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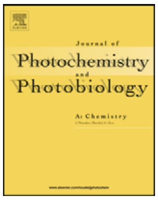

Thioxanthone-benzotriazole: Initiator and stabilizer properties in one component

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ABSTRACT

The initiation efficiency of 3H-5-Thia-1,2,3-triaza-cyclopenta[b]anthracene-10-one (TX-BT) for free radical polymerization of methyl methacrylate (MMA), is enhanced by the addition of N-methyldiethanolamine (MDEA) to the initiator formulation. Photodegradation of polymethylmethacrylate (PMMA), which was prepared with and without TX-BT, was examined according to its weight loss. The beneficial effects of TX-BT as initiator and stabilizer for polymerization of methyl methacrylate was determined.

1. Introduction

Photoinitiators, which are used to start a radical photoinduced polymerization reaction upon exposure to UV light, have been known as playing one of the most important roles in reaching high conversions of the monomer [1,2]. Photoinitiated radical polymerization may be initiated by both α-cleavage (type I) and H-abstraction (type II) initiators. Photoinitiated free radical polymerization is of enormous commercial importance [1,3–7]. Techniques such as the curing of coatings on various materials, adhesives, printing inks, and photoresists are based on photoinitiated radical vinyl polymerization [1,3–7]. Weather resistant systems have a very important part in the application of these technologies especially their ability to withstand sunlight exposure. Thus, photooxidation reactions need to be stopped or slowed down. The photostability of polymers is one of their most important properties. Photostabilization is the well known, main strategy to prevent photooxidation [8–14]. Light stabilizers, UV absorbers, quenchers, or hindered amine light stabilizers (HALS) are added to the photopolymerizable formulations to solve the problem of polymer stabilization. Among them, both 2-hydroxyphenylbenzotriazoles and hindered amines such as 2,2,6,6-tetramethylpiperidines are of great interest due to their high photostability [8–14].

As a consequence of the strong absorption of UV absorbers in the UV-A, a significant reduction of the photoinitiation efficiency is observed [2].

An attractive approach towards UV cured coatings with enhanced light stability is the combination of the photoinitiator and UV absorber properties in one molecule. A research program aimed at the design of such compounds was therefore initiated. The synthesis of a first new photoinitiator structure possessing a benzotriazol fragment as part of its structure and an investigation of the influence of these structural features on the efficiency of the new compound as a photoinitiators for the polymerization of MMA as well as the photostability of the polymer (PMMA) thus obtained fragment is reported in the following.

2. Experimental

2.1. Materials

Thiosalicylic acid (98%, Aldrich), benzotriazole (Aldrich), isopropylthioxanthone (ITX, Aldrich), N,N-dimethylformamide (DMF; Riedel) and 2-methyltetrahydrofuran (Merck) were used as received. Methyl methacrylate (MMA) (99%, Aldrich) was washed with 5% aqueous NaOH solution and dried over Na_2SO_4 just before use. N-methyldiethanolamine (MDEA) was also obtained from Aldrich and used as received. Ethanol (96%, Merck) was used as received to take fluorescence and phosphorescence spectra. Methanol, which was used to precipitate the polymers, was supplied by Merck and purified by conventional drying and distillation procedures.

2.2. Instruments

Gel permeation chromatography (GPC) analyses of the polymers were performed with a set-up consisting of a pump (Waters) and

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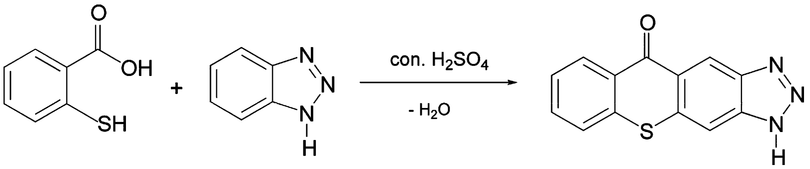


Scheme 1. Synthesis of thioxanthone-benzotriazole (TX-BT).

four ultrastyragel columns of different porosities. Tetrahydrofuran (THF) was used as the eluent (flow rate 3 mL min^{-1}) and detection was carried out with the aid of a differential refractometer. The number average molecular weights were determined using polystyrene standards. ^{1}H 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 a Varian UV–Visible Carry 50 Spectrophotometer. Also, IR spectra were taken on an ATI Unicam Mattson 1000 FTIR Spectrophotometer. Fluorescence and phosphorescence spectra were recorded on a Jobin Yvon–Horiba Fluoromax-P in cold finger at 77 K. The photolyzing light was generated by a medium pressure mercury lamp (Flexicure UV system) and was conducted through a flexible fiber optic for the photolysis of TX-BT.

