

Water-Soluble and Polymerizable Thioxanthone Photoinitiator Containing Imidazole

Jun Qiu, Jun Wei

Department of Polymer Materials and Engineering, School of Material Engineering, Key Laboratory for Ecological-Environment Materials of Jiangsu Province, Yancheng Institute of Technology, Yancheng City, 224051, People's Republic of China
Correspondence to: J. Wei (E-mail: fngpl@163.com)

ABSTRACT: A novel free radical photoinitiator, 3-allyl-1-[2-hydroxy-3-(thioxanthen-9-one-2-yl)oxypropyl]imidazolium chloride ([AIPTX]Cl), is synthesized by the addition reaction of 2-(2,3-epoxy)propoxylthioxanthone (ETX) with a heterocyclic compound imidazole firstly, and the achieved intermediate 1-[2-hydroxy-3-(thioxanthen-9-one-2-yl)oxypropyl]imidazole (IPTX) is then reacted with allyl chloride. IPTX is chosen to evaluate the photoefficiency of [AIPTX]Cl. FTIR and $^1\text{H-NMR}$ confirm the structures of [AIPTX]Cl and IPTX. UV-Vis spectra of the two photoinitiators are similar and both exhibit the maximal absorption about 400 nm. Fluorescence spectra show [AIPTX]Cl/IMZ has slightly higher fluorescence intensity than IPTX system. Photopolymerization studies indicate that [AIPTX]Cl/IMZ is more efficient for the polymerization of water-soluble monomer than IPTX. Moreover, due to its advantages of water solubility and polymerizability, [AIPTX]Cl is an environmental-friendly photoinitiator and has potential for application in UV-curing systems. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40659.

KEYWORDS: photochemistry; photopolymerization; radical polymerization

Received 5 December 2013; accepted 27 February 2014

DOI: 10.1002/app.40659

INTRODUCTION

At present, free radical photocuring technology has gained a wide range of industrial applications.^{1–3} The traditional photocuring systems are usually organic-soluble systems, using reactive diluents to reduce the viscosity of the resin.^{4–6} Because of environmental and legislation constrains, many efforts have been made to develop water as a substitute of conventional organic diluents in the last 20 years. Water-soluble system has many advantages, such as none volatile organic solvents (VOCS), easily adjusting the viscosity, no skin irritation, and unpleasant odor. In water-soluble photocuring system, a photoinitiator is an extremely important component.^{7–10} Currently, the traditional organic-soluble photoinitiators have been widely used in water-soluble photocuring systems. However, the poor compatibility between organic-soluble photoinitiators and water-soluble resins would inevitably affect the final performances of the curing products.^{11–15} Great attention has been paid to synthesize new and highly efficient water-soluble photoinitiators in recent years.^{16–20} On the other hand, in order to overcome the inherent defect of migration of low molecular weight photoinitiators, many researchers have concentrated on preparing polymeric or polymerizable photoinitiators.^{21–23} To give consideration to both water solubility and no migration, J. Yin group synthesized the water-soluble polymeric photoinitiator.^{24,25}

To our knowledge, thioxanthone photoinitiator containing both the advantages of water solubility and polymerizability has seldom been reported.

In this article, imidazole (IMZ), an odorless compound, was introduced into the structure of 2-(2,3-epoxypropoxyl)thioxanthone (ETX) to achieve 1-[2-hydroxy-3-(thioxanthen-9-one-2-yl)oxypropyl]imidazole (IPTX), which was further reacted with allyl chloride to obtain 3-allyl-1-[2-hydroxy-3-(thioxanthen-9-one-2-yl)oxypropyl]imidazolium chloride ([AIPTX]Cl). Because of the existence of quaternary ammonium ion and double bond, [AIPTX]Cl possesses the advantages of water-solubility and polymerizability simultaneously. Therefore, [AIPTX]Cl may have good compatibility with water-soluble resins, and may copolymerize with the photocurable resins. IPTX was chosen as a model compound to evaluate the photoefficiency of [AIPTX]Cl/IMZ (a mixture of [AIPTX]Cl with IMZ at 1 : 1 molar ratio). FTIR and $^1\text{H-NMR}$ were used to characterize the structure of [AIPTX]Cl and IPTX. UV-Vis and Fluorescence spectra were used to investigate their photochemical behavior. The photopolymerization of trimethylolpropane triacrylate (TMPTA) and acrylamide (AM), initiated by [AIPTX]Cl/IMZ and IPTX systems, was studied by differential scanning photocalorimetry (photo-DSC).

