2-Mercapto Thioxanthone as a Chain Transfer Agent in Free-Radical Polymerization: A Versatile Route to Incorporate Thioxanthone Moieties into Polymer Chain-ends

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ABSTRACT: 2-Mercapto thioxanthone (TX-SH) was used as a chain transfer agent in free-radical polymerization of methyl methacrylate (MMA) and styrene (St), by using 2,2′-azobisisobutyronitrile (AIBN) as an initiator at 70°C. Chain transfer constants were found to be 1.41 and 0.12 for St and MMA, respectively. The use of TX-SH as a chain transfer agent leads to the formation of polymers with thioxanthone (TX) end groups. The incorporation TX moiety was con-firmed by spectral measurements. Polymers obtained this way were used as triplet photosensitizer in free-radical polymerization of MMA in the presence of a hydrogen donor such as N-methyldiethanolamine (MDEA). © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3766–3770, 2007

Key words: radical polymerization; photopolymerization; initiator; functionalization of polymers; mechanical properties

INTRODUCTION

The use of chain transfer agents to control the molecular weights of polymers obtained by free-radical polymerization is a well-known phenomena and of continuous interest.[1–3] This interest is mainly due to the increased use of low molecular weight polymers and the control of polymer chain length, since the final physical and mechanical properties of the polymers depend on their molecular weights. Thiols are taken very big part among the chain transfer agents due to their efficiency in the obtainment of polymers with desired molecular weights. The weakness of the S—H bond and the high reactivity of the thiyl radicals are two important parameters for the efficiency of thiols as chain transfer agents.[4–6]

We have recently reported the use of a thiol derivative of thioxanthone as photoinitiator for free-radical polymerization.[6] A great advantage of this initiator is related to its one component nature. It can serve as both triplet photosensitizer and a hydrogen donor. Thus, this photoinitiator does not require an additional coinitiator, i.e., a separate molecular hydrogen donor. Moreover, the new mercaptothioxanthone photoinitiator has no odor of characteristic of thiol compounds

and is only slightly inhibited by oxygen. 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 initiate the polymerization (Scheme 1).

Most of the studies on the behavior of thiols as chain transfer agents deal with aliphatic thiols. Although, because of the low energy of the S—H bond, the aromatic thiols are expected to act more efficient chain transfer agents, the corresponding studies on the use of these compounds are scarce. Only recently, Encinas and coworkers systematically studied the behavior of 4-substituted thiphenols as chain transfer agents in free-radical photopolymerization of vinyl monomers both in aqueous solution and organic media.[2–3]

In addition to the initiator-controlled polymer functionalization, chain transfer reactions may result in functional polymers.[7–10] Monofunctional polymers have been successfully prepared by using functional thiols. For example, carboxylic acid[11,12] and hydroxyl[13,14] functionalities were introduced to the polymer chain ends by using 3-mercaptopropionic acid and 2-mercapto-ethanol as a functional chain transfer agents, respectively. Polymeric photoinitiators[15–22] have attracted much attention in the past years, for they combine properties of polymers with those of low molecular weight photoinitiators. Solubility or miscibility problems, often observed with coatings containing low molecular weight photoinitators, 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
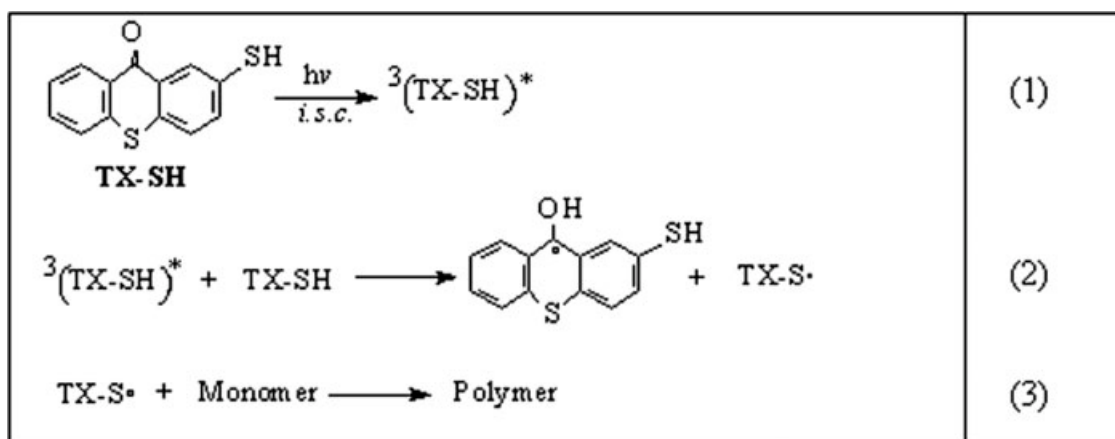
Scheme 1 Photoinitiated polymerization by using TX-SH. i.s.c: Intersystem crossing.

