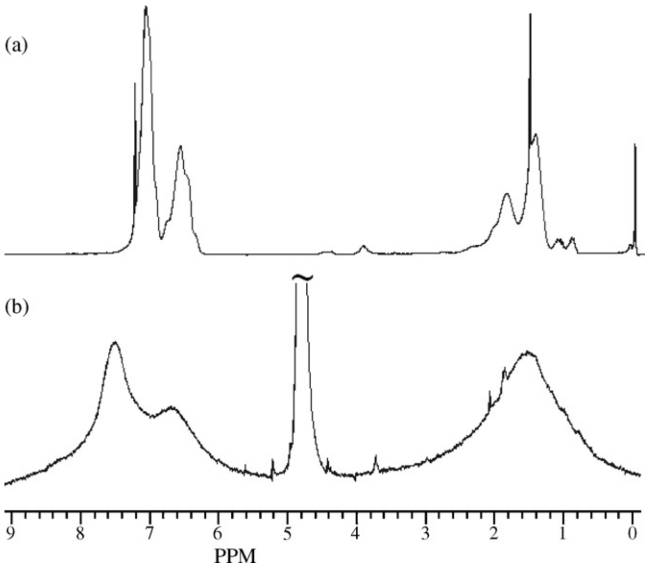


Fig. 1. ^1H NMR spectra of PSt in $CDCl_3$ (a) and PSt-TX-WS in D_2O (b).

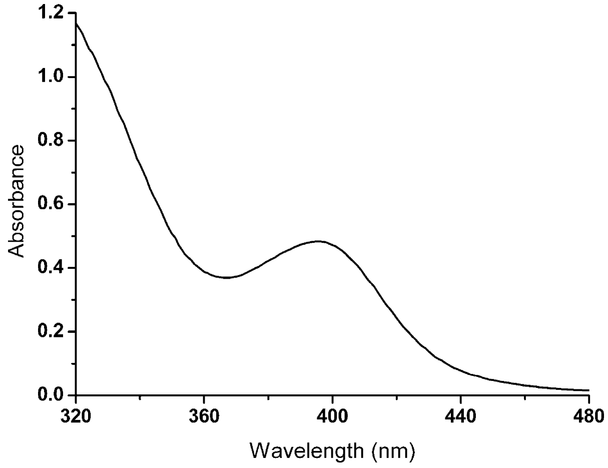


Fig. 2. Absorption spectrum of PSt-TX-WS (5×10^{-5} M) in water.

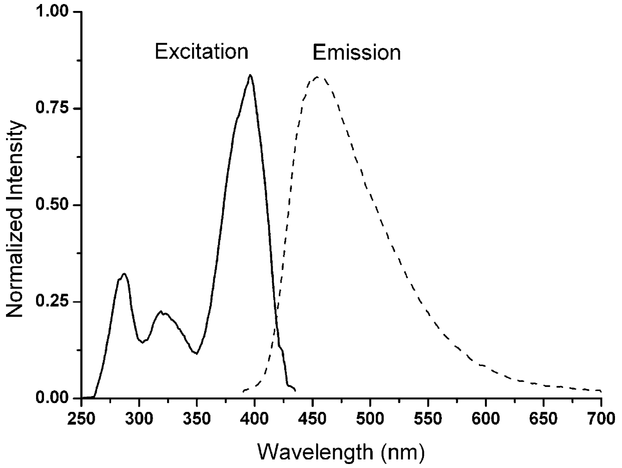


Fig. 3. Fluorescence excitation and emission spectra of PSt-TX-WS in water at 25 °C, $\lambda_{exc} = 380$ nm.