2.3. Synthesis of 3H-5-Thia-1,2,3-triaza-cyclopenta[b]anthracene-10-one (TX-BT) [14–16]

Concentrated sulphuric acid (4.5 ml) was slowly added to thiosalycylic acid (0.8 g, 5 mmol) at 0 °C and benzotriazole (2.621 g, 22 mmol) was added to the solution in a two-necked round-bottomed flask. After the addition, the reaction mixture was left stirring at room temperature for 15 min and then heated to 80 °C and then 3.5 ml concentrated sulphuric acid was added to the mixture. After 3 h, this solution was precipitated in hot distilled water and filtered and dried in vacuo. The residue was washed with ether and hot water (mp: 265 °C).

- 1H NMR (250 MHz) in DMSO: δ 6.60–6.90 (m, 2H), 7.42–8.13 (m, 4H), 8.42 (bs, 1H) ppm.
- IR (KBr): 3431 (s, N-H), 3067 (w, phenyl); 1695 (vs, C=O); 1631 (s, C=C); 1579 (s, C=C); 1456 (s, C=C); 727 (s, disubstituted aromatic) cm^{-1}.

2.4. Photopolymerization

Appropriate solutions of monomer and the different concentrations of initiator (TX-BT) were irradiated in a photoreactor equipped with 12 Philips lamps emitting nominally at $\lambda = 350$ nm for 60 min in the presence and absence of N-methyldiethanolamine in either an air or N_2 atmosphere. The light intensity was measured with a Radiometer (Macam UV203 Ultraviolet Radiometer) and was found as $I = 12.0$ mW/cm^2. Polymers were obtained after precipitation in methanol and drying in vacuo. The conversion % and polymerization rates were calculated gravimetrically for all samples.

3. Results and discussion

Our study can be expressed in two ways: (i) synthesis of TX-BT as the one component initiator with a stabilizer unit and investigation of the photophysical properties of TX-BT.

(ii) Obtaining polymers of MMA with TX-BT and AIBN and changing the molecular characteristics of both polymers after irradiation.

In order to achieve our aims, photoinitiated polymerization experiments were performed with 3H-5-Thia-1,2,3-triaza-cyclopenta[b]anthracene-10-one (TX-BT) which was synthesized and characterized by elemental and spectral analysis (see Scheme 1).

The absorption spectrum of the initiator has a maxima at 393 nm ($\varepsilon = 1208\,\mathrm{l} \times \mathrm{mol}^{-1} \times \mathrm{cm}^{-1}$).

The photobleaching of TX-BT was followed by detecting spectral changes upon photolysis. The UV spectra of the TX-BT in DMF,

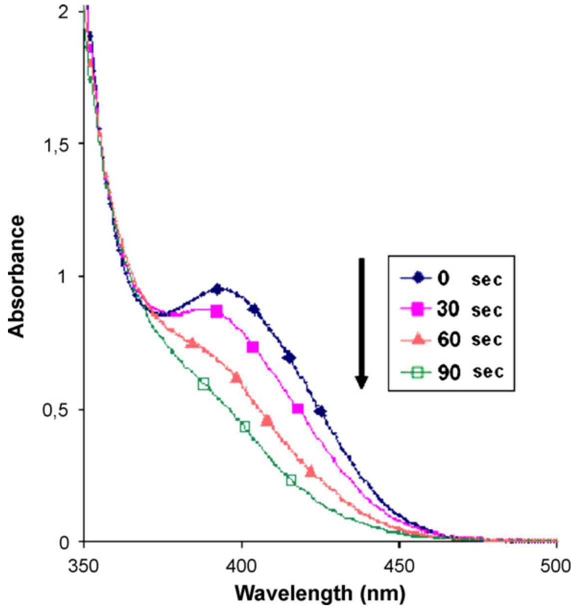


Fig. 1. UV spectral changes of TX-BT [1×10^{-3} M] with MDEA [5×10^{-2} M] on irradiation at $\lambda > 300$ nm under air atmosphere in DMF (90 s).