EXPERIMENTAL

Materials

Ethanol ($\geq 99.8\%$), chloroform ($\geq 99.5\%$), petroleum ether (bp 30–60°C), benzene ($\geq 98.0\%$), allyl chloride ($\geq 99.8\%$), Ammonia water ($\geq 27.5\%$), *N,N*-dimethyl formamide (DMF; $\geq 99.5\%$), IMZ ($\geq 99.0\%$, Jiangsu Kangle new material), TMPTA (Nantong Litian Chemical Company), AM (Guangzhou Gao Jian chemical limited) were used as received. ETX was synthesized in our lab according to the procedure described in literature.²⁶ Other chemicals were of analytical grade except as noted.

Characterization

¹H-NMR spectra were recorded on a Mercury Plus 400MHz spectrometer with CDCl₃ and DMSO-*d*₆ as solvent. ¹³C-NMR spectra were recorded on a Bruker Avance 300MHz spectrometer with DMSO-*d*₆ as solvent. FTIR spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer. The samples were prepared as KBr disk. Elemental analysis was conducted on an Elementary Varioel apparatus. Mass spectra were recorded on a HP5989A mass spectrometer at 70 eV. UV-Vis spectra were recorded in chloroform solution by a Perkin-Elmer Lambda 20 UV-Vis spectrophotometer. Fluorescence spectra were recorded in chloroform solutions with a PerkinElmer LS50B luminescence spectrophotometer.

Photopolymerization of AM and TMPTA was studied by means of DSC 6200 (Seiko Instrument Inc) photo-DSC with a high-pressure Hg lamp. Approximately 2 mg sample mixture was placed in the aluminum DSC pans. In the polymerization of AM, the solvent is water, and the concentration [AM] = 2.0 mol/L. Whether in AM or in TMPTA, the concentration [PI] = 0.02 mol/L. Heat flow versus time (DSC thermogram) curves were recorded in an isothermal mode under a nitrogen flow of 50 mL/min, cured at 25°C by UV light with an intensity of 35 mW/cm². 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

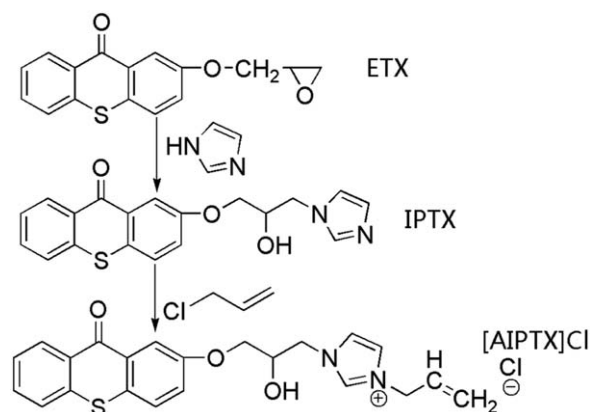
$$C = \Delta H_t / \Delta H_0^{\text{theor}} \quad (1)$$

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, $\Delta H_0^{\text{theor}} = 86$ kJ/mol, and for an acrylamide bond, $\Delta H_0^{\text{theor}} = 82.5$ kJ/mol.²⁷ The polymerization rate (R_p) is directly related to the heat flow (dH/dt) according to

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

Photoinitiators Preparation

Synthesis of IPTX. IMZ (3.41 g, 0.05 mol) and ethanol (50 mL) were added to a three-necked flask with magnetic stirring under a nitrogen atmosphere. When the mixture was heated to 70°C, ETX (5.69 g, 0.02 mol) was added slowly to the mixture. After the addition was completed, the mixture was further reacted for 7 h, and then cooled down to room temperature. The mixture was filtered through a thin layer of activated charcoal. The filtrate was evaporated to remove ethanol, and the residual liquid was poured into mixed solvent of water and chloroform. The chloroform phase was separated and evaporated to give yellow liquid. The yellow liquid was dissolved in diluted hydrochloric acid and washed with benzene in a separating funnel. Ammonia was used to adjust the pH value of the aqueous layer to 8–9, and the solution was extracted with chloroform. The chloroform solution was evaporated to give crude product, which was then recrystallized and dried under vacuum at 50°C for 48 h to yield 5.34 g IPTX. Yield: 75.8%.



