Polymer Communication

A novel amphipathic polymeric thioxanthone photoinitiator

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ABSTRACT

A novel amphipathic polymeric photoinitiator based on thioxanthone (TX) (APTX) containing coinitiator amine was synthesized by introducing TX, amine and short poly(ethylene oxide) (PEO) chain into the backbone of polymeric chain together. APTX can be not only dispersed easily in many solvents and acrylate monomers but also is soluble in water. In comparison to low-molecular weight analogues photoinitiators, APTX is very efficient for photoinitiation of acrylate monomers 2,2-bis[4-(acryloxy-polyethoxy)phenyl] propane (ABPE-10) and trimethylolpropane triacrylate (TMPTA), and acrylamide (AM) in aqueous solution.

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1. Introduction

Photopolymerization science and technology have assumed an increasing relevance in extensive applications such as manufacture of printed circuits, encapsulation of electronic components, coatings, and printing inks [1–3]. This technology is based on photoinitiator systems which can generate free radicals to initiate polymerization. Compared with low-molecular weight analogues, polymeric photoinitiators have obtained much attention recently due to several advantages, such as low odor, nontoxicity, and compatibility improved with formulation components [4–16]. According to the mechanism of radical generation, polymeric photoinitiators can be divided into two classes: cleavable (Type I) and hydrogen abstraction (Type II). As one of Type II photoinitiators, thioxanthone (TX) derivatives have been widely used because of their high photoinitiation efficiency and absorption characteristics at near-UV range [17–26]. As a very planar molecular, however, TX is difficult to be dispersed in photo-curing systems, and can migrate out of the cured systems to cause some problems. Therefore, most efforts have been focused on how to increase its compatibility with different photo-curing systems [27,28]. Yagci et al. [29] and Encinas et al. [20,30] have introduced TX moieties into polystyrene and polyacrylate chain to obtain polymeric photoinitiator. Corrales [31] developed water-soluble polymeric photoinitiators based on TX by free radical copolymerization of TX derivatives and two water-soluble monomers: acrylamide and tetra ammonium. However, these polymeric

photoinitiators were limited to be used only in one type of photo-curing system: oil or aqueous.

Because of its good hydrophility and hydrophobility, PEO chain is of our interest in the preparation of polymeric photoinitiators of good compatibility in photo-curing systems. Moreover, PEO chain can act as hydrogen donor due to its structure of ether [1]. In this text, we successfully developed a novel amphipathic polymeric photoinitiator as a part of our continuous interest in polymeric thioxanthone photoinitiators [23,25]. This polymeric photoinitiator based on TX has good solubility in both oil and aqueous medium, and can photoinitiate polymerization very efficiently without the presence of other coinitiator amine.

2. Experimental part

2.1. Materials

Poly(ethylene oxide) diglycidyl ether (PEO-DE, $M_n = 526$), dihydroxylethyl piperazidine (DHEP) (from Aldrich), acrylamide (AM), piperazidine (PP) (from Chinese Medicine Group). 2,2-Bis[4-(acryloxypolyethoxy)phenyl] propane (ABPE-10) and trimethylolpropane triacrylate (TMPTA) (from Shin-Nakamura Chemical Co. Ltd). Other chemicals are of analytical grade except as noted.

2.2. Synthesis of APTX

The amphipathic polymeric photoinitiators were synthesized according to Scheme 1. DETX (0.5 mmol, synthesized in our laboratory according to Ref. [23]), PEO-DE (1.0 mmol) and piperidine (1.5 mmol) were dissolved in ethanol (20 ml). The mixture was refluxed at 80 °C for 12 h, and then poured into 10-fold ether. The

