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2-Methylol-thioxanthone as a free radical polymerization initiator

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Abstract

2-Methylol-thioxanthone (TX-M) was synthesized and characterized as a new photoinitiator. Photopolymerization experiments were performed with methyl methacrylate and also trimethylolpropanetriacrylate (TMPTA) as a multifunctional monomer in the presence of TX-M with *N*-methyl diethanol amine. Polymerization did not occur in an air atmosphere with TX-M without adding MDEA. The inhibiting effect of oxygen on the rate of polymerization was observed to be due to quenching of the triplet radicals by the carbonyl compound (TX-M).

Keywords: Thioxanthone; Photoinitiator; Type II system; Free radical polymerization

1. Introduction

Photopolymerization science and technology have assumed an increasing relevance in many applications. This technology is based on the use of photoinitiator systems suited to absorbing a light to produce primary radical species, which are able to initiate polymerisation [1–5]. Photoinitiated radical polymerization may be initiated by both α-cleavage (type I) and H-abstraction (type II) intiators [1]. Type I photoinitiators undergo an α-cleavage process to form two radical species. Type II photoinitiators are based on a bimolecular reaction with hydrogen donors in order to produce initiating radicals. Typical type II photoinitiators are benzophenone and derivatives, thioxanthones, benzil, quionones, and organic dyes, while alcohols, ethers, amines and thiols are used as hydrogen donors [6–8].

Although type II photoinitiators are slower than type I photoinitiators due to the bimolecular initiation reaction, they have better optical absorption properties near the UV spectroscopic region. Photopolymerization of vinyl monomers is generally initiated by the radicals produced from the hydrogen donor. The ketyl radicals are not reactive toward vinyl monomers because of steric hindrance and the delocalization of an unpaired electron.

In this study, 2-methylol-thioxanthone was synthesized and its structure and photophysical characteristics were determined. This photoinitiator was used in the free radical polymerization of methylmethacrylate and multifunctional monomer, and the results were compared to the photopolymerization and RT-FTIR results of thioxanthone in appropriate concentrations.

2. Experimental

2.1. Materials

Thiosalicylic acid (98%, Aldrich), Benzyl Alcohol (98+%, Across), *N*-methyldiethanolamine (MDEA, 99%, Aldrich) were used as received and methyl methacrylate (MMA, 99%, Aldrich) was washed with 5% aqueous NaOH solution, dried over $CaCl_2$, and distilled over CaH_2 under vacuum just before use. Dimethylformamide (DMF, 99+%, Aldrich) was distilled over CaH_2 under reduced pressure. All other reagents were purchased from Aldrich and used as received.

2.2. Synthesis of 2-methylol-thioxanthone (TX-M)

Thiosalicylic acid 1.6 g (10 mmol) was slowly added to 15 ml concentrated sulfuric acid, and the mixture was stirred for 10 min in ice bath. Five milliliters (55 mmol) benzyl alcohol was added slowly to the stirred mixture over a period of 1 h. After the addition, the reaction mixture was stirred at room temperature for 1 h and then at 70 °C for 3 h. At the end of the period, the mixture was left to stand at room temperature overnight. The resulting mixture was poured while stirring into a 10-fold excess of boiling water, and it was then boiled for a further 30 min. The warm

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solution was filtered, and the same process was repeated three times. The crude product was dissolved in 100 ml DMF, and then filtered through a thin layer of activated charcoal. Vacuum distillation was applied to clear liquid to remove excess DMF. At the end of the distillation process, the wet solid product was washed with water several times. The excess water was decanted and the solid was dried under vacuum. Yield: 30%.

Anal. Calcd. for $C_{14}H_{10}O_2S$ (242 g mol^{-1}): C, 69.40%; H, 4.16%; S, 13.23% Found, C, 68.53%; H, 4.00%; S, 13.05%. ^1H NMR (d-DMSO): δ, ppm 8.2–7.25 (7H, aromatic), δ 3.30 (2H, CH_2), δ 3.76 (1H, OH). IR (cm^{-1}): 3430 (OH); 3019 (aromatic, C–H); 2917 (aliphatic, C–H) 1690 (C=O); 1036 (C-S).

2.3. Photopolymerization

Typical procedure: appropriate solutions of MMA and TX-M with MDEA in DMF 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. Conversions were calculated gravimetrically.

2.4. Real-time infrared spectroscopy photopolymerization studies

Uniform samples of photocurable formulations consisting of a photoinitiator and multifunctional monomer; trimethylolpropane triacrylate (TMPTA) in the presence of MDEA were prepared by casting on a KBr pellet. The samples were placed in the compartment of a 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.

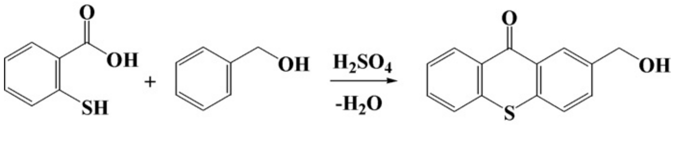
The light intensity (4.37×10^{16} photons s^{-1}) was determined by potassium ferrioxalate actinometry. The spectrometer was operated in the absorbance mode, and the detection wavelength was set at 810 cm^{-1} (C=C–H twist) to monitor the disappearance of double bonds. The degree of conversion, R, can be expressed by the following relation:

$$\alpha = \frac{A_0 - A_t}{A_0} \tag{1}$$

where A_0 is the initial absorbance at 810 cm^{-1} and A_t the absorbance value at irradiation time t.