Scheme 1. Synthesis route for IPTX and [AIPTX]Cl.

rated to give yellow liquid. The yellow liquid was dissolved in diluted hydrochloric acid and washed with benzene in a separating funnel. Ammonia was used to adjust the pH value of the aqueous layer to 8–9, and the solution was extracted with chloroform. The chloroform solution was evaporated to give crude product, which was then recrystallized and dried under vacuum at 50°C for 48 h to yield 5.34 g IPTX. Yield: 75.8%.

m.p.: 170°C (DSC in N₂); EIMS (70 eV) $m/e = 352$; ¹H-NMR (CDCl₃, 400 MHz): $\delta = 8.68$ –7.50 (7H, aromatic), 7.11–6.83 (3H, heterocyclic), 4.32–4.21 (2H, OCH₂), 4.25–4.13 (2H, CH₂), 4.07 (1H, CH), 2.40 (1H, OH); ¹³C-NMR (DMSO-*d*₆, 300MHz): $\delta = 178.2$ (C=O), 157.09 (Ar–O), 137.73–111.41 (14C, aromatic and heterocyclic), 69.77 (OCH₂), 68.11 (CHOH), 49.23 (CH₂-N); FTIR (KBr): $\nu = 3440$ (–OH), 3020, 2920 (CH, CH₂), 1630 (C=O). C₁₉H₁₆N₂O₃S: Calcd. C 64.76, H 4.58, N 7.95, S 9.10; Found C 64.81, H 4.48, N 7.79, S 9.06.

Synthesis of [AIPTX]Cl. IPTX (3.52 g, 0.01 mol), allyl chloride (10 mL), and chloroform (50 mL) were added in a three-necked flask with magnetic stirring and reflux condenser under nitrogen atmosphere, the mixture was heated to 60°C for 8 h. After cooled down to ambient temperature, the resultant solution was evaporated by a spinning evaporator to remove chloroform and excessive allyl chloride. The crude product was washed by petroleum ether twice and dried under vacuum at 50°C for 48 h to yield 3.07 g [AIPTX]Cl. Yield: 71.6%.

m.p.: 93 °C (DSC in N₂); ¹H-NMR (CDCl₃, 400MHz): $\delta = 8.49$ –7.82 (7H, aromatic), 7.60–7.31 (3H, heterocyclic), 6.01 (1H, CH=), 5.40–5.29 (2H, =CH₂), 4.92 (1H, OH), 4.50–4.41 (2H, NCH₂), 4.32–4.28 (2H, OCH₂), 4.21–4.14 (2H, CH₂N), 4.07 (1H, CH); ¹³C-NMR (DMSO-*d*₆, 300MHz): $\delta = 178.43$ (C=O), 157.12 (Ar-O), 136.84–111.59 (16C, aromatic, heterocyclic, and CH=CH₂), 69.68 (OCH₂), 67.14 (CHOH), 52.01 (N-CH₂), 50.77 (CH₂-N); FT-IR (KBr): $\nu = 3430$ (–OH), 3040, 2920 (CH, CH₂), 1633 (C=O); C₂₂H₂₁ClN₂O₃S: Calcd. C 61.60, H 4.93, Cl 8.27, N 6.53, S 7.48; Found C 61.71, H 4.87, Cl 8.29, N 6.49, S 7.44.

RESULTS AND DISCUSSION

Photoinitiators Synthesis

The main purpose of this article is to investigate the photoinitiating efficiency difference between oil-soluble photoinitiator

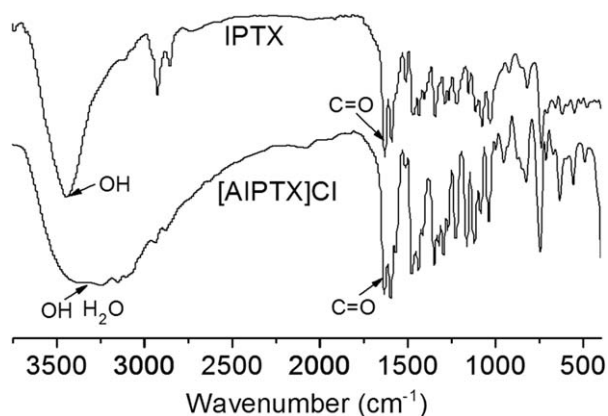


Figure 1. FTIR spectra of IPTX and [AIPTX]Cl.

