



Amphipathic hyperbranched polymeric thioxanthone photoinitiators (AHPTXs): Synthesis, characterization and photoinitiated polymerization

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ABSTRACT

Amphipathic hyperbranched polymeric thioxanthone (TX) photoinitiators (AHPTXs) were synthesized by introducing TX, and polyethylene glycol monoethylether glycidyl ether (E-PEO), which contained short poly(ethylene oxide) (PEO) chain, into periphery of hyperbranched poly(ethylene imine) (HPEI), as well as low-molecular weight analogue 2-(2-hydroxy-3-(methyl(2,3,4,5,6-pentahydroxyhexyl)amino)propoxy) thioxanthone (MGA-TX). AHPTXs possess UV-vis absorption spectra similar to TX derivatives, and weaker fluorescence emission in comparison to low-molecular weight analogues. AHPTXs can be not only dispersed easily in many solvents and acrylate monomers, but also are soluble in water. AHPTXs are very efficient in photopolymerization of acrylamide (AM), poly(ethylene glycol) diacrylate (PEGDA) and 2,2-bis[4-(acryloxypropoxy)phenyl] propane (A-BPE-10). In comparison to low-molecular weight analogues photoinitiator systems 2-(2,3-epoxypropyloxy) thioxanthone/triethylamine (ETX/TEA) and MGA-TX/TEA, AHPTX1 is very efficient for photoinitiation of A-BPE-10 and AM in aqueous solution

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1. Introduction

Photopolymerization science has been obtaining much attention because of its widespread applications [1,2]. This technology is based on the photoinitiator systems suited to absorb a light radiation of the appropriate wavelength, which can produce primary radical species able to convert a multifunctional monomer into a cross-linked network [3,4]. In the development of this technology, photoinitiator systems play a very important role. In order to get photoinitiator systems of high performance, one of the important ways is to develop polymeric photoinitiators, which have some advantages derived from polymeric structure, in comparison with low-molecular weight analogues [5–11]. Thioxanthone derivatives are widely used as bimolecular photoinitiators in processes such as printing inks, coatings, microelectronics and photoresists, and their photoinitiation activity can be promoted by the presence of coinitiator amine [12–15]. 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 [16,17]. Yagci [18] and Encinasc, et al. [19] have introduced TX moieties into polystyrene and polyacrylate chain to obtain polymeric photoinitiator. Corrales [20] developed water-soluble polymeric photoinitiators based on TX by free radical

copolymerization of TX derivatives and two water-soluble monomers: acrylamide and tetraammonium. However, these polymeric photoinitiators were limited to be used only in one type of photo-curing system: oil or aqueous.

Recently, we have developed a novel linear amphipathic polymeric thioxanthone photoinitiators (APTxs) containing poly(ethylene oxide) (PEO) short chain in backbone, which exhibited good solubility in organic solvent and water, and high efficiency in photopolymerization of acrylamide in aqueous solution and oil-soluble acrylate monomers in bulk [21]. PEO chain is of our interest in preparation of polymeric photoinitiators of good compatibility in photo-curing systems, due to its good amphipathic property, commercial availability and biocompatibility. As a continuous study, we tried to develop amphipathic hyperbranched polymeric thioxanthone photoinitiators (AHPTXs) based on hyperbranched poly(ethylene imine) (PEI). Hyperbranched polymeric photoinitiators are expected for some advantages such as small fluid volume, low viscosity, high reactivity, good solubility and compatibility [22,23]. As a novel commercial hyperbranched polymer, PEI is comprised of tertiary amine groups in the core and secondary or primary amine groups in the periphery. Therefore, PEI is very good hyperbranched polymer backbone, which can be easily further functionalized by reaction with amine groups. In this text, novel amphipathic hyperbranched polymeric thioxanthone photoinitiators (AHPTXs) were synthesized by introducing TX moieties and PEO short chain into hyperbranched PEI backbone. AHPTXs are expected potential in application due to their good solubility in

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water and organic solvent, and high performance in photoinitiated polymerization of monomer.

2. Experimental section

2.1. Materials

Hyperbranched poly(ethylene imine) (HPEI, $M_n = 600$) and polyethylene glycol diacrylate (PEGDA) (from Aldrich), Polyethylene glycol monomethylether (PEGM, $M_n = 350$) (from Alfa Aesar), Epichlorohydrin, *N*-methyl-*D*-glucamine, acrylamide and tetrabutyl ammonium bromide (from Sinopharm Chemical Reagent Co., Ltd.) 2,2-bis[4-(acryloxypolyethoxy)phenyl]propane (A-BPE-10) (from Shin-Nakamura Chemical Co., Ltd) were used as-received. 2-(2,3-Epoxypropyloxy) thioxanthone (ETX) was synthesized in our lab according to the procedure described in literature [24]. Other chemicals are of analytical grade except as noted.