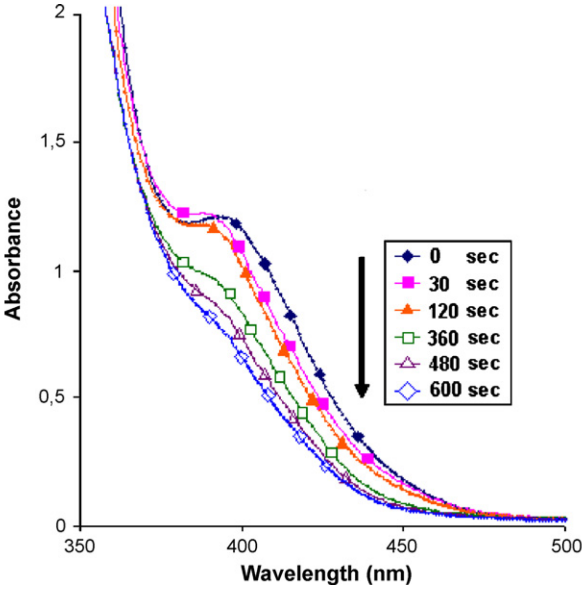


Fig. 2. UV spectral changes of TX-BT [1×10^{-3} M] without MDEA on irradiation at $\lambda > 300$ nm under air atmosphere in DMF (600 s).

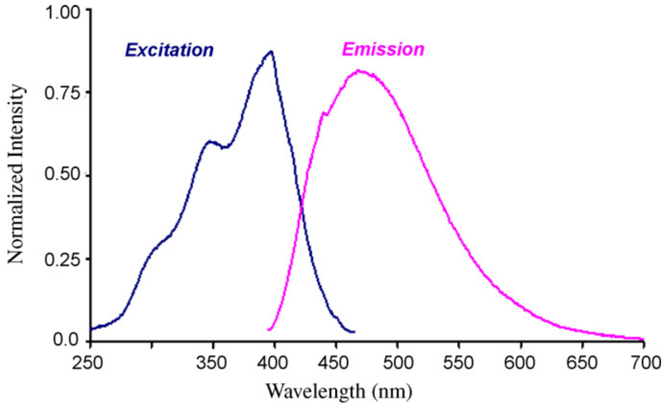


Fig. 3. Fluorescence excitation and emission spectra of TX-BT in ethanol at 25 °C, λ_{exc} = 390 nm.

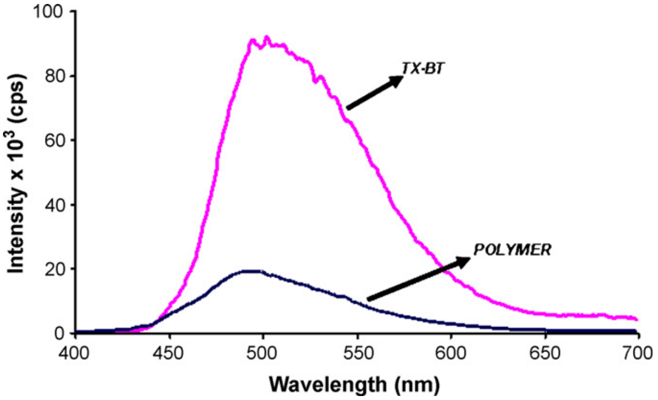


Fig. 4. Phosphorescence spectrum of TX-BT (in ethanol) and polymer (in 2-methyl tetrahydrofuran) at 77 K.

with and without MDEA, were recorded after the solution had been exposed to the light of the UV-lamp at different irradiation times (Figs. 1 and 2).

The consumption of the photoinitiator in the oxygen atmosphere took 600 s while addition of MDEA to the photoinitiator solution helped to decrease the irradiation time to 90 s (see Figs. 1 and 2). The addition of amines is known to decrease the deleterious effects of oxygen [17–21].