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.

It seemed therefore appropriate to use TX-SH as an aromatic thiol in the same manner, since it contains thiol group attached to the thoxathone chromophoric moiety. In the present work, we studied the chain transfer property of TX-SH on the free-radical polymerization of styrene (St) and methyl methacrylate (MMA). As it will be shown later, because of the consequence of the chain transfer reactions, this process leads to the formation of polymers with TX end groups capable of acting as a photosensitizer in a subsequent free-radical polymerization.

EXPERIMENTAL

Materials

2-Mercapto thioxanthone (TX-SH) was synthesized and crystallized as given in the literature.[6] 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. N-methyldiethanolamine (MDEA) was obtained from Aldrich and used without any purification. All solvents and monomers were purified by conventional drying and distillation procedures.

Analysis

GPC analyses of the polymer were performed at room temperature with a setup consisting of a pump (Agilent 1100) and three columns (Zorbax PSM); THF was used as the eluent (flow rate 0.3 mL min^{-1}), and the detection was carried out with the aid of a Agilent 1100s differential refractometer. The number–average molecular weights were determined using Polymer Laboratories polystyrene standards. UV–vis spectra were taken on an Agilent 8453. Fluorescence spectra were recorded on a Jobin Yvon-Horiba Floromax-P.

Free-radical polymerization

Monomers, methyl methacrylate (MMA) or styrene (St) containing a given amount of AIBN and TX-SH, were placed in a constant temperature bath at 70°C. Reactions were carried out in inert atmosphere at 70°C for 1 h. At the end of the reaction, the mixtures were poured into a 10-fold excess of methanol and precipitated polymers were filtered and dried.
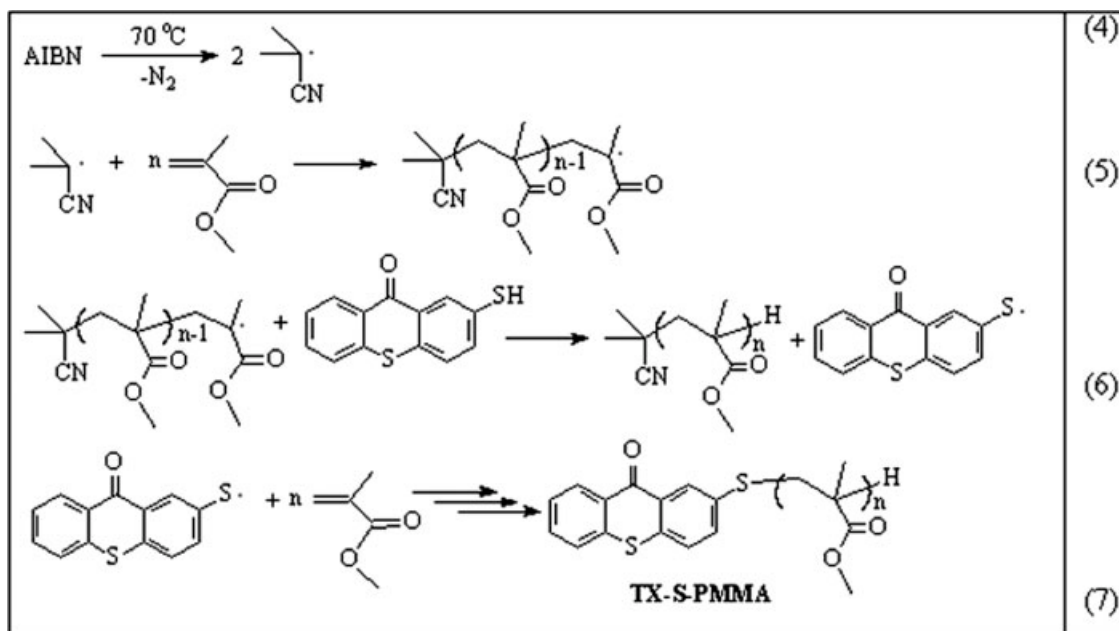
Photopolymerization