2.2. Synthesis of polyethylene glycol monoethylether glycidyl ether (E-PEO)

17.5 g (0.05 mol) PEGM, 27.8 g (0.3 mol) epichlorohydrin, 2.8 g (0.05 mol) potassium hydroxide and 0.5 g tetrabutyl ammonium bromide were added to dichloromethane (50 ml). The mixture was

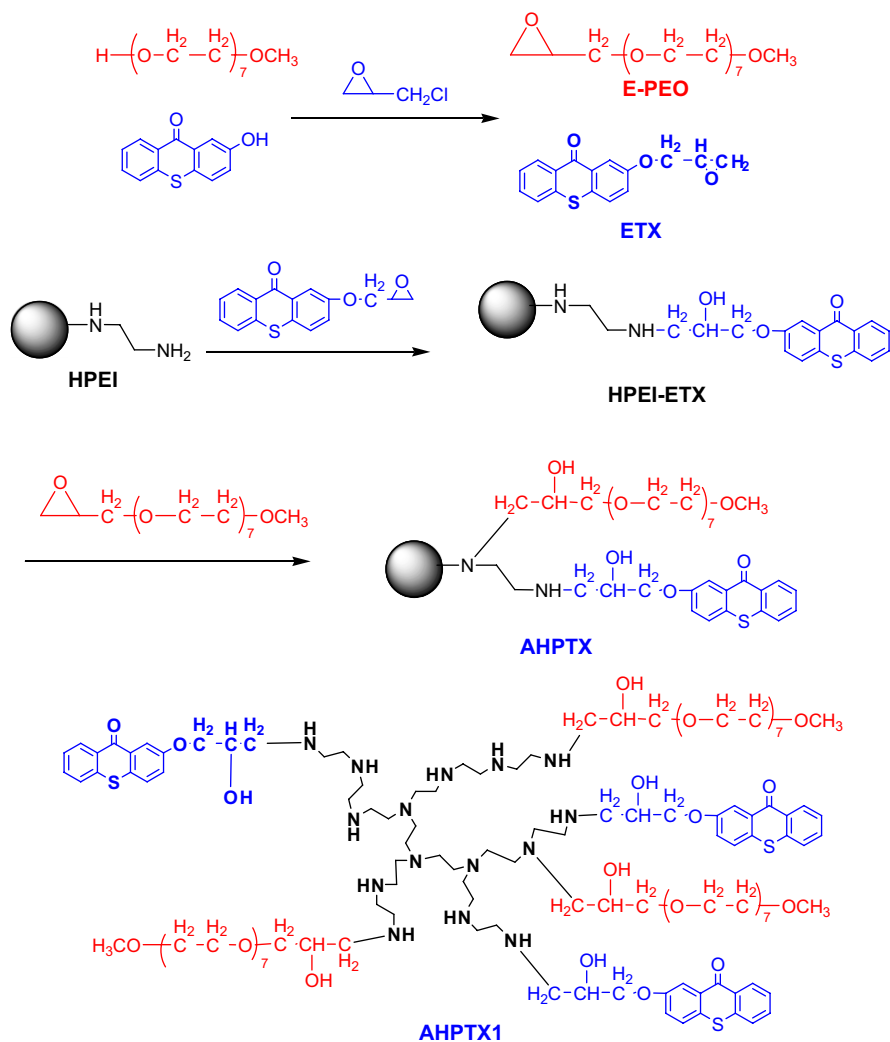
heated to 55 °C for 8 h, then cooling to room temperature, filtered and washed three times by water, rotated the solvent and get E-PEO (5.0 g). Yield: 24.6%.

2.3. Synthesis of amphiphilic hyperbranched thioxanthone photoinitiator (AHPTXs)

The amphiphilic hyperbranched thioxanthone photoinitiators (AHPTXs) were synthesized according to Scheme 1. AHPTXs were synthesized by incorporating E-PEO and ETX into the same HPEI and changing the molar ratio of HPEI/E-PEO/ETX, which are listed in Table 1. Taking AHPTX1 as an example, the detail synthesis procedure is as follows.

ETX (0.284 g, 1 mmol) and HPEI (0.215 g, 5 mmol in terms of $-\text{CH}_2\text{CH}_2\text{N}-$ repeat unit) were added to ethanol (10 ml), the mixture refluxed for 24 h at 80 °C under nitrogen, then E-PEO (0.406 g, 1 mmol) and ethanol (10 ml) were added to the mixture and continued to reflux for 24 h at 80 °C under nitrogen. Then the solution was dropped into 10-fold anhydrous ether and filtered to get the product, then dried in vacuum.