Fig. 3 shows the fluorescence spectra of TX-BT in ethanol at room temperature and a nearly mirror-image-like relation exists between the absorption and emission spectra of TX-BT. The fluorescence quantum yield (ϕ_f = 0.151 for TX-BT and (ϕ_f = 0.238 for ITX) was estimated by using 9,10-Diphenyl anthracene as the standard (ϕ_f = 0.95) [22–23].

Table 1
Photoinitiated polymerization of methyl methacrylate (MMA) in dimethylformamide (DMF) with TX-BT in the absence and presence of MDEA in air and nitrogen atmospheres during 60 min of irradiation time.

Run[a]	[PI] (mM)	MDEA (mol L^{-1})	N$_2$	Conversion (%)	$M_n \times 10^{-4}$ (g mol^{-1})[b]	M_w/M_n[b]
1	0.5	–	–	2.4	–	–
2	0.5	5×10^{-2}	–	8.4	3.6	1.6
3	0.5	–	+	8.0	6.9	3.0
4	1	–	–	3.9	8.4	2.5
5	1	5×10^{-2}	–	12.1	3.5	1.7
6	1	–	+	7.8	6.0	4.5
7	1	5×10^{-2}	+	15.9	2.9	1.4
8	4	–	–	6.3	5.4	3.3
9	4	5×10^{-2}	–	8.2	3.5	2.3
10	4	–	+	10.1	7.0	3.2

[a] [MMA] = 4.68 mol L^{-1}

[b] Determined by GPC using polystyrene standards

Table 2
Photoinitiated polymerization of methyl methacrylate (MMA) in dimethylformamide (DMF) with ITX in the presence of MDEA in air and nitrogen atmospheres during 60 min of irradiation time.

Run[a]	[ITX] (mM)	MDEA (mol L^{-1})	N$_2$	Conversion (%)
1	1	–	–	3.8
2	1	5×10^{-2}	–	8.4
3	1	–	+	3.9
4	1	5×10^{-2}	+	10.0

[a] [MMA] = 4.68 mol L^{-1}.

Table 3
Molecular characteristics of polymers: PMMA1 and PMMA2.

Polymer	Before irradiation			After irradiation		
	M_{n0}	M_{w0}	M_{w0}/M_{n0}	M_n	M_w	M_w/M_n
PMMA1	226.710	472.880	2.09	28.772	40.857	1.42
PMMA2	39.690	96.636	2.43	35.910	58.197	1.62

PMMA1: Prepared by thermal polymerization of MMA with AIBN. PMMA2: TX-BT attached to PMMA and prepared by photoinduced polymerization of MMA with TX-BT.

The phosphorescence spectra of the initiator was taken in ethanol and PMMA obtained in 2-methyl tetrahydrofuran at 77 K. TX-BT exhibits phosphorescence emissions in ethanol at 77 K upon excitation with 400 nm light (see Fig. 4).

The (0,0) emission bands for TX-BT occur at 502 nm, corresponding to an approximate triplet energy of ca 238 kJ/mol. The phosphorescence possesses a lifetime of 73 ms for TX-BT. Moreover, phosphorescence measurements are useful to gain information on the triplet configurations of TX-BT. The phosphorescence lifetime for n–π^* triplets is significantly shorter (in the order of several milliseconds) compared with π–π^* triplets (more than 100 ms). The results obtained from the phosphorescence measurements indicate a mixture of n–π^* and π–π^* natures of the lowest triplet state [24–26].

Photopolymerization experiments were performed for different initiator concentrations, with or without amine, either in a nitrogen or air atmosphere.

The conversions of monomer (MMA) into polymer were determined gravimetrically and the results are shown in Table 1.