A solution of TX-attached PMMA in CH_2Cl_2 with MDEA and MMA [4.68M] as hydrogen donor and monomer, respectively, was put into a pyrex tube (i.d: 9 mm) and irradiated for 15 min in a photoreactor equipped with 400 W medium pressure mercury lamp. Polymer formed at the end of irradiation was precipitated in 10-fold excess methanol and dried *in vacuo*.

TABLE I
Thermal Polymerization[a] of the Styrene and Methyl Methacrylate in DMF with AIBN in the Presence of TX-SH at 70°C

TX-SH (10^{-3} mol/L)	Styrene		Methyl methacrylate	
	Conversion (%)	M_n[b] (10^{-3})	Conversion (%)	M_n[b] (10^{-3})
0	4.3	18.5	10.5	273.4
0.5	4.6	18.4	12.1	239.6
1	4.5	17.5	11.7	177.5
2	4.3	16.2	10.8	171.2
6	4.1	13.5	15.8	163.6
8	4.1	12.2	18.8	153.2
10	4.2	12.1	18.7	147.9

[a] [MMA] = 4.68M; [St] = 4.36M; [AIBN] = 1 × 10^{-3} M, t = 60 min.
[b] Determined by GPC according to the polystyrene standards.

Scheme 2 Chain transfer reactions of TX-SH.

RESULTS AND DISCUSSION

As stated previously, TX-SH is an efficient one-component photoinitiator for the polymerization of methyl methacrylate (MMA) and styrene (St). As the thiyl radicals were found to be responsible for the initiation of polymerization, TX-SH may also act as chain transfer agent when the polymerization is initiated by other means such as thermal polymerization by using AIBN as an initiator. Thermal polymerization of MMA in the presence of TX-SH and in the absence of AIBN did not form significant amount of polymer, confirming that TX-SH is thermally stable and does not initiate itself. The addition of millimolar concentrations of TX-SH to the polymerization of both monomers decreased the molecular weight of the polymers formed (Table I). The rate of polymerization of St did not significantly change upon addition of TX-SH. In the case of MMA, however, some increase in the rate may be due to the difference in the electronic nature of the respective monomers.[23] Nucleophilic thiyl radicals are expected to be more reactive towards MMA because of the higher electrophilic character. Typical chain transfer reactions involving the interaction of growing macroradicals
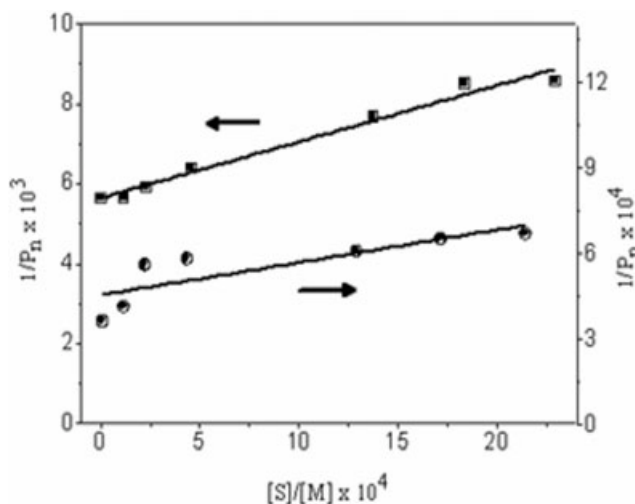