2.5. Characterization

Gel permeation chromatography (GPC) measurements were performed at room temperature with a setup consisting of a pump (Agilent 1100), a refractive index detector (Agilent 1100s), and three high resolution Zorbax PSM columns (60S, 300S and 1000S). The effective molecular weight ranges were 500–10,000, 3000–300,000, and 10,000–1,000,000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at room temperature. Data analyses were performed with Polymer Laboratories Caliber Software Calibration with linear polystyrene standards (Polymer Laboratories) was used to estimate the molecular weights.



Scheme 1. Synthesis of 2-methylol-thioxanthone.

UV–vis spectra were taken on an Agilent 8453. IR spectra were recorded on an ATI Unicam Mattson 1000 FT/IR-3 spectrophotometer on a KBr disc.

Elemental analysis was performed on a CHNS-932 LECO instrument.

3. Results and discussion

2-Methylol-thioxanthone photoinitiator was synthesized by the modified literature [9] procedure described for the synthesis of 2-hydroxy-thioxanthone according to Scheme 1.

Structure of the photoinitiator was confirmed by spectral analysis. 2-Methylol-thioxanthone possesses similar absorption chacteristics to thioxanthone with a maximum at 385 nm (Fig. 1).

TX-M was used as a photoinitiator in the free radical polymerization of MMA in the presence of air. The results obtained from polymerization of MMA with either TX or TX-M in the presence of MDEA are compiled in Table 1.

Photoinitiated polymerization of MMA in DMF solution was achieved in the presence of the initiator TX-M with MDEA (see Table 1). When polymerization of MMA was performed with MDEA in DMF as a control experiment, no polymer were obtained.

In order to determine the concentration of initiator required to optimize the rate of polymerization, experiments using different concentrations of initiator were performed. The degree of polymerization of formulation increased with increasing photoinitiator concentration. Further increase in the TX-M (1×10^{-2} M) concentration results in a decrease in the rate of polymerization (see Table 1).

Many aromatic ketones possess nπ* triplet states which have relatively long lifetimes (10^{-6} s). A consequence of the carbonyl

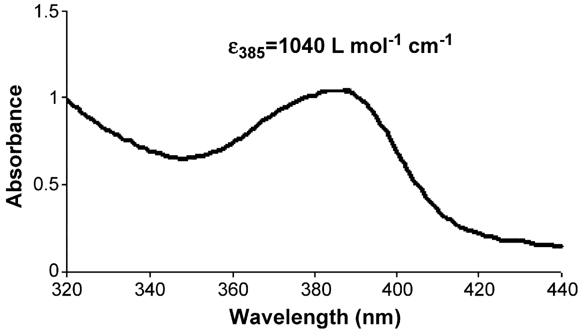


Fig. 1. Absorption spectra 2-methylol-thioxanthone (1.0×10^{-3} M) in DMF.

Table 1
Photoinitiated polymerization of MMA by TX-M and TX with MDEA (*N*-methyldiethanolamine) in DMF

Run[a]	Photoinitiator (PI)[b]	[PI] (mol L^{-1})	Conversion (%)	M_n[c] ($\times 10^{-3}$ g mol^{-1})	M_w/M_n
1	TX-M	5×10^{-4}	5.0	39.80	1.99
2	TX-M	1×10^{-3}	7.0	36.47	1.89
3	TX-M	5×10^{-3}	17.4	19.51	1.43
4	TX-M	1×10^{-2}	15.5	25.29	1.64
5	TX	1×10^{-2}	14.0	22.65	1.55
4	TX	5×10^{-3}	10.0	23.97	1.57

t_{irr} = 15 min.

[a] [MMA] = 4.68 mol L^{-1}; TX = Thioxanthone; TX-M = 2-methylolthioxanthone.

[b] [MDEA] = 1×10^{-2} mol L^{-1}.

[c] Determined by GPC using polystyrene standards.

compounds having long triplet lifetimes is that they are very susceptible to oxygen quenching.

Type I photoinitiators usually have very short triplet lifetimes and hence do not suffer extensively from oxygen inhibition [10–12]. This is not the case for Type II systems which involve a bimolecular reaction between the triplet initiator and the synergist. Oxygen will also compete with the amine synergist for the triplet ketone. In combination with Type II photoinitiators, amines react as coinitiators and produce the initiating radicals (see Scheme 2) [2–4,13–16].