IPTX and water-soluble photoinitiator [AIPTX]Cl. Through the ring-opening reaction of epoxy group of ETX with IMZ, the intermediate IPTX was achieved. Then, IPTX was further reacted with allyl chloride to give [AIPTX]Cl. The synthesis route is presented in Scheme 1. The structures of IPTX and [AIPTX]Cl were characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FTIR spectra, mass spectra, and elemental analysis.

From the FTIR spectra (Figure 1), in addition to the absorption of carbonyl group from TX moieties (Ar-CO-Ar) around 1630 cm^{-1} , the appearance of absorption at 3440 cm^{-1} verified the formation of hydroxyl group in IPTX and [AIPTX]Cl. Meanwhile, the absorptions around 1100 cm^{-1} indicate that C—N bond was successfully introduced to the target products. Moreover, the expected structure of IPTX and [AIPTX]Cl were further confirmed by the signals in $^1\text{H-NMR}$ spectra (Figure 2),

as well as the results of mass spectra, $^{13}\text{C-NMR}$, and elemental analysis.

UV-Vis Spectra

UV absorption spectra of IPTX and [AIPTX]Cl were measured in chloroform, as shown in Figure 3. The absorption maximum (λ_{max}) and the logarithm of molar extinction coefficients at λ_{max} ($\log \epsilon$) are summarized in Table I. From Figure 3 and Table I, the maximum of absorption of IPTX and [AIPTX]Cl are all about 400 nm, which is the common characteristic of TX. Moreover, according to the value of $\log \epsilon$, these absorptions should belong to the $\pi-\pi^*$ transition of $\text{C}=\text{O}$.^{28,29}

Fluorescence Spectra

Fluorescence spectra of IPTX and [AIPTX]Cl/IMZ were measured in chloroform, as shown in Figure 4. According to Figure 4, the fluorescence emission wavelengths of the two photoinitiator systems are all about 440 nm, a typical emission characteristic of TX.³⁰ The emission intensity of IPTX is slightly weaker than that of [AIPTX]Cl/IMZ, which can be ascribed to the quenching effect of coinitiator imidazole on the excited TX. Imidazole can transfer an electron to excited TX moiety, which can generate active free radicals. The active free radicals have quenching effect on the excited TX. Therefore, the higher the concentration of coinitiator imidazole is, the better the quenching effect is. Though the whole ratio of TX moiety with coinitiator imidazole in [AIPTX]Cl/IMZ is the same as that in IPTX, the partial concentration of coinitiator imidazole moiety around TX moiety in IPTX is much higher than that in [AIPTX]Cl/IMZ, which results that the excited TX moiety of IPTX is quenched more easily than that of [AIPTX]Cl/IMZ.