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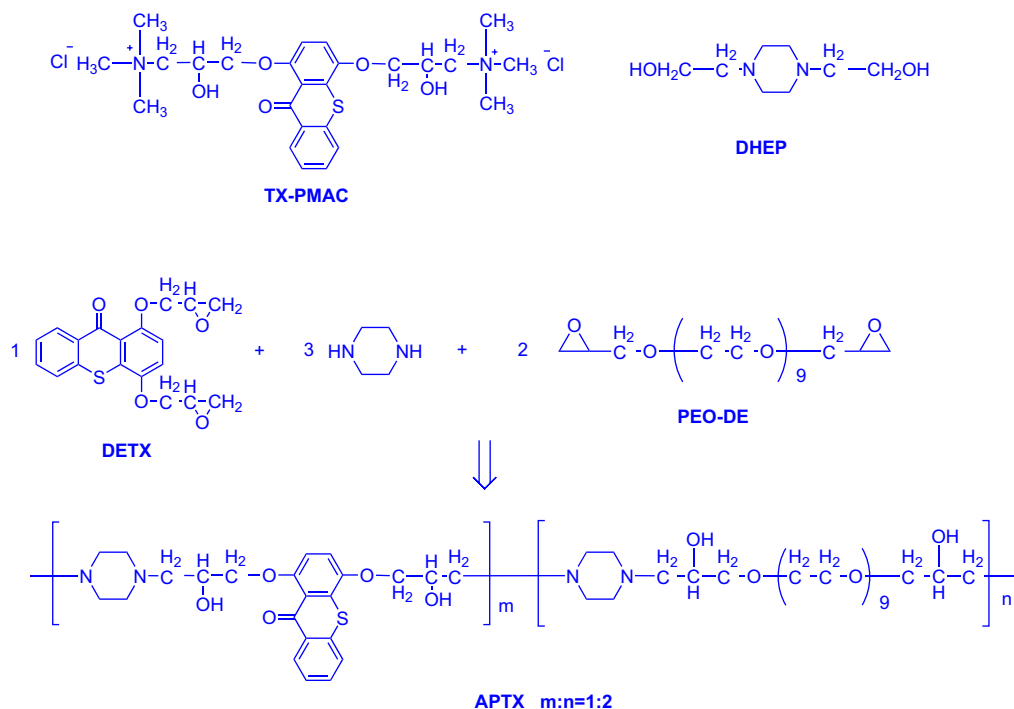
Scheme 1. Synthesis of amphipathic polymeric thioxanthone photoinitiator.

solution was filtered to give product, which was dried in vacuo to obtain paste APTX.

UV: $\lambda_{max} = 401$ nm $\varepsilon = 4196$ L mol^{-1} cm^{-1} (in water); $M_w = 5.7 \times 10^3$, $M_w/M_n = 2.12$. ^{1}H NMR ([$-d_6$] DMSO, 400 MHz): $\delta = 8.24$–7.08 (aromatic), 4.86 (–OH), 4.10–3.93 (–OCH$_2$, –OCH), 2.48–2.41 (–NCH$_2$). FT-IR (KBr): 3401 (O–H), 2923, 2813 (C–H), 1628 cm^{-1} (C=O).

2.3. Analysis

The concentration of photoinitiator system is in terms of TX moieties and the molar ratio of TX-PMAC/DHEP, DETX/DHEP in the low-molecular weight analogue systems (DHEP as coinitiator) is always 1:3 in measurement.

Molecular weights were determined by gel permeation chromatography (GPC) on a Perkin Elmer Series 200 apparatus on the basis of linear polystyrene (PS) standards using N,N-dimethylformamide (DMF) or water as eluent.

^{1}H NMR spectra were recorded on a Mercury Plus 400 Hz spectrometer with DMSO ($-d_6$) as solvent.

FT-IR spectra were recorded on a Perkin–Elmer Paragon1000 FTIR spectrometer.

UV–vis spectra were recorded in aqueous and ethanol solution by Perkin–Elmer Lambda 20 UV–vis spectrophotometer (concentration $= 5 \times 10^{-5}$ mol L^{-1} in terms of thioxanthone moieties).

2.4. Photopolymerization of acrylamide (AM) in aqueous solution

Photopolymerization of AM in aqueous solution were performed in a bottle at 25 °C. The concentration of AM and photoinitiator is 4.0 M and 0.004 M, respectively. The light source was a high-pressure Hg lamp (400 W) with a cut-off filter of 365 nm, and the intensity of light was about 10 mW/cm^2. After exposure for 2 h, aqueous solution was poured into 10-fold methanol, and polyacrylamide (PAM) was filtered and dried. The final conversions were calculated gravimetrically.