UV: $\lambda_{\text{max}} = 404 \text{ nm}$ $\epsilon = 1.65 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ (in water); $^1\text{H NMR}$ (CDCl_3): $\delta = 8.58\text{--}7.21$ (aromatic), $4.10\text{--}3.80$ ($-\text{OCH}_2-$, $-\text{OCH}$), $3.72\text{--}3.40$ ($-\text{OCH}_2\text{CH}_2-$), 3.35 ($-\text{OCH}_3$), $2.8\text{--}2.4$ ($-\text{NCH}_2\text{CH}_2-$). FTIR (KBr): 3326 ($-\text{OH}$), 2880 ($-\text{CH}$), 1630 ($\text{C}=\text{O}$).



Scheme 1. Synthesis of AHPTXs and possible structure of AHPTX1.

Table 1
The content molar ratio of AHPTXs in feed and obtained photoinitiators.

Photoinitiators	HPEI/E-PEO/ETX ^a	
	In feed	In polymer ^b
AHPTX1	1.8/5/5	1.8/5/5
AHPTX2	1.8/2/10	1.8/2/10

^a Ratio of molar.

^b Estimated from ¹H NMR.

2.4. Synthesis of low-molecular weight compound MGA-TX

MGA-TX was synthesized according to Scheme 2 [25]. ETX (0.568 g, 2 mmol), *N*-methyl-*D*-glucamine (0.39 g, 2 mmol), and ethanol (30 ml) were stirred at 90 °C for 24 h, then distilled to remove solvent. Then the residue was recrystallized from ethanol to get MGA-TX.

UV: $\lambda_{\max} = 404 \text{ nm}$ $\epsilon = 1.98 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ (in water); EIMS (70 eV): m/z 479.6. C₂₃H₂₉NO₈S (480); Calcd. C 57.61, H 6.10, N 2.92, S 6.69. Found C 57.24, H 5.99, N 2.80, S 6.53. ¹H NMR (CDCl₃): $\delta = 8.52$ – 7.43 (aromatic), 4.60–3.94, 3.72–3.30 (–OCH₂, –OCH), 2.60–2.20 (–NCH₂). FTIR (KBr): 3386 (–OH), 2920 (–CH), 1630 (C=O).

2.5. Measurement

2.5.1. Physicochemical measurements

We used MGA-TX/TEA as water-soluble low-molecular weight analogue and ETX/TEA as oil-soluble low-molecular weight analogue according to Scheme 2. In all measurement, the concentration of photoinitiator system is in terms of TX moieties and the molar ratio of TX/TEA is always 1:5.

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 DMF as an eluent.

¹H NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with CDCl₃ as the solvent.

FT-IR spectra were recorded on a Perkin-Elmer Paragon1000 FT-IR spectrometer. The samples were prepared as KBr disc.

UV-vis spectra were recorded in CHCl₃ and H₂O solution by Shimadzu UV-2450 spectrophotometer (The concentration is $5.0 \times 10^{-5} \text{ M}$ in terms of thioxanthone moieties.).

Elemental analysis was conducted on an Elementar Varioel apparatus.

Fluorescence spectra were recorded in CHCl₃ and H₂O solution on Perkin-Elmer LS50B luminescence spectrophotometer (The concentration is $1.0 \times 10^{-5} \text{ M}$ in terms of thioxanthone moieties.).

Solubility test was measured according to following step: A certain amount of polymer was dissolved in solvent at room temperature. The result was decided after 1 h. The solubility was classified into three types: insoluble, partial soluble and completely soluble. The solubility less than 0.1% (weight) is considered as insoluble.

2.5.2. Photopolymerization of acrylamide (AM) in aqueous solution

Photopolymerization of AM in aqueous solution was performed in a bottle at 10 °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 2 mW/cm². 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.

2.5.3. Photocalorimetry

The photopolymerization of PEGDA and A-BPE-10 was carried out by photo-DSC (DSC 6200, Seiko Instrument Inc.) with incident light of 365 nm, which intensity can be changed from 5 to 75 mW. Approximately 2.0 mg sample mixture was placed in the aluminum DSC pan.