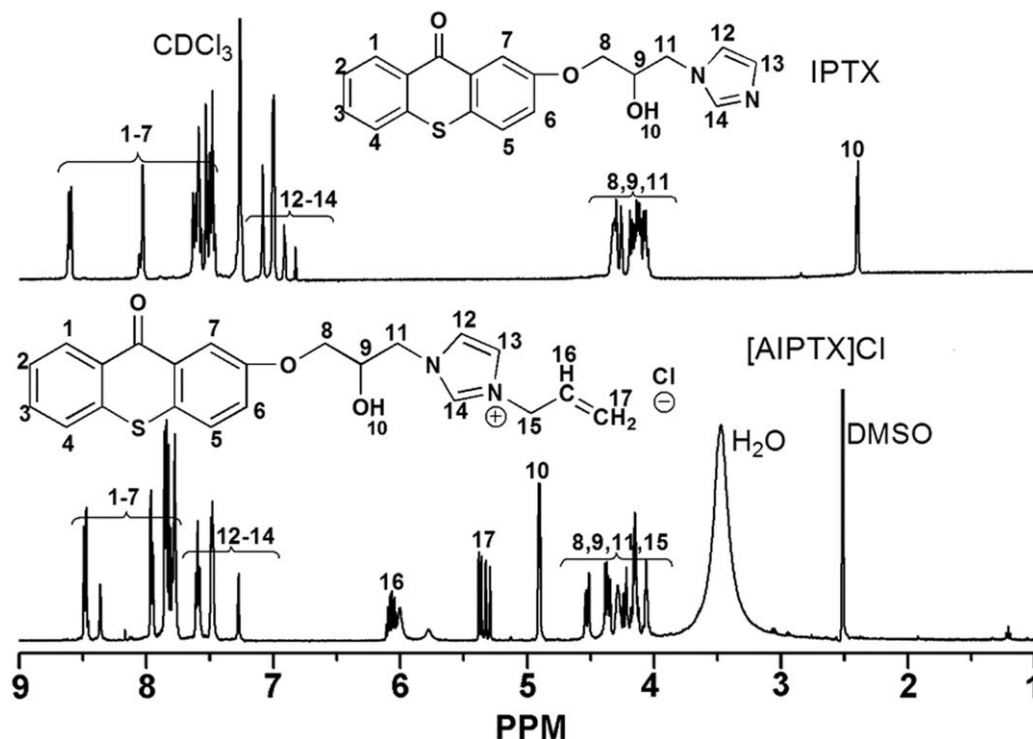


Figure 2. $^1\text{H-NMR}$ spectra of IPTX and [AIPTX]Cl.

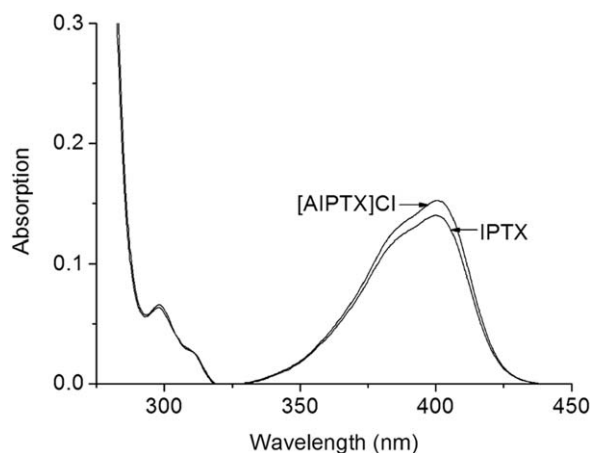


Figure 3. UV-Vis absorption spectra of IPTX and [AIPTX]Cl in chloroform solution (the concentration is $2.5 \times 10^{-5} M$).

As a result, the emission intensity of IPTX is weaker than that of [AIPTX]Cl/IMZ.

Photopolymerization of TMPTA and AM

Figures 5 and 6 show the photo-DSC profiles of AM and TMPTA initiated by IPTX and [AIPTX]Cl/IMZ systems. Their polymerization behaviors appear to be similar. The data for the maximal polymerization rate ($R_{p, \max}$) and the final conversion of TMPTA (C_{\max}) are summarized in Table II.

According to Figures 5, 6, and Table II, IPTX is a little more efficient than [AIPTX]Cl/IMZ in initiating TMPTA. This result can be ascribed to the efficiency of the photoinitiator system, which is mostly determined by the efficiency of electron and proton transfer between photoinitiator and coinitiator. TX is a well-known hydrogen-abstraction type photoinitiator, and its photoefficiency can be greatly promoted in the presence of a hydrogen donor.^{31,32} In this study, IMZ (group) was used as a hydrogen donor or coinitiator. In [AIPTX]Cl, the alkaline nitrogen atom in imidazole ring was quaternized and lost its alkalinity. Thus, [AIPTX]Cl needs an additional IMZ as coinitiator. Upon irradiation, the photoreduction reaction occurs between [AIPTX]Cl and IMZ, resulting in producing ketyl radical and imidazole free radical, and the later can initiate photopolymerization of vinyl monomers (as shown in Scheme 2). Therefore, for [AIPTX]Cl/IMZ system, the electron and proton transfer belongs to intermolecular transfer. However, as for IPTX, aside from the intermolecular hydrogen abstraction, the intramolecular reaction will also take place (as shown in Scheme 3). As is well known, the efficiency of intramolecular electron and proton transfer is higher than that of intermolecular electron and proton transfer.^{33,34} Hence, the efficiency of producing free radicals

Table I. Absorption Properties of IPTX and [AIPTX]Cl in Chloroform Solution (The Concentration is $2.5 \times 10^{-5} M$)

Photoinitiator	λ_{\max} (nm)	$\log(\epsilon/L\text{mol}^{-1} \text{cm}^{-1})$
IPTX	401	3.750
[AIPTX]Cl	401.4	3.758