2.5. Photopolymerization of TMPTA and ABPE-10 by Photo-DSC

The photopolymerization of TMPTA and ABPE-10 was carried out by DSC 6200 (Seiko Instrument Inc.) photo-DSC with incident light of 365 nm. Approximately 2 mg sample mixture was placed in the aluminum DSC pans. The concentration of initiator [PI] is 8×10^{-3} mol L^{-1} in term of thioxanthone moiety.

Heat flow vs time (DSC thermogram) curves were recorded in an isothermal mode under a nitrogen flow of 50 ml/min. The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to:

$$C = \Delta H_t / \Delta H_0^{theor} \tag{1}$$

where ΔH_t is the reaction heat evolved at time t, and ΔH_0^{theor} is the theoretical heat for complete conversion. $\Delta H_0^{theor} = 86$ kJ/mol for an acrylic double bond [32]. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:

$$R_p = dC/dt = (dH/dt)/\Delta H_0^{theor} \tag{2}$$

3. Results and discussion

Amphipathic polymeric thioxanthone photoinitiator (APTX) was synthesized according to Scheme 1. Through addition of pronuclear between epoxy and amine groups, thioxanthone and coinitiator amine moieties, and amphipathic PEO chain can be introduced into the same polymeric chain, resulting in hydrophily and hydrophobility of APTX. Compared to DETX, the disappearance of the signals related to epoxy group, accompanied by the occurrence of the hydroxyl signal in the IR and ^{1}H NMR spectra of APTX,
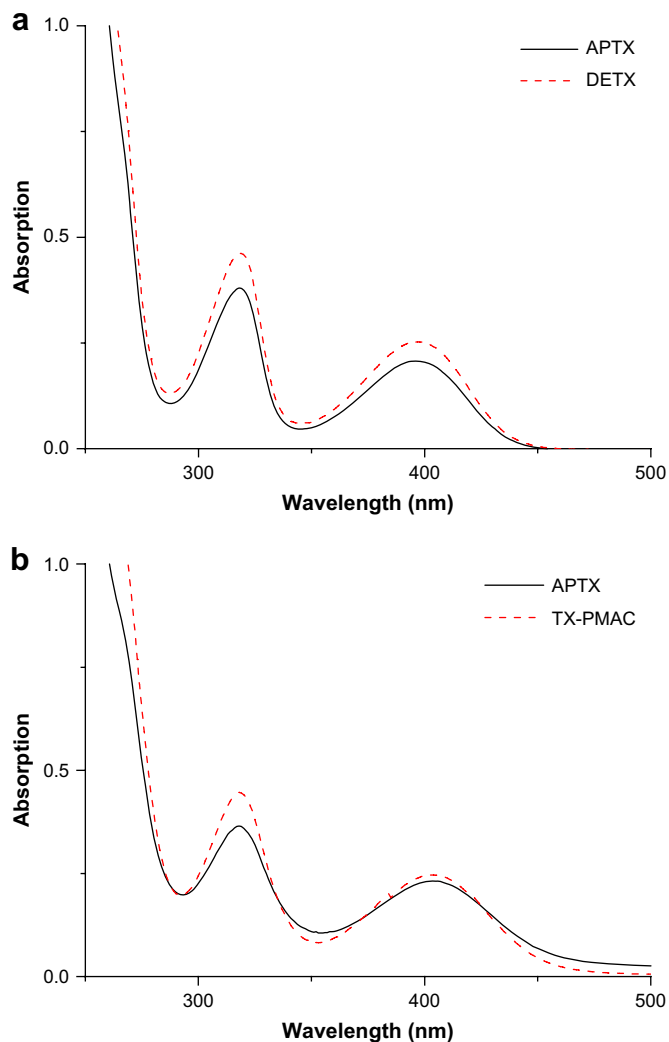
Fig. 1. UV–vis absorption spectra: (a) DETX and APTX in ethanol, (b) TX-PMAC and APTX in aqueous solution (concentration $= 5 \times 10^{-5}$ mol L^{-1}).