Heat flow versus 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 double bond conversion (DBC) of the vinyl groups or the extent of reaction could be determined according to:

$$\text{DBC} = \Delta H_t / \Delta H_0^{\text{theor}} \quad (1)$$

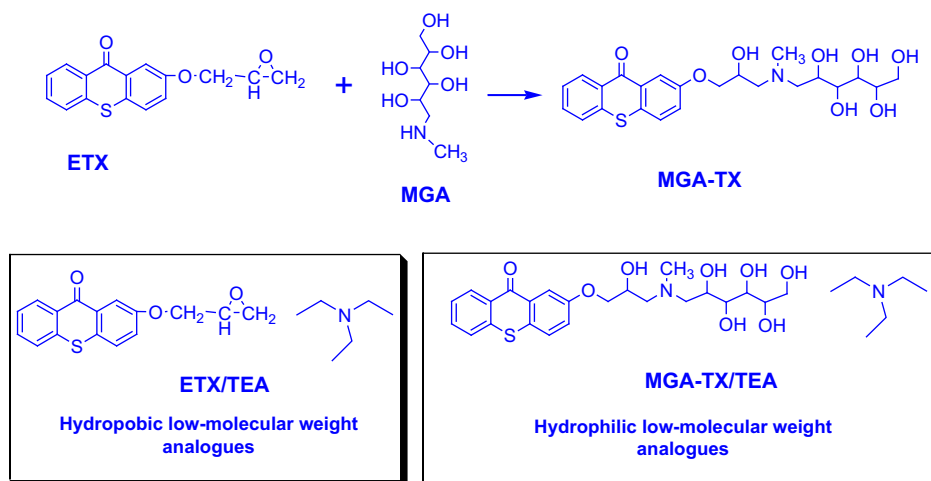
where ΔH_t is the reaction heat evolved at time t , and $\Delta H_0^{\text{theor}}$ is the theoretical heat for complete conversion. For an acrylic double bond, $\Delta H_0^{\text{theor}} = 86 \text{ kJ/mol}$ [26]. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:

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

3. Results and discussion

3.1. Synthesis of AHPTXs

Through reactions between epoxy and amine group, TX moieties and PEO chain can be incorporated into periphery of HPEI according to Scheme 1. Because nucleophilic substitution/ring-opening



Scheme 2. Synthesis of MGA-TX and the structure of low-molecular weight analogues.

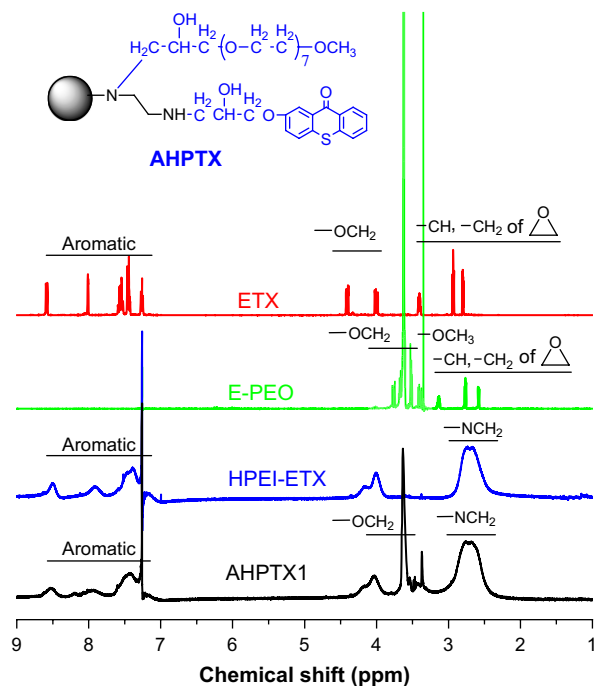


Fig. 1. ^1H NMR spectra for ETX, E-PEO, HPEI-ETX and AHPTX1 in CDCl_3 .

reactions between epoxy and amine groups possesses characterization of “click-chemistry”, the process for synthesis of AHPTX is very simple and “green” in ethanol as solvent, in which no small molecules were produced. The resulted polymeric thioxanthone photoinitiators were confirmed by ^1H NMR and FT-IR. ^1H NMR spectra for ETX, E-PEO, HPEI-ETX and the final obtained polymeric photoinitiator AHPTX1 are shown in Fig. 1. As for ETX, the peak between 2 and 3 ppm and 3.4 ppm can be assigned to the $-\text{CH}_2$ and $-\text{CH}$ of epoxy ring, respectively, and the two peaks at 3.95 ppm and 4.45 ppm can be assigned to $-\text{OCH}_2$. Compared with ETX, the signal related to epoxy disappeared in ^1H NMR spectra of intermediate HPEI-ETX, which can be evidence of successful introduction of TX moieties into HPEI. The disappearance of signals related to the epoxy groups, accompanied with the occurrence of the signals at 7.2–8.5 ppm (phenyl ring from TX) and 3.6 ppm ($-\text{OCH}_2$ from PEO) in ^1H NMR of AHPTX1, can be considered as evidence of successful introduction of TX moieties and PEO chains into HPEI backbone. Moreover, the component of AHPTXs can be determined by calculating the intensity ratio of signals related to TX, E-PEO and HPEI. We can calculate the content ratio by the intensity of aromatic hydrogen, $-\text{OCH}_3$ and $-\text{NCH}_2$ in ^1H NMR spectra, which are the characteristic signals of TX, E-PEO and HPEI, respectively. As for AHPTX1, we assigned the aromatic hydrogen intensity as 7, based on which the intensity of $-\text{OCH}_3$ and $-\text{NCH}_2$ is 3 and 20, so the content ratio of HPEI/ETX/E-PEO should be $\{20/[(600/43)*4]\}: [7/7]: [3/3] = 0.36:1:1 = 1.8:5:5$. The results are summarized in Table 1. The content of TX, PEO and HPEI in obtained AHPTXs is similar to them in feed, which might be ascribed to high efficiency of nucleophilic substitution/ring-opening reactions between epoxy and amine groups. To compare the performance of the obtained AHPTXs with low-molecular analogue, water-soluble MGA-TX was synthesized according to Scheme 2.