Figure 1 Thermal polymerization of styrene (■) and methyl methacrylate (●) in the presence of TX-SH as chain transfer agent.
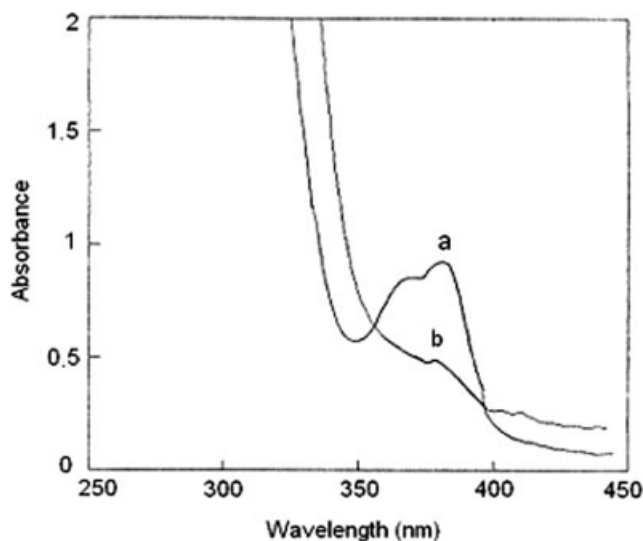

Figure 2 Absorption spectra of 2-mercaptothioxanthone-([TX-SH] $= 1 \times 10^{-3}$ M) (a) and polystyrene obtained by thermal polymerization by using AIBN in the presence of TX-SH as chain transfer agent (b) in CHCl$_3$.
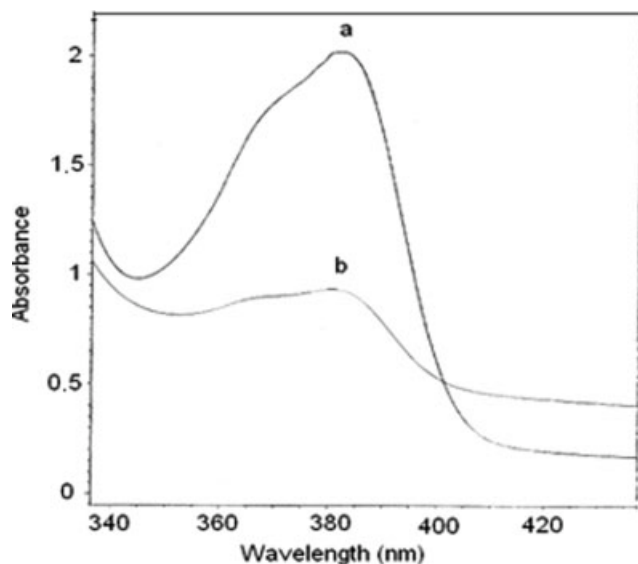
Figure 3 Absorption spectra of 2-mercaptothioxanthone ([TX-SH] $= 1 \times 10^{-3}$ M) (a) and PMMA obtained by thermal polymerization by using AIBN in the presence of TX-SH as chain transfer agent (b) in $CHCl_3$.

with TX-SH are presented on the example of MMA polymerization (Scheme 2).

Chain transfer constants (C_s) were found to be 1.41 and 0.12 for St and MMA, respectively, from the slope of $1/P_n$ against [S]/[M] as shown in Figure 1, by using the classical Mayo equation:

$$1/P_n = 1/P_n^0 + C_s[S]/[M]$$

where P_n and P_n^0 are the degree of polymerization in the presence and absence of TX-SH, respectively, C_s is the chain transfer constant for TX-SH, and [S] and [M] are TX-SH and monomer concentrations, respectively.

These values are much lower than those of simple 4-substituted thiophenols. This is expected since TX-SH contains strong electron withdrawing carbonyl group in the structure. It was found that chain transfer constants are well correlated with the electron donor–acceptor ability of the substituents, decreasing with acceptor groups.