Table 2
Polymerization of AM initiated by APTX and TX-PMAC/DHEP in aqueous solution for 2 h at 25 °C ([TX] $= 4 \times 10^{-3}$ mol L^{-1}, [AM] $= 4$ mol L^{-1}).

Photoinitiator	Conversion (%)	R_p (mol L^{-1} s^{-1}) $\times 10^4$	M_n[a] (g mol^{-1}) $\times 10^{-4}$	M_w/M_n
APTX	54.2	3.0	3.8	2.1
TX-PMAC/ DHEP	34.3	1.9	2.9	1.9

[a] Determined by GPC using water as eluent.

APTX possesses very good compatibility with hydrophobic commercial multi-functional monomers ABPE-10 and TMPTA, due to amphipathic PEO chain. This indicates that introduction of PEO chain into polymeric TX can really increase solubility of TX in different solvents and enhance compatibility of TX with multi-functional acrylate crosslinker.

Photopolymerization of AM initiated by APTX and TX-PMAC/ DHEP in aqueous solution was studied, and the results are summarized in Table 2. Water-soluble low-molecular weight molecule TX-PMAC was used as reference. The quarternized amine group was introduced into TX moiety to make TX-PMAC water-soluble, and has no obvious influence on photo-efficiency of TX in the presence of other coinitiator amine [31,33,34]. Compared to
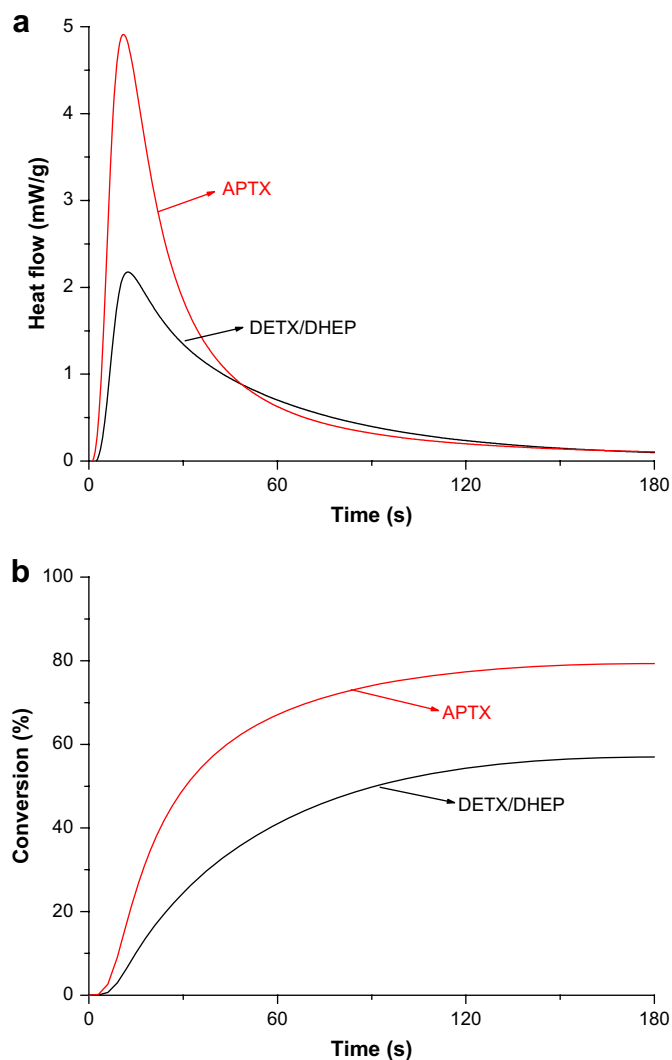
was considered as indicative of success of addition reaction. UV–vis spectra of APTX in ethanol and water are shown in Fig. 1, as well as low-molecular weight analogues DETX and water-soluble TX-PMAC (synthesized in our laboratory according to Ref. [33]). APTX exhibits the usual characteristic absorption of thioxanthone, and possesses an absorption similar to DETX in ethanol ($\lambda_{max} = 398$ nm, Fig. 1(a)) and TX-PMAC in water ($\lambda_{max} = 403$ nm, Fig. 1(b)). This also indicates that TX moiety and PEO short chain have been successfully introduced into polymeric chain of APTX.

