

Copolymeric dendritic macrophotoinitiators

Xuesong Jiang, Hongjie Xu, Jie Yin*

State Key Laboratory for Composite Materials, School of Chemistry and Chemical Technology, Research Institute of Polymer Materials, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Received 9 June 2005; received in revised form 28 August 2005; accepted 6 September 2005

Available online 22 September 2005

Abstract

Three kinds of copolymeric dendritic macrophotoinitiator DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC were synthesized by introducing thioxanthone (TX) and octene (OC) moieties into the periphery of dendrimer poly(propylene imine) (PPI), in order to get photoinitiators systems of high performance. The maximum of absorption (λ_{\max}) red-shifted slightly, and the fluorescence emission intensity and the lifetime of the triplet state for TX decreased, with the PPI's generation. Photopolymerization of methyl methacrylate (MMA) and trimethylolpropane triacrylate (TMPTA) initiated by these copolymeric dendritic photoinitiators shows that different photoinitiators exhibit different behaviors towards different monomers: DAB-64-TX-OC is the most efficient for MMA, and DAB-16-TX-OC is the most efficient for TMPTA.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Copolymeric; Photoinitiator; Dendritic

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 [3–5]. 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 macrophotoinitiators, which have some advantages derived from macromolecular nature, in comparison with low-molecular weight analogues [6–13]. 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 [14–17].

Dendritic poly(propylene imine) (PPI) is highly branched, well-defined macromolecules with a number of interesting characteristics and can be used as hydrogen donor because of its high density of amino groups [18–20]. The introduction of

thioxanthone and the vinyl monomer into the periphery of PPI can lead to the novel copolymeric dendritic macrophotoinitiators, which have some obvious advantages such as intramolecular energy transfer between thioxanthone and amine, no need of low-molecular weight coinitiator amine, the higher cross-linking density, and good solubility and compatibility in the curing systems [21–23].

In this context, we further synthesized copolymeric dendritic macrophotoinitiator by introducing vinyl monomer into the dendritic macrophotoinitiators, which have been synthesized in our lab recently and can photoinitiate the polymerization of acrylamide more efficiently than its low-molecular weight counterpart [22]. Two representatives of unsaturated monomer with different functionality, methyl methacrylate (MMA) and trimethylolpropane triacrylate (TMPTA) were chosen to be initiated by these macromolecular photoinitiators in order to obtain information on the influence of macromolecular dendritic structure on photoinitiating and photochemical properties.

2. Experimental part

2.1. Materials

Poly(propylene imine) (generation 1.0, 3.0 and 5.0, named as DAB-4, DAB-16 and DAB-64, respectively) were purchased from Aldrich and 1,2-epoxy-7-octene was purchased from Acros; methyl methacrylate (MMA) was washed

* Corresponding author. Tel.: +86 21 54746215; fax: +86 21 54741297.

E-mail address: jiyin@sjtu.edu.cn (J. Yin).

with 5% aqueous NaOH solution, dried over Na₂CO₃ and distilled. TMPTA was purchased from Nantong Litian Chemical Company; 2-(2,3-epoxy)propoxylthioxanthone (synthesized according to Ref. [15] in our lab); Other chemicals are of analytical grade except as noted.

2.2. Synthesis

Synthesis of copolymeric dendritic macromolecular photoinitiators (DAB-4-TX-OC, DAB-16-TX-OC, DAB-64-TX-OC).

DAB-4-TX, DAB-16-TX and DAB-64-TX were synthesized and fully characterized according to Ref. [22]. A mixture of 0.85 g 1,2-epoxy-7-octene and 0.91 g DAB-4-TX, 0.89 g DAB-16-TX or 0.86 g DAB-64-TX dendritic macromolecule was dissolved in 40 ml ethanol, and then stirred at 80 °C for 48 h. The solution was poured into 400 ml benzine. The precipitate was filtered to give the copolymeric dendritic macrophotoinitiators.