3.2. Solubility of AHPTXs

Table 2 summarizes the solubility of AHPTXs in different solvents and acrylate monomers, as well as low-molecular weight

Table 2

The solubility of photoinitiators in different solvents.

Photoinitiator	Water	DMF	CHCl_3	CH_2Cl_2	AMP-10G	PEGDA
AHPTX1	++	++	++	++	+	++
AHPTX2	+	++	++	++	+	++
MGA-TX	++	++	+	+	–	++
ETX	–	++	++	++	++	++

Note: “–” is insoluble, “+” is partial soluble, “++” is completely soluble.

analogues MGA-TX and ETX. From Table 2, the solubility of AHPTXs in water increased with the increasing content of PEO chain. Compared with AHPTX2, AHPTX1 containing more PEO chains are completely soluble in water, indicating that introduction of PEO chain can really enhance the water-solubility. Compared with MGA-TX and ETX, AHPTX1 are not only soluble in water, but also exhibit good solubility in non-polar and polar solvents such as dichloromethane, chloroform, and DMF. In particular, water-soluble AHPTX1 possesses very good compatibility with commercial multifunctional monomers ABPE-10 and PEGDA, due to amphipathic PEO chain. This indicates that introduction of PEO chain can really increase solubility of TX in different solvents and enhance compatibility of TX with multifunctional acrylate crosslinkers. From this point, AHPTX1 is expected to be efficient in photoinitiation of acrylate crosslinkers.

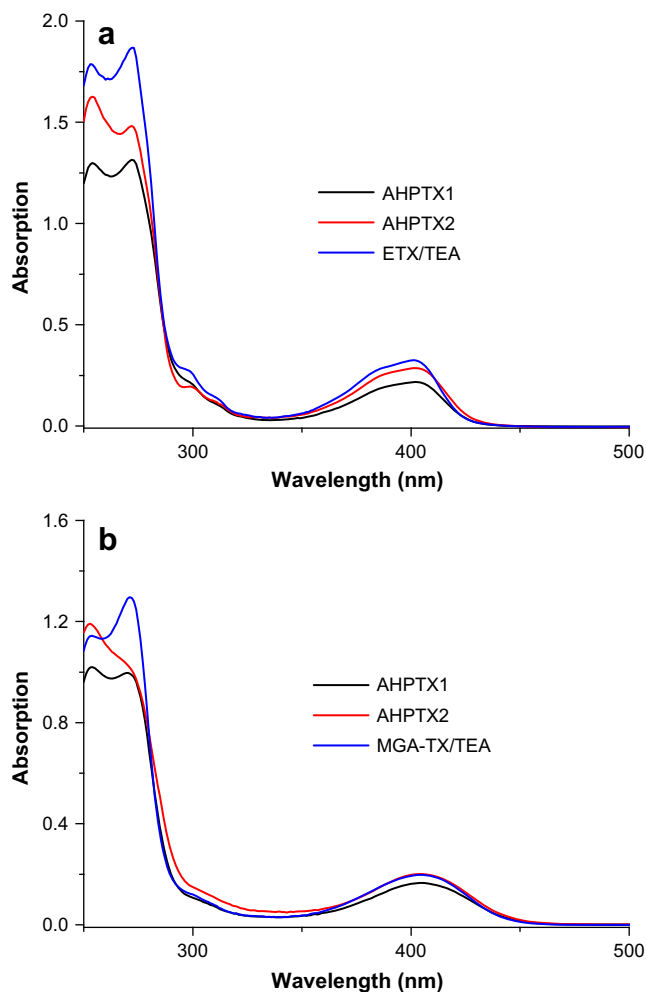


Fig. 2. UV-vis spectra of photoinitiator in (a) CHCl_3 and (b) aqueous solution (the concentration is 5.0×10^{-5} mol/L in terms of TX moiety).