Table 1 summarizes solubility of APTX in different solvents and acrylate monomers, as well as DETX and TX-PMAC. Compared with DETX and TX-PMAC, APTX is not only soluble in water but also exhibits good solubility in non-polar and polar solvents such as ethanol, chloroform, DMF and benzene. In particular, water-soluble

Table 1
Solubility of thioxanthone photoinitiator in different solvents and crosslinkers.[a]

Photoinitiator	Solvent						
	Water	Ethanol	Chloroform	DMF	Styrene	ABPE-10	TMPTA
A-PTX	++	++	++	++	+	++	++
DETX	+−	+	+	++	+	++	+
TX-GMAC	++	++	+	+	+	+−	+-

[a] ++: Well soluble, +: soluble, +−: partly soluble.

Fig. 2. (a) Photo-DSC profiles; (b) conversion vs time curves, for photopolymerization of APBE-10 initiated by DETX/DHEP, and APTX, irradiated at 25 °C by UV light with an intensity of 25 mW/cm^2 ([PI] $= 8 \times 10^{-3}$ mol L^{-1}).

Table 3
Photopolymerization of ABPE-10 and TMPTA initiated by APTX and DETX/DHEP, cured at 25 °C by UV light with an intensity of 25 mW/cm².

Photoinitiator[a]	ABPE-10			TMPTA		
	$Rp_{max} \times 10^{3b}$ (s^{-1})	Conversion[c] (%)	T_{max}[d] (s)	$Rp_{max} \times 10^3$ (s^{-1})	Conversion (%)	T_{max}[d] (s)
APTX	22.2	79.3	10.9	27.2	54.1	8.8
DETX/DHEP	9.8	57.0	12.2	18.2	40.8	11.3

[a] The photoinitiator concentration is 8×10^{-3} M in term of TX moieties.
[b] The maximal polymerization rate.
[c] The final conversion of double bond.
[d] Time to reach maximal polymerization rate.

low-molecular weight analogues TX-PMAC/DHEP, APTX can photo-initiate polymerization of AM more efficiently, which might be ascribed to efficient intramolecular hydrogen abstraction between TX and coinitiator amino group in APTX. The photolysis of thioxanthone, in the presence of hydrogen donors such as amines, leads to the formation of a radical produced from carbonyl compound (ketyl-type radical) and another amino radical through hydrogen abstraction [9]. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization

of unpaired electron. The photopolymerization of vinyl monomers is usually initiated by the amino radicals. Therefore, hydrogen abstraction between TX and amine is the key step to the generation of amino radicals, which determines the speed of photo-polymerization. Because of TX and coinitiator amino groups in the same polymeric chain of APTX, the excited state of TX can abstract hydrogen from amino groups along polymeric chain, resulting in effective generation of radicals. Therefore, APTX can initiate pho-topolymerization of AM more efficiently than TX-PMAC/DHEP.

To understand the photoinitiating efficiency of APTX in hydro-phobic medium, we studied the photopolymerization of two commercial acylate crosslinkers ABPE-10 and TMPTA initiated by APTX, as well as low-molecular weight analogues DETX/DHEP. The photo-DSC profiles of the polymerization of ABPE-10 for APTX and DETX/DHEP are shown in Fig. 2, and the results are summarized in Table 3. The polymerization behavior appears similar to other multi-functional monomers [25,29]. From Fig. 2 and Table 3, both final conversion and Rp_{max} of polymerization ABPE-10 photo-initiated by APTX are higher than that of DETX/DHEP, indicating that APTX is more efficient for photoinitiation of ABPE-10. Rp_{max} for APTX is 22.2×10^{-3} s^{-1}, about 1.3 times higher than that for DETX/DHEP (9.8×10^{-3} s^{-1}). This may be ascribed to two factors related to polymeric structure of APTX. Firstly, thioxanthone is difficult to be dispersed in most acylate monomers, especially crosslinkers of high viscosity, due to its planar structure. Amphipathic PEO chain in APTX can enhance the compatibility of TX moiety with ABPE-10 (See Table 1), resulting in better solubility in ABPE-10 compared to DETX/DHEP. Secondly, APTX might generate more radicals than DETX/DHEP, due to efficient hydrogen abstraction along polymeric chain of APTX.