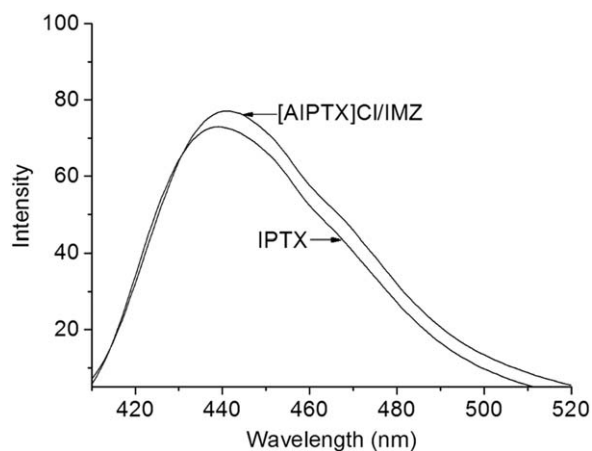


Figure 4. Fluorescence spectra of IPTX and [AIPTX]Cl/IMZ in chloroform solution (the concentration is $2.5 \times 10^{-5} M$).

from IPTX is higher than that of [AIPTX]Cl/IMZ system. As a result, the photopolymerization rate and the final conversion of TMPTA of IPTX system is higher than those of [AIPTX]Cl/IMZ system.

As for the photopolymerization of AM initiated by IPTX and [AIPTX]Cl/IMZ systems, the result is completely opposite to that of TMPTA. [AIPTX]Cl/IMZ exhibits much better initiating performances than IPTX, whether photopolymerization rate or final conversion of AM. This result can be mainly attributed to the compatibility of the photocuring systems. [AIPTX]Cl, due to the introduction of the structure of quaternary ammonium salt, is water-soluble, and has good compatibility with the water-soluble monomer AM. Meanwhile, the coinitiator IMZ is also water-soluble. Therefore, the compatibility of [AIPTX]Cl system will be better than that of IPTX system, because IPTX belongs to organic-soluble initiator. As a result, [AIPTX]Cl/IMZ has better initiating effect on AM than IPTX. Similarly, as shown in Figures 5, 6, and Table II, IPTX is more efficient for the photopolymerization of TMPTA than that for AM, while

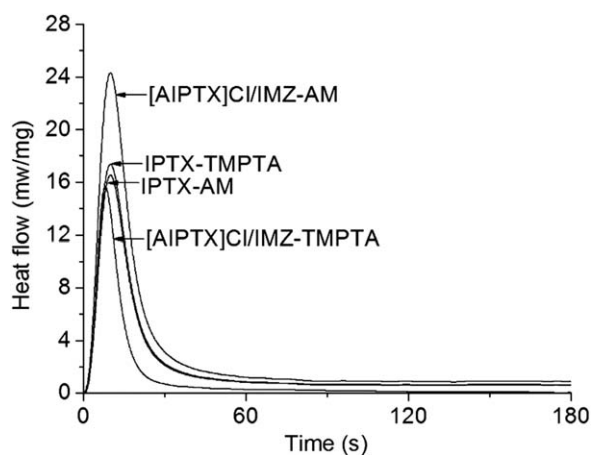


Figure 5. Photo-DSC profiles for IPTX and [AIPTX]Cl/IMZ in AM and in TMPTA, cured at 25°C by UV light with an intensity of 35 mW/cm^2 (The photoinitiator concentration is $0.02M$).