As stated in the "Introduction" section, in addition to the chain length control, chain transfer reactions are often used as a versatile route for polymer functionalization.[7–9] As a consequence of the reaction 7 depicted in Scheme 2, thioxanthone moiety should be incorporated into the polymer chain end. Indeed, the UV–vis spectra of the resulting polymethylmethacrylate (PMMA) and polystyrene (PSt) purified by several reprecipitation presents an absorption with a maximum at 380 nm similar to that of the low molecular weight precursor, TX-SH (Figs. 2 and 3).

NMR spectra of the polymer also presents weak resonances of the aromatic protons indicative of the presence of the thioxanthone moiety. Fluorescence

spectra of TX covalently attached polymers may also provide further evidence for the chain transfer process. As can be seen from Figure 4, fluorescence spectra in CH_2Cl_2 of TX-SH (spectrum a) and PMMA obtained from the thermal polymerization initiated by AIBN in the presence of TX-SH (spectrum b) are very similar. Expectedly, the intensity is lower in the case of polymer bound thioxanthone.

Polymers containing thioxanthone terminal groups can act as bimolecular photoinitiators when used in conjunction with hydrogen donors analogous to the low molecular weight thioxanthones. UV irradiation of TX-S-PMMA with N-methyldiethanolamine (MDEA) serving as a hydrogen donor initiates the polymerization of MMA. In this case, the triplet TX moiety abstracts hydrogen from MDEA to form α-aminoalkyl radicals capable of initiating free-radical polymerization. The overall process is shown in Scheme 3.

The polymeric ketyl radicals formed concomitantly do not initiate the polymerization due to the steric hinderance and radical stabilization. Although not entirely elucidated, presumably these radicals undergo bimolecular termination. These assumptions were proved by the GPC analysis of the polymeric products obtained by the photopolymerization of MMA by using TX-S-PMMA. The GPC trace of the crude product exhibits a bimodal molecular weight distribution. After fractionation, the curve at higher elution volume does not contain spectral characteristics of thioxanthone moiety as was confirmed by UV absorption measurements, indicating that the short chains are initiated from
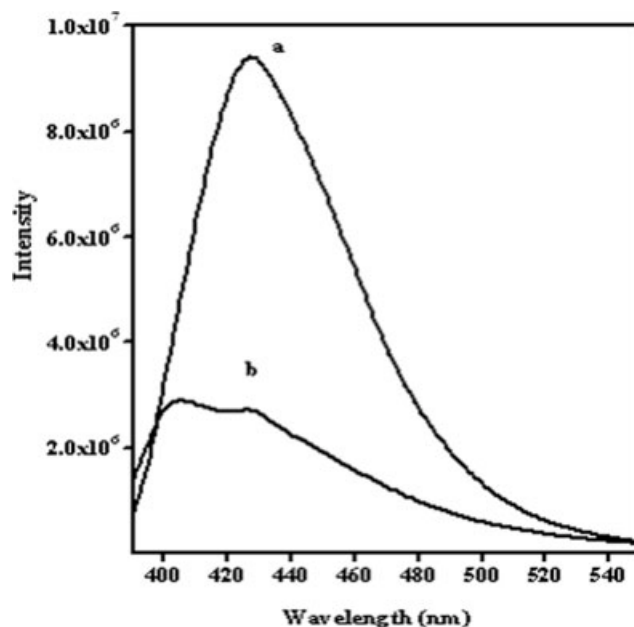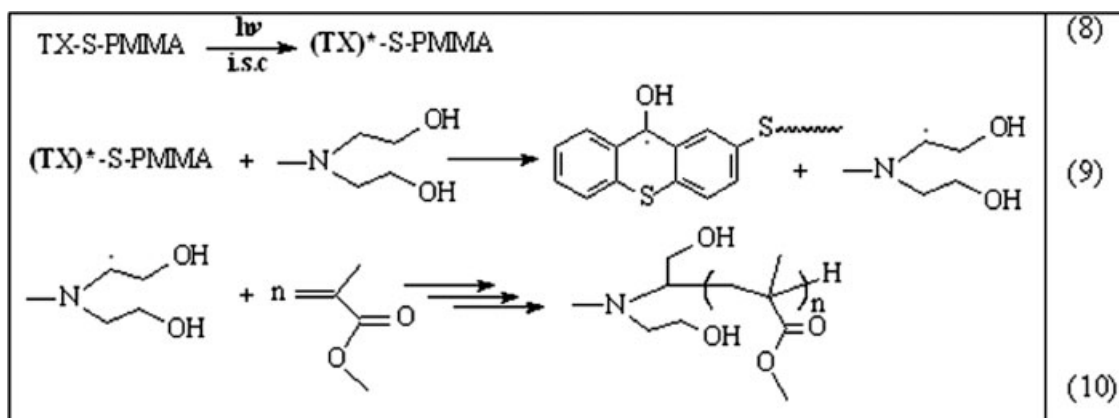