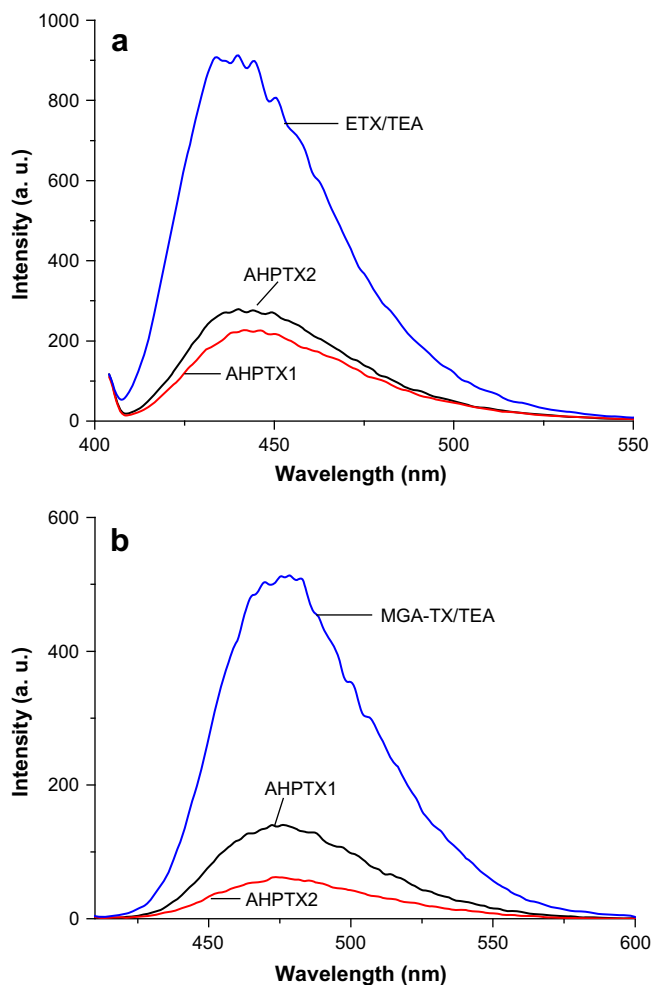


Fig. 3. Fluorescence spectra of photoinitiators in (a) CHCl_3 solution, $\lambda_{\text{ex}} = 402$ nm and (b) aqueous solution, $\lambda_{\text{ex}} = 404$ nm (the concentration is 1.0×10^{-5} mol/L in terms of TX moiety).

3.3. Photochemical and photophysical properties

UV–vis spectra of AHPTXs in chloroform and water are shown in Fig. 2, as well as low-molecular weight analogues ETX and water-soluble MGA-TX. AHPTXs exhibit the usual characteristic absorption of thioxanthone, and possesses an absorption similar to ETX in chloroform ($\lambda_{\text{max}} = 402$ nm, Fig. 2(a)) and MGA-TX in water ($\lambda_{\text{max}} = 404$ nm, Fig. 2(b)). This also indicates that TX moiety and PEO short chain have been successfully introduced into polymeric chain of AHPTXs.

Although emission from AHPTXs has a similar maximum at 475 nm to ETX and MGA-TX, the emission of AHPTXs is obviously weaker than that of ETX/TEA in chloroform and MGA-TX/TEA in aqueous solution according to Fig. 3. The weaker emission of AHPTXs, which shows a more effective energy transition between the excited state of the TX moieties and the coinitiator amine, may be ascribed to both intramolecular and intermolecular quenching

Table 3

Polymerization of AM initiated by photoinitiators in aqueous solution for 2 h at 10°C ($[\text{AM}] = 4$ mol/L, $[\text{TX}] = 4 \times 10^{-3}$ mol/L).