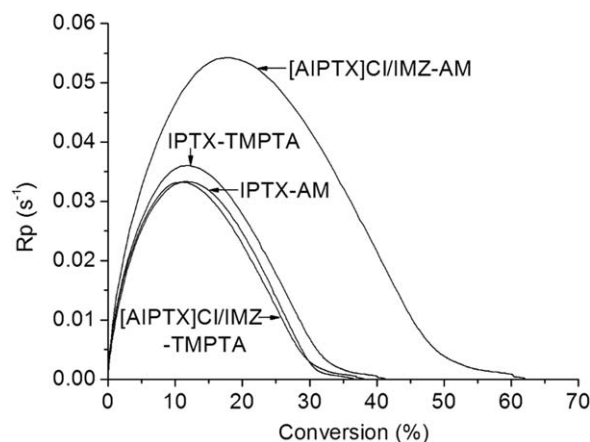


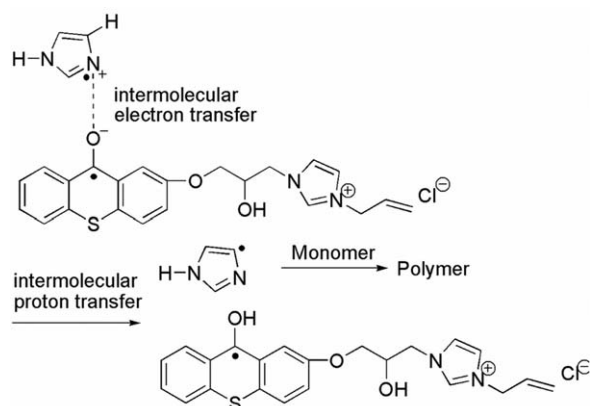
Figure 6. Rate vs. conversion for photopolymerization of AM and TMPTA for IPTX and [AIPTX]Cl/IMZ, cured at 25°C by UV light with an intensity of 35 mW/cm² (The photoinitiator concentration is 0.02M).

Table II. Results for Photopolymerization of TMPTA and AM Initiated by Photoinitiator Systems, Cured at 25°C by UV Light with an Intensity of 35 mW/cm² (The Photoinitiator Concentration is 0.02M)

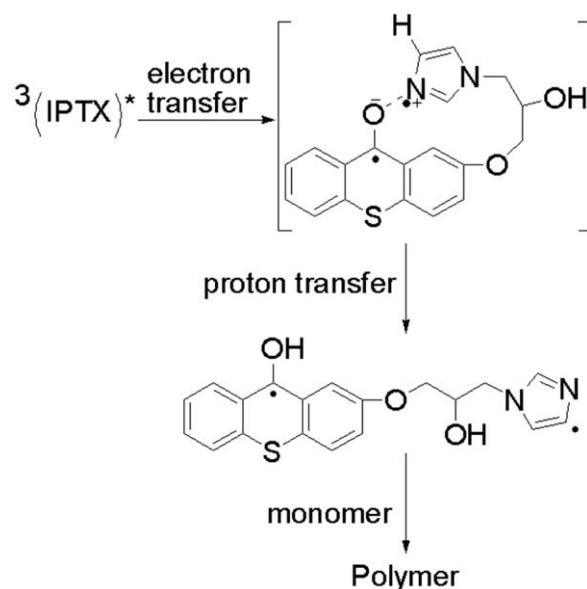
Photoinitiator-Monomer	$R_{p,max} \times 10^2$ (s ⁻¹)	C_f (%)	H_{max} (mW/mg)	T_{max} (s)
[AIPTX]Cl/IMZ-AM	5.416	62.08	24.31	8.3
IPTX-AM	3.352	38.08	16.54	8.1
[AIPTX]Cl/IMZ-TMPTA	3.322	36.60	15.68	6.1
IPTX-TMPTA	3.598	41.25	17.28	7.2

$R_{p,max}$, maximal polymerization rate; C_f , final conversion; H_{max} , maximal heat flow; T_{max} , time to reach maximal heat flow.

[AIPTX]Cl/IMZ is quite the opposite. In addition, due to the existence of double bond, [AIPTX]Cl may copolymerize with the photo-curable monomers or resins. Thus, [AIPTX]Cl may not migrate to the surface of the cured product any more, which will certainly favor to improve the quality of the photo-curing products.



Scheme 2. Proposed initiation mechanisms for [AIPTX]Cl/IMZ.



Scheme 3. Proposed initiation mechanisms for IPTX.

CONCLUSIONS

UV-Vis spectra indicate that [AIPTX]Cl possesses a slightly red-shifted UV maximum of absorption as compared with IPTX. Fluorescence spectra show IPTX has a little lower intensity of fluorescence than [AIPTX]Cl. Photopolymerization of TMPTA and AM, initiated by IPTX and [AIPTX]Cl/IMZ systems, was studied by photo-DSC. The results indicate that [AIPTX]Cl/IMZ is much more efficient for the water-soluble monomer AM than IPTX, and it is a little lower efficient for the organic-soluble monomer TMPTA than IPTX. In a word, [AIPTX]Cl/IMZ is a good efficient photoinitiator whether for the water-soluble monomer or for the organic-soluble monomer, especially for water-soluble monomer. Due to the advantages of water solubility and polymerizability of [AIPTX]Cl, it might have great potential applications in UV-curing systems.

ACKNOWLEDGMENTS

The authors express our gratitude to the education department of Jiangsu Province (Qing-Lan project and key project of natural science research for colleges and universities, NO: 11KJA430010), the key Laboratory for Ecological-Environment Materials of Jiangsu Province (Open project, NO: EML201205), and Yancheng Institute of Technology (Natural research fund, NO: XKY2011001) for their financial support.