Figure 4 Fluorescence spectra (a) of 2-mercaptothioxanthone([TX-SH] $= 2.5 \times 10^{-6}$ M) and (b) PMMA obtained via thermal polymerization of MMA in the presence of AIBN and TX-SH as chain transfer agent in CH_2Cl_2, $\lambda_{exc.} = 380$ nm.

Scheme 3　Photoinitiated free-radical polymerization using polymer with thioxanthone groups in the presence of *N*-methyl-diethanol amine.

α-aminoalkyl radicals. Notably, the fraction at lower elution volume corresponds almost exactly to the molecular weight of the precursor polymer (Fig. 5).

In conclusion, TX-SH acts as a chain transfer agent in free-radical polymerization. The chain transfer efficiency is lower than simple aromatic phenols, particularly from those with electron donating substituents. Chain transfer reactions lead to the formation of polymers with TX moieties, which can be used as polymeric photoinitiator in hydrogen abstraction type initiation.

Such polymeric photoinitiators may be useful when solubility, miscibility, migration, and odor problems are of prime importance.

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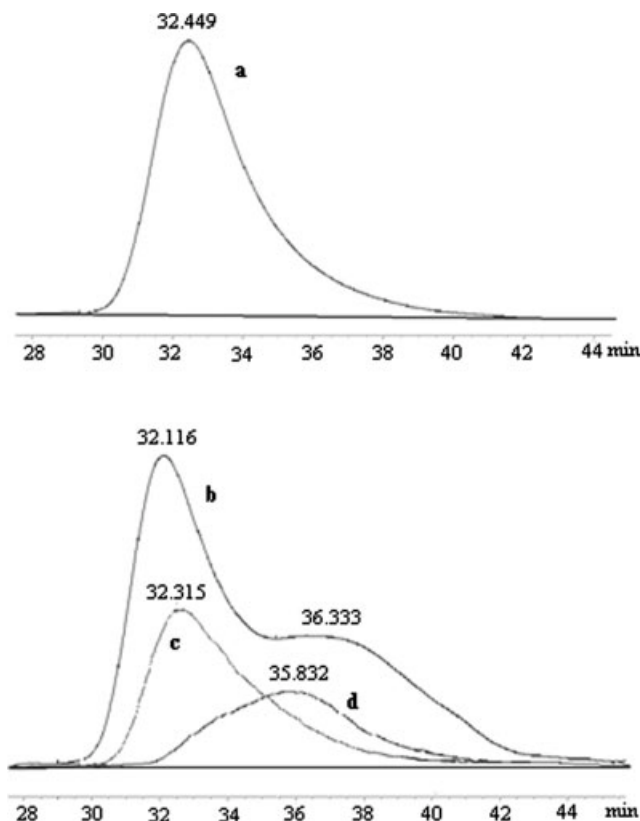23. Odian, G. Principle of Polymerization; Wiley-Interscience: New York, 1991; pp 233–237.

Figure 5　GPC traces of TX-S-PMMA, before irradiation (a), and after irradiation in the presence of MMA, crude product (b), the first fraction (c) and second fraction (d).