Photoinitiator	Conversion (%)	R_p ($\text{mol L}^{-1} \text{s}^{-1}$) $\times 10^4$	M_n (g mol^{-1}) $\times 10^{-5}$	M_w/M_n
AHPTX1	83.4	4.6	7.0	4.5
AHPTX2	62.3	3.5	6.6	4.6
MGA-TX/TEA	65.0	3.7	6.9	4.6

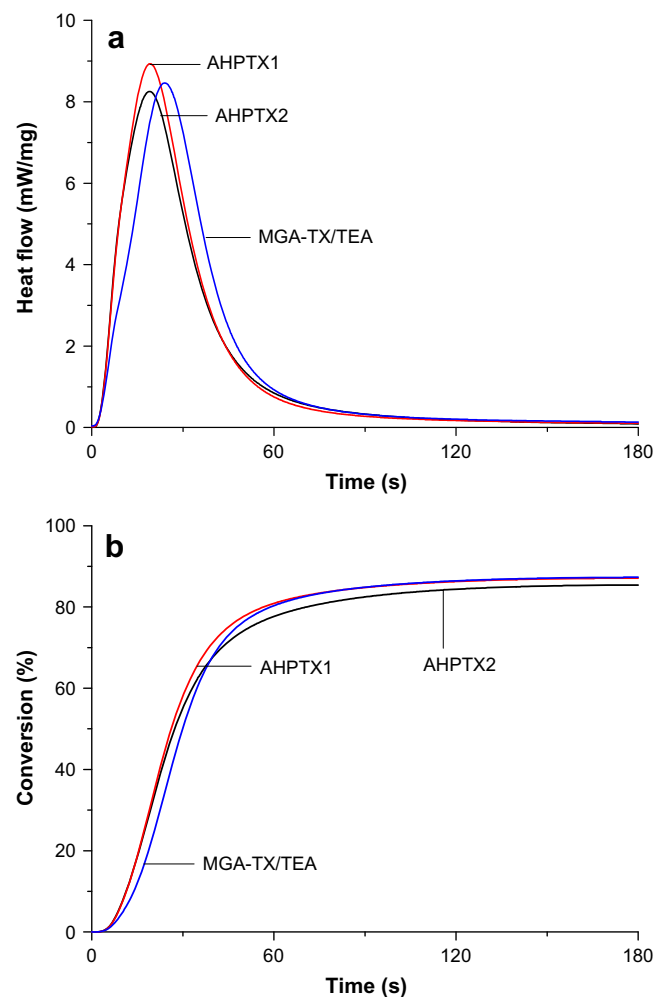


Fig. 4. (a) Photo-DSC profile, (b) conversion versus time curves, for polymerization of PEGDA initiated by AHPTX1, AHPTX2 and MGA-TX/TEA, irradiated at 25°C by UV light with an intensity of 20 mW/cm^2 ($[\text{PI}] = 0.01$ mol/L).

of the aromatic ketone by the amino groups of HPEI backbone. Compared with low-molecular weight analogues ETX/TEA and MGA/TEA, the local amino concentration around TX moieties in AHPTXs is higher and the excited TX moieties can be more effectively quenched, which might be resulted from polymeric effect.

3.4. Photopolymerization

Photopolymerization of AM initiated by AHPTXs and MGA-TX/TEA in aqueous solution was studied, and the results are summarized

Table 4

Photopolymerization of PEGDA and A-BPE-10 initiated by AHPTXs and low-molecular weight analogues, cured at 25°C by UV light with an intensity of 20 mW/cm^2 .

Photoinitiator ^a	PEGDA			A-BPE-10		
	$R_{p,\text{max}} \times 10^{3b}$ (s^{-1})	t_{max}^c (s)	DBC ^d (%)	$R_{p,\text{max}} \times 10^3$ (s^{-1})	t_{max} (s)	DBC (%)
AHPTX1	29.8	19.2	87.1	37.9	15.1	86.0
AHPTX2	27.6	19.1	85.4	35.3	17.2	78.7
MGA-TX/TEA	28.3	24.0	87.3			
ETX/TEA				27.3	34.9	80.2

^a The photoinitiator concentration was 0.01 M in terms of TX moieties.

^b $R_{p,\text{max}}$: the maximal polymerization rate.

^c t_{max} : time to reach maximal polymerization rate.

^d DBC: final conversion.

in Table 3. Compared to low-molecular weight analogues MGA-TX/TEA, AHPTXs can photoinitiate polymerization of AM more efficiently, which might be ascribed to efficient intramolecular hydrogen abstraction between TX and coinitiator amino group in AHPTXs. 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 [27]. 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 photopolymerization. Because of TX and coinitiator amino groups in the same hyperbranched polymeric backbone, the excited state of TX can abstract hydrogen from amino groups along polymeric chain, resulting in effective generation of radicals. Therefore, AHPTXs can initiate photopolymerization of AM more efficiently than MGA-TX/TEA. From Table 3, AHPTX1 is more efficient for photopolymerization of AM than AHPTX2, which might be ascribed to its better water-solubility.