A significant increase in the conversion was achieved by the addition of MDEA (run 1,2 and 4,5 and 7,8). The highest conversion was achieved at a concentration level of 4 mM of TX-BT. A more significant improvement in the efficiency of photopolymerization was

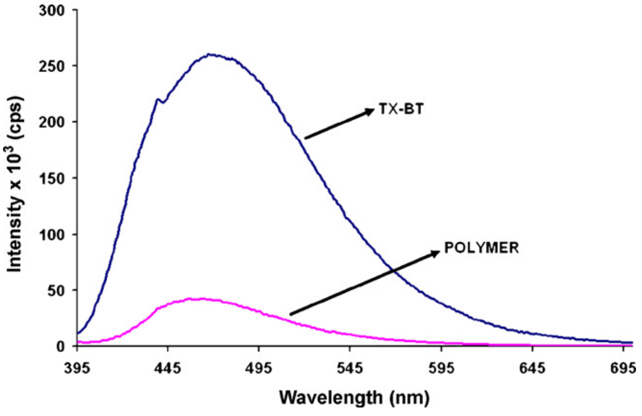
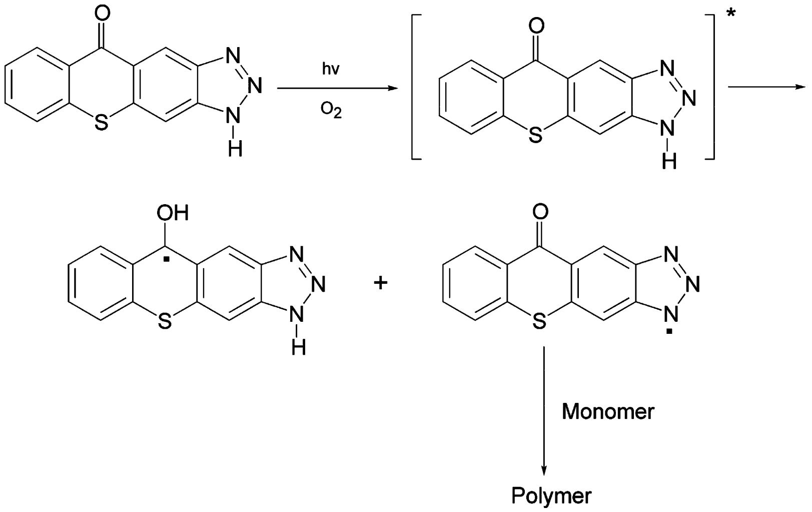


Fig. 5. Fluorescence emission spectra of TX-BT (in ethanol) and polymer (in 2-methyl tetrahydrofuran) at 25 °C, λ_{exc} = 390 nm.



Scheme 2. Photoinitiated radical polymerization mechanism of TX-BT.

achieved by conducting the experiment with the addition of MDEA under a nitrogen atmosphere (run 7). The photoinitiated polymerization of MMA with ITX in the presence of MDEA in air and nitrogen atmosphere was also performed. The results are given in Table 2. The initiation efficiency of TX-BT was found higher than ITX for all irradiation conditions (see Tables 1 and 2).

To elucidate the initiation mechanism of TX-BT, the phosphorescence and fluorescence emission spectra of PMMA were taken and are given in Figs. 4 and 5.

Incorporation of the thioxanthone moiety to the polymer chain, due to the proposed initiation mechanism, can be seen from the spectroscopic results and the phosphorescence lifetime was found to be 69 ms for TX covalently attached PMMA and the fluorescence spectra of PMMA also give additional evidence for incorporation of TX into the polymer (see Scheme 2).

In order to clarify the effect of photodegradation on the structure of polymers, the change in molecular weight distribution of the photodegraded polymers was investigated. PMMA1 was prepared by thermal polymerization of MMA with AIBN. PMMA2 is TX-BT attached to PMMA and was prepared by photoinduced polymerization of MMA with TX-BT. The molecular weights, M_w and M_n, of both polymers were determined before and after irradiation, where M_{n0} and M_n are the number average molecular weights before and after irradiation respectively. The results are given in Table 3.

Both polymers were irradiated by UV light for 2 h and the molecular weight distribution of PMMA1 changed significantly: 87% reduction in the M_n value of PMMA1 was detected, compared with 9% reduction in the M_n value of PMMA2. It is suggested that bond breaking reactions occur after the absorption of UV light and the concomitant loss of useful physical properties (see PMMA1 results). For polymer PMMA2, TX-BT incorporated to PMMA, photooxidative degradation was not as drastic as PMMA1 because TX-BT protected or stabilized PMMA2 against the harmful effects of light.