REFERENCES

- Moszner, N.; Salz, U. *Prog. Polym. Sci.* **2001**, *26*, 535.
- Nguyen, K. T.; West, J. L. *Biomaterials* **2002**, *23*, 4307.
- Aydin, M.; Arsu, N.; Yagci, Y. *Macromol. Rapid Commun.* **2003**, *24*, 718.
- Green, W. A. J. *Eur. Coat.* **1994**, *5*, 274.
- Gacal, B.; Akat, H.; Balta, D. K.; Arsu, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 2401.

6. Green, P. N.; Green, W. A. *J. Polym. Paint Colour* **1990**, *180*, 42.
7. Liska, R. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1504.
8. Balta, D. K.; Cetiner, N.; Temel, G.; Turgut Z.; Arsu, N. *J. Photochem. Photobiol. A: Chem.* **2008**, *199*, 316.
9. Kojima, K.; Ito, M.; Morishita, H.; Hayashi, N. *Chem. Mater.* **1998**, *10*, 3429.
10. Lougnot, D. J.; Fouassier, J. P. *J. Polym. Sci. A: Polym. Chem.* **1988**, *26*, 1021.
11. Cokbaglan, L.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2003**, *36*, 2649.
12. Allen, N. S.; Catalina, F.; Mateo, J. L.; Sastre, R.; Green, P. N.; Green, W. A. *J. Photochem. Photobiol. A: Chem.* **1988**, *44*, 171.
13. Yang, J.; Zeng, Z.; Chen, Y. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 2563.
14. Ritter, H.; Schwarz-Barac, S.; Stein, P. *Macromolecules* **2003**, *36*, 318.
15. Jiang, X. S.; Xu, H. J.; Yin, J. *Polymer* **2005**, *46*, 11079.
16. Alupej, I. C.; Alupej, V.; Ritter, H. *Macromol. Rapid. Commun.* **2002**, *23*, 55.
17. Li, S. J.; Wu, F. P.; Li, M. Z.; Wang, E. J. *Polymer* **2005**, *46*, 11934.
18. Temel, G.; Arsu, N. *J. Photochem. Photobiol. A: Chem.* **2009**, *202*, 63.
19. Balta, D. K.; Temel, G.; Aydin, M.; Arsu, N. *Eur. Polym. J.* **2010**, *46*, 1374.
20. Yilmaz, G.; Acik, G.; Yagci, Y. *Macromolecules* **2012**, *45*, 2219.
21. Liska, R.; Herzog, D. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 752.
22. Angiolini, L.; Caretti, D.; Salatelli, E. *Macromol. Chem. Phys.* **2000**, *201*, 2646.
23. Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. *J. Photochem. Photobiol. A: Chem.* **2003**, *159*, 103.
24. Wang, Y. L.; Jiang, X. S.; Yin, J. *J. Appl. Polym. Sci.* **2007**, *105*, 3817.
25. Jiang, X. S.; Yin, J. *Macromol. Chem. Phys.* **2008**, *209*, 1593.
26. Yang, J. W.; Zeng, Z. H.; Chen, Y. L. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 2563.
27. Andrejewska, E.; Andrzejewski, M. *J. Polym. Sci. Part A: Polym. Chem.* **1998**, *36*, 665.
28. Degirmenci, M.; Hizal, G.; Yagci, Y. *Macromolecules* **2002**, *35*, 8265.
29. Angiolini, L.; Caretti, D.; Carlini, C.; Corelli, E.; Salatelli, E. *Polymer* **1999**, *40*, 7197.
30. Temel, G.; Parali, T.; Tulu, M.; Arsu, N. *J. Photochem. Photobiol. A: Chem.* **2010**, *213*, 46.
31. Valderas, C.; Bertolotti, S.; Previtali, C. M.; Encinas, M. V. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 2888.
32. Temel, G.; Aydogan, B.; Arsu, N.; Yagci, Y. *Macromolecules* **2009**, *42*, 6098.
33. Corrales, T.; Catalina, F.; Allen, N. S.; Peinado, C. *J. Photochem. Photobiol. A: Chem.* **2005**, *169*, 95.
34. Jiao, H.; Goh, S. H.; Valiyaveettil, S. *Macromolecules* **2001**, *34*, 8138.