To understand the efficiency of AHPTXs in photoinitiation of commercial acrylate crosslinkers, we studied the photopolymerization of hydrophilic PEGDA and hydrophobic A-BPE-10 initiated by AHPTXs, as well as low-molecular weight analogues MGA-TX/TEA

and ETX/TEA. As one of important hydrophilic difunctional acrylate crosslinker, PEGDA are widely used in photo-curing hydrogel and biomaterials. The photo-DSC profiles of the polymerization of PEGDA initiated by AHPTXs and MGA-TX/TEA are shown in Fig. 4, and the results are summarized in Table 4. The polymerization behavior appears similar to other multifunctional monomers [28,29]. From Fig. 4 and Table 4, both final conversion and $R_{p,max}$ of polymerization PEGDA photoinitiated by AHPTXs are almost as high as that of MGA-TX/TEA, indicating that AHPTXs are efficient for photoinitiation of PEGDA. The final conversion for AHPTXs is higher than 80%.

Photo-DSC curves for polymerization of hydrophobic A-BPE-10 initiated by AHPTXs and ETX/TEA are shown in Fig. 5. From Fig. 5 and Table 4, AHPTXs are obvious more efficient than low-molecular weight analogues ETX/TEA, which is different from the polymerization of PEGDA. $R_{p,max}$ for AHPTXs is higher than ETX/TEA, and increases with the increasing content of PEO chain in AHPTX, which may be ascribed to polymeric structure of AHPTXs. Compared with PEGDA, the viscosity and the double bond content of A-BPE-10 are much higher, which leads to very high crosslinking density in the whole polymerization process of A-BPE-10. In this condition, the mobility of radicals becomes very important factor to the polymerization of A-BPE-10. Due to its planar structure, thioxanthone is difficult to disperse in crosslinkers of high viscosity, especially cross-linked network in the late state of photo-curing. Because of the introduction of flexible amphipathic PEO chain into AHPTXs, the mobility and solubility of the obtained AHPTXs in acrylate crosslinker increase with the increasing content of PEO chain. Therefore, AHPTXs are more efficient in polymerization of A-BPE-10 than ETX/TEA, and their photoinitiation efficiency can be enhanced by introduction of more PEO chain.

4. Conclusion

We successfully synthesized amphipathic hyperbranched polymeric thioxanthone (TX) photoinitiators (AHPTXs) by introducing TX, and short poly(ethylene oxide) (PEO) chain into periphery of hyperbranched poly(ethylene imine) (HPEI). AHPTXs can be not only dispersed easily in many solvents and acrylate monomers, but also are soluble in water. AHPTXs are very efficient in photopolymerization of acrylamide (AM), PEGDA and A-BPE-10. AHPTXs will be expected very potential in application such as coatings, inks and photo-curing hydrogel.

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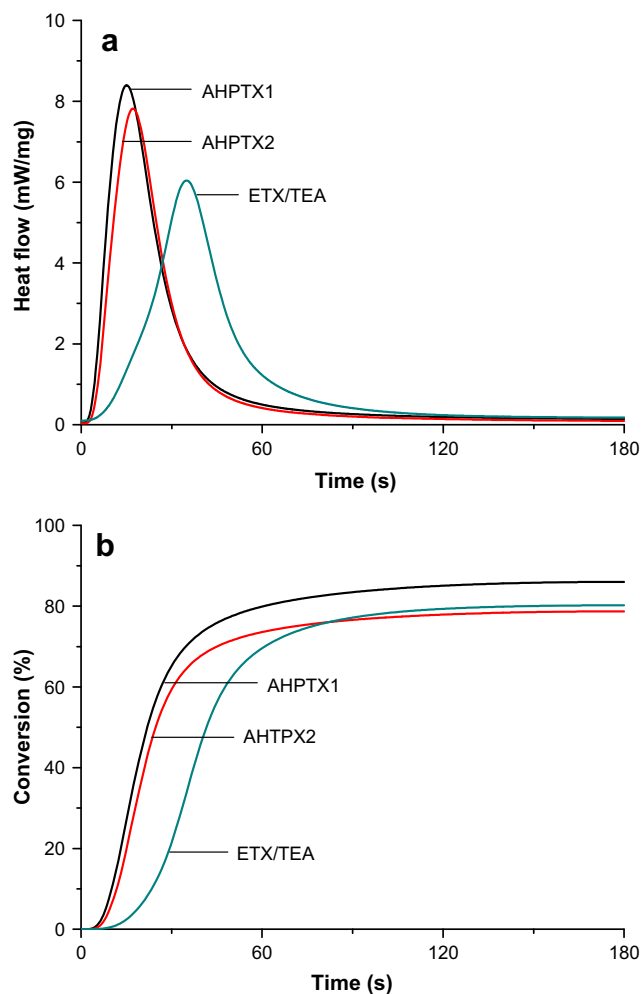


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