4. Conclusion

Photoinitiated polymerization of MMA with TX-BT was achieved in an air atmosphere. Some experiments were performed in the presence of MDEA in either an air or nitrogen atmosphere. The inhibition due to oxygen is reduced by the addition of MDEA as co-initiator. However, photopolymerization using TX-BT as initiator in the absence of MDEA yielded a low conversion. The photostabilization effect of TX-BT was also examined.

Acknowledgements

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References

[1] J.P. Fouassier, N.S. Allen (Eds.), Photopolymerization and Photoimagining Science and Technology, Elsevier Applied Science, London, 1989, 2 pp.
[2] J.P. Fouassier, D. Ruhlmann, A. Erddalane, Macromolecules 26 (1993) 721–728.
[3] S.P. Pappas, UV Curing Science and Technology, Technology Marketing Corp., Norwalk, CT, 1978.
[4] H.J. Timpe, S. Ulrich, C. Decker, J.P. Fouassier, Macromolecules 26 (1993) 4560–4566.
[5] K. Dietliker, Chemistry & Technology of UV & EB Formulation for Coatings, vol. III, Inks & Paints, SITA Technology Ltd., London, 1991.
[6] R.S. Davidson, Exploring the Science, Technology and Applications of UV and EB Curing, SITA Technology Ltd., London, 1999.
[7] M.K. Mishra, Y. Yagci, Handbook of Radical Vinyl Polymerization, Marcel Dekker Inc., New York, 1998 (Chapter 7).
[8] N.S. Allen, Chem. Soc. Rev. 15 (1986) 373–404.
[9] B. Ranby, J.F. Rabek, Photodegradation, Photooxidation and Photostabilization of Polymers, Wiley, London, 1975.
[10] D.M. Wiles, Pure Appl. Chem. 50 (1978) 291–297.
[11] J.F. Rabek, Photodegradation of Polymers; Physical Characteristics and Applications, Springer-Verlag, Berlin Hendelberg, 1996.
[12] J.P. Fouassier, N.S. Allen (Eds.), Photopolymerization and Photoimagining Science and Technology, Elsevier Applied Science, London, 1989, pp. 227–237.
[13] V. Bojinov, Photochem. Photobiol. Sci. 1 (2002) 340–346.
[14] J. Pospisil, S. Nespurek, Prog. Polym. Sci. 25 (2000) 1261–1335.
[15] F. Catalina, J.M. Tercero, C. Peinado, R. Sastre, J.L. Mateo, N.S. Allen, J. Photochem. Photobiol A: Chem. 50 (1989) 249.
[16] L. Cokbaglan, N. Arsu, Y. Yagci, S. Jockusch, N.J. Turro, Macromolecules 36 (2003) 2649–2653.
[17] R.S. Davidson, R. Foster (Eds.), In Molecular Association, Academic Press, New York, 1975.
[18] J.P. Fouassier, N.S. Allen (Eds.), Photopolymerization and Photoimagining Science and Technology, Elsevier Applied Science, London, 1989, 153 pp.
[19] R.S. Davidson, Exploring the Science, Technology and Applications of UV and EB Curing, SITA Technology Ltd., London, 1999, 134 pp.
[20] N. Arsu, M. Aydin, Angewandte Macromolekulare Chemie 266 (1999) 70–74.
[21] N. Arsu, J. Photochem. Photobiol. A Chem. 153 (2002) 129–133.
[22] J.V. Morris, M.A. Mahaney, J.R. Huber, J. Phys. Chem. 80 (1976) 969–974.
[23] J.C. Dalton, F.C. Montgomery, J. Am. Chem. Soc. 96 (1974) 6230–6232.
[24] N.J. Turro, N. Modern, Molecular Photochemistry, University Science Books, Sausalito, CA, 1991.
[25] I. Carmichael, G.L. Hug, in: J.C. Scaiano (Ed.), CRC Handbook of Organic Photochemistry, vol. 1, CRC Press, Boca Raton, FL, 1989.
[26] X. Allonas, C. Ley, C. Bibaut, P. Jaques, J.P. Fouassier, Chem. Phys. Lett. 322 (2000) 483–490.