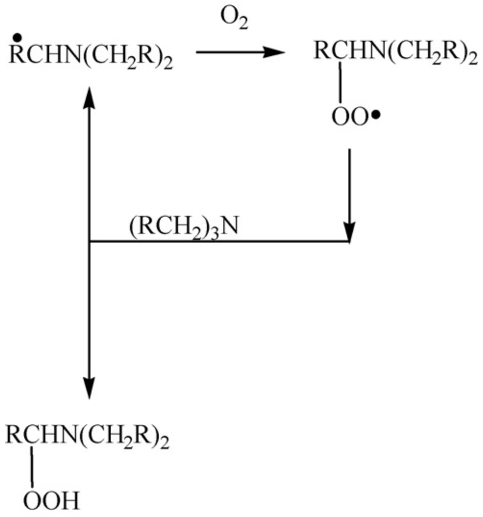
The α-aminoalkyl radical produced in the quenching cycle is also involved in the initiation process under these conditions, since it is the same species as formed by the reaction with the excited sensitiser, and other more reactive radicals are not produced at the same time. Therefore, the addition of amines to many photoinitiators is an effective means of reducing oxygen inibition [3,4,16]. When polymerization of MMA was performed with TX-M without adding MDEA, polymerization did not occur, possibly because of quenching the excited state of TX-M with oxygen. According to the behaviour of this initiator, TX-M was categorized as a Type II initiating system.

The high activity of amines can be attributed to their ability to act as electron donors in the formation of exciplexes with triplet excited ketones, as well as to their high chain transfer reactivity for peroxide radicals and for acrylates. In this study we have used *N*-methyl diethanol amine because amines are by far, the most important coinitiators for aromatic ketones and MDEA has readily transferrable hydrogens.

Due to steric bulk and delocalisation, the ketyl radical is insufficiently reactive to initiate polymerization. This intermediate mainly undergoes dimerization giving pinacol type products. On the other hand, α-aminoalkyl radicals are efficient initiators for acrylates (Scheme 3).

The influence of the resin constituents on the kinetic parameters can be readily evaluated by RT-FTIR spectroscopy which seems to be an ideal tool for assessing the new initiators [17–18]. A very important constituent in a photopolymerizable formulation is certainly the photoinitiator, since even the most reactive acrylate hardly polymerizes when exposed in pure form to UV light. Photocuring formulations containing the multifunctional monomer (TMPTA) and TX-M as photoinitiator with MDEA were prepared and the results obtained were compared with a formulation consisting of TMPTA and TX with MDEA.

The disappearance of double bonds during the photocuring of the formulations was followed by Fourier's transform real-time infrared spectroscopy (RT-FTIR). Monitoring the changes in the characteristic monomer IR absorption bands, allowed continuous direct monitoring of the fast polymerization process [17,18]. In Fig. 2, kinetic profiles referring to the polymerization of the



Scheme 2. Oxygen quenching by amines.

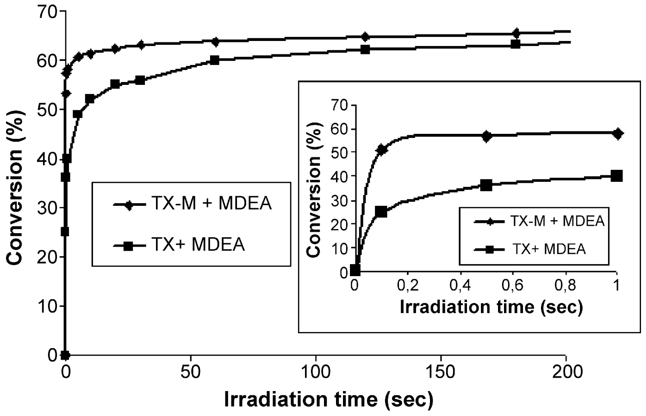
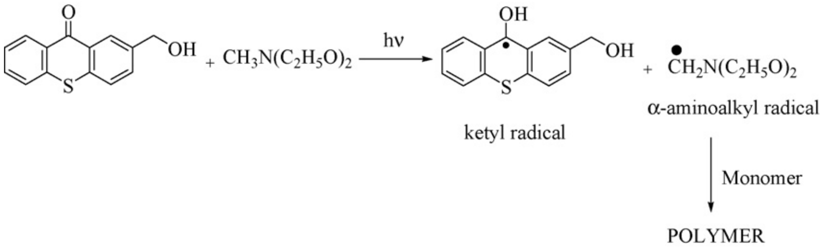


Fig. 2. Real-time FTIR kinetic profiles demonstrating the photopolymerization of TMPTA containing TX-M (1%) and TX (1%) with MDEA (10%) in an air atmosphere.



Scheme 3. General mechanism of Type II photoinitiation.

TMPTA under polychromatic light are shown. The curves were obtained by monitoring the absorption decrease of the band at 810 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 polymerization takes place more rapidly with TX-M/MDEA than that of the corresponding one with TX/MDEA. The curve for the polymerization with the TX-M/MDEA system indicates the highest conversion percentage values, both for the initiation period and prolonged irradiation times. The curve for the polymerization with TX/MDEA system is also provided for comparison.

4. Conclusion

TX-M is efficient photoinitiator for free radical polymerization. This photoinitiator requires an additional co-initiator (NMDEA) and resulted α-aminoalkyl radical initiates the polymerization of acrylates and methacrylates. These properties suggest that it may find use in a variety of practical applications.

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