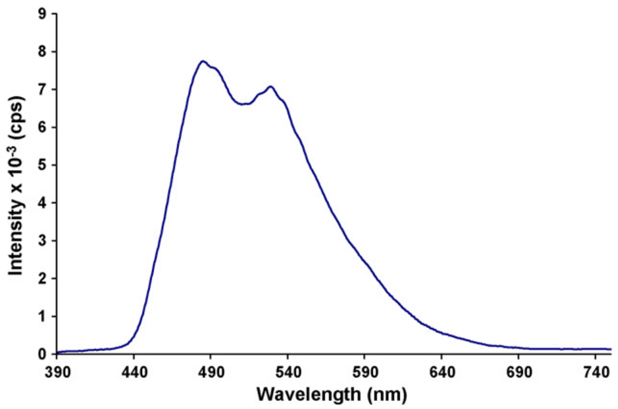


Fig. 4. Phosphorescence spectrum of PSt-TX-WS in ethanol at 77 K.

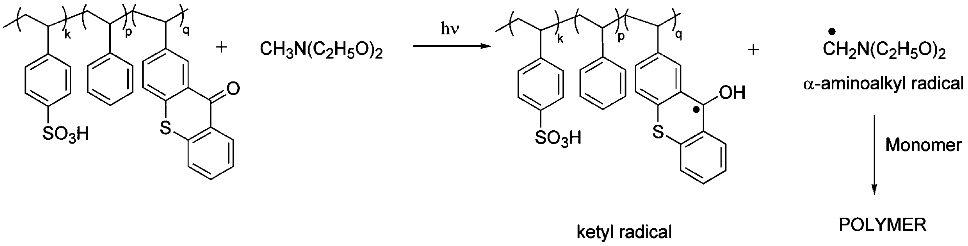
phorescence spectra of the initiators were taken in ethanol due to problems with freezing water cracking the quartz tubes at 77 K. The excitation spectrum of PSt-TX-WS in water is given in Fig. 3.

The singlet excited state energy of PSt-TX-WS, estimated from the intersection of the emission and excitation spectrum at 441 nm, is ca 271 kJ/mol (see Fig. 3). The fluorescence quantum yield of PSt-TX-WS was estimated by using 9,10-diphenyl anthracene as the standard ($\phi_f = 0.95$) [22] ϕ_f was found to be 0.021 for PSt-TX-WS. It is well known that the polarity of a solvent greatly influences the fluorescence lifetime and fluorescence quantum yield of thioxanthone derivatives. As reported elsewhere, the fluorescence quantum yield of thioxanthone increases with increasing solvent polarity [23–26]. Phosphorescence measurements are useful to gain information on the triplet configuration of PSt-TX-WS. The water-soluble PSt-TX macrophotoinitiator exhibits phosphorescence emission in ethanol at 77 K upon excitation with 400 nm light (see Fig. 4). The (0,0) emission band occurs at 515 nm, corresponding to approximate triplet energy of ca 232 kJ/mol.

The phosphorescence lifetime at 77 K is 95 ms (Fig. 4). The phosphorescence spectra of ketones with an 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. In addition, the phosphorescence lifetime for n-π^* triplets are significantly shorter (in the order of several ms) compared to π-π^* triplets. The results obtained from phosphorescence measurements indicate 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.

Quenching experiments were performed by adding MDEA at different concentrations, and changes in the emission spectrum of PSt-TX-WS in water solution were recorded. The Stern–Volmer representation (i.e. I_0/I vs. $[Q]$) is shown in Fig. 5. It can be observed that the least squares fit of the experimental results produce a straight line with reasonable point scattering. The linearity of the corresponding plot was always excellent ($R^2 > 0.98$) and no deviation was detected at high quencher concentrations. The Stern–Volmer quenching constant, K_{SV} obtained from the slope, is 2.28 M^{-1}.

This novel water-soluble polymeric photoinitiator was used for photopolymerization of two different concentrations (1 and 4.68 M) of acrylamide with MDEA in the presence of air and the results are given in Fig. 6. Although photoinitiated polymerization of AAm in water with PSt-TX-WS in the absence of MDEA was attempted, it was observed that polymerization did not occur in air without the aid of an amine. One can say that PSt-TX-WS behaves like a typical Type II photoinitiator in combination with MDEA it produces the initiating radical (α-aminoalkyl radical) as shown in Scheme 3.