Fig. 3 shows photo-DSC profiles of the polymerization of ABPE-10 for APTX and DETX/DHEP. Photopolymerization of TMPTA behaves similarly to ABPE-10. From Fig. 3 and Table 3, APTX is more efficient for the polymerization of TMPTA than DETX/DHEP. Both final conversion and Rp_{max} for photopolymerization of TMPTA initiated by APTX are higher than that for DETX/DHEP. It might be the same factors, polymeric structure containing PEO chain, that result in higher efficiency of APTX than DETX/DHEP for polymeri-zation of TMPTA.

4. Conclusion

In conclusion, we have obtained a novel amphipathic polymeric thioxanthone photoinitiator (APTX) by introducing TX moiety, coinitiator amino group and PEO short chain into the same poly-meric chain. APTX is not only soluble in water and other solvents but also possesses good compatibility with multi-functional acry-late crosslinkers. APTX can photoinitiate polymerization of acryl-amide in aqueous solution, and acylate crosslinkers ABPE-10 and TMPTA very efficiently, and will find wide potential applications in the field of UV-curing.

Acknowledgement

Fig. 3. (a) Photo-DSC profiles; (b) conversion vs time curves, for photopolymerization of TMPTA initiated by DETX/DHEP, and APTX, irradiated at 25 °C by UV light with an intensity of 25 mW/cm²([PI] = 8×10^{-3} mol L^{-1}).

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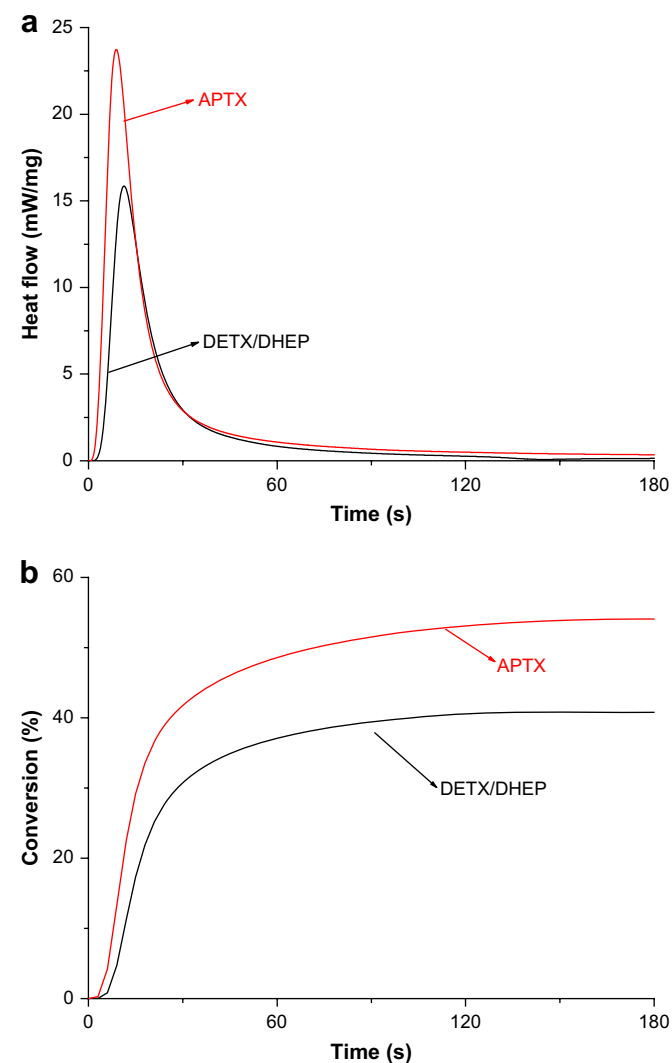[5] Corrales T, Catalina F, Peinado C, Allen NS. J Photochem Photobiol A Chem 2003;159:103–14.

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