Scheme 3. Photoinduced radical generation mechanism of PSt-TX-WS photoinitiator with coinitiator.

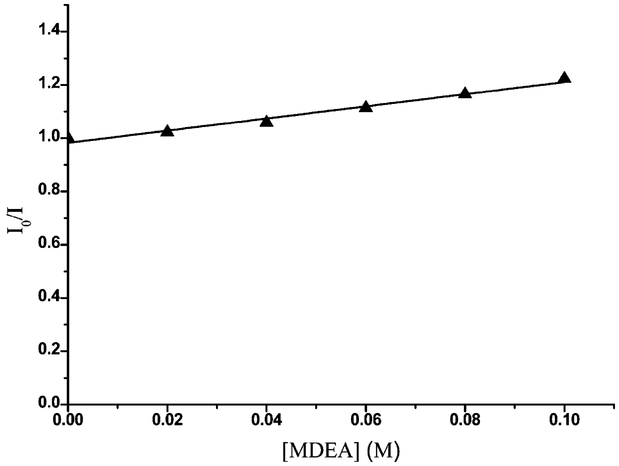


Fig. 5. Stern–Volmer plot of the quenching of PSt-TX-WS (1.95×10^{-6} mol L^{-1}) by MDEA in water (λ_{exc} = 380 nm). I_0 = fluorescence intensity of PSt-TX-WS, I = fluorescence intensity of PSt-TX-WS in the presence of MDEA.

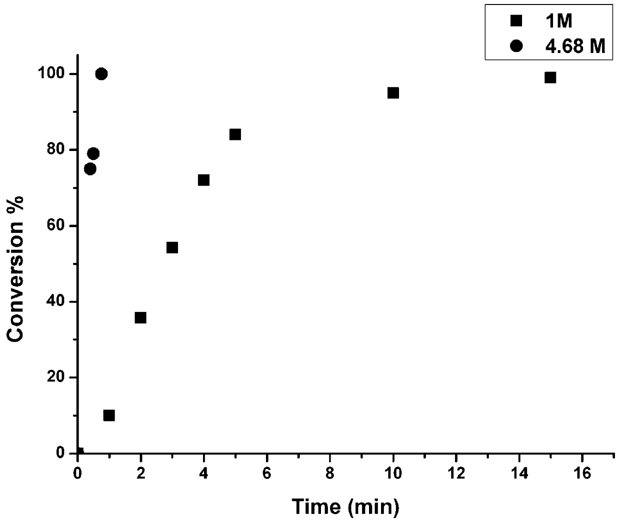


Fig. 6. Conversion vs. time curves of 1 and 4.68 M AAm in water with PSt-TX-WS in the presence of air. [PI] = 2.2×10^{-4} M, [MDEA] = 5×10^{-2} M.

Another important benefit of adding amines to the formulations is the decrease in the deleterious effects of oxygen. MDEA scavenges oxygen and the α-aminoalkyl radical produced in the quenching cycle is also involved in the initiation process.

4.68 M of AAm monomer with photoinitiator was polymerized faster (completely polymerized in 40 s) than 1 M of AAm monomer (completely polymerized in 15 min of irradiation).

4. Conclusion

Well-defined low molecular weight polystyrene was transformed into "completely water soluble" macrophotoinitiator form by the thioxanthonation and sulfonation methods in one-pot synthesis.

This photoinitiator is efficient for free radical polymerization in 1 and 4.68 M concentrations of AAm but requires an additional co-initiator (MDEA) to start polymerization. The resulting α-aminoalkyl radical initiates polymerization of the acrylamide monomer after addition of MDEA to the formulation.

Acknowledgements

The authors would like to thank to TUBITAK (project no: 106T407) and Yildiz Technical University Research Fund and DPT for financial support.

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