DAB-4-TX-OC: yield ratio: 92%; UV, $\lambda = 399$ nm $\epsilon = 4096$ L mol⁻¹ cm⁻¹. Melting point: 45 °C. Elemental analysis, C₁₁₂H₁₄₄N₆O₁₃S₄ Calcd C 70.41, H 7.54, N 4.40, S 6.70; found: C 69.98, H 7.32, N 4.78, S 6.95; ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.60$ – 7.10 (28H, aromatic), 5.80–5.65 (4H, CH=CH₂) 5.0–4.82 (8H, CH=CH₂) 4.20–3.60 (16H, –OCH₂, –OCH), 2.70–2.25 (36H, N–CH₂), 2.0–1.85 (8H, CH₂–C=C) 1.78–1.20 (34H, –CH₂–); FT-IR (KBr): 3419 (O–H), 2933, (C–H), 1630 (C=O), 905 cm⁻¹ (CH=CH₂).

DAB-16-TX-OC: yield ratio: 89%; UV, $\lambda = 400$ nm $\epsilon = 4058$ L mol⁻¹ cm⁻¹; elemental analysis: C₄₇₂H₆₂₄N₃₀O₆₄S₁₆, Calcd C 68.70, H 7.56, N 5.09, S 6.21; found, C 68.90, H 7.42, N 5.21, S 6.58; ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.60$ – 7.10 (7H, aromatic), 5.80–5.65 (1H, CH=CH₂), 5.0–4.82 (2H, CH=CH₂), 4.20–3.60 (4H, –OCH₂, –OCH), 2.70–2.25 (9H, N–CH₂), 2.0–1.85 (2H, CH₂–C=C), 1.78–1.20 (8.5H, –CH₂–); FT-IR (KBr): 3402 (O–H), 2933, (C–H), 1630 cm⁻¹ (C=O), 905 cm⁻¹ (CH=CH₂).

DAB-64-TX-OC: yield ratio: 93%; UV, $\lambda = 402$ nm $\epsilon = 3995$ L mol⁻¹ cm⁻¹. Elemental analysis: Calcd C 68.69, H 7.61, N 5.28, S 6.13; found, C 69.03, H 7.52, N 5.34, S 5.98; ¹H NMR (CDCl₃, 400 MHz): $\delta = 8.40$ – 6.98 (6.5H, aromatic), 5.80–5.65 (1H, CH=CH₂), 5.0–4.82 (2H, CH=CH₂), 4.20–3.60 (3.9H, –OCH₂, –OCH), 2.70–2.25 (11.5H, N–CH₂), 2.0–1.85 (2H, CH₂–C=C) 1.78–1.20 (10H, –CH₂–); FT-IR (KBr): 3402 (O–H), 2933, (C–H), 1630 cm⁻¹ (C=O), 905 cm⁻¹ (CH=CH₂).

2.3. Analysis

The concentration of photoinitiator system is in terms of TX moieties.

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

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

Elemental analysis was conducted on an Elementar Varioel apparatus.

UV–vis spectra were recorded in ethanol solution by Perkin–Elmer Lambda 20 UV–vis spectrophotometer (concentration is 5×10^{-5} mol L⁻¹ in terms of thioxanthone moieties).

Fluorescence spectra were recorded in ethanol solution by Perkin–Elmer LS50B luminescence spectrophotometer (concentration is 2×10^{-5} mol L⁻¹ in terms of thioxanthone moieties, $\lambda_{\text{ex}} = 400$ nm).

Transient absorption spectra were determined using a Nd:YAG laser, which provides 355 nm pulses with a duration of 5 ns and a maximum energy of 120 mJ/pulse. The laser and analyzing light beam passed perpendicularly through a quartz cell. The transmitted light entered a monochromator equipped with a R955 photomultiplier. The signals were collected using an HP54510B digital oscilloscope and then transferred to computer to be treated.

2.4. Photopolymerization

Photopolymerization kinetic studies were performed dilatometrically in a recording dilatometer by irradiating about 12 ml of 3.0 M MMA DMF solution at 30 °C. The concentration of photoinitiator is 0.001 M. The light source was a high-pressure Hg lamp (400 W, wavelength is 365 nm), set at a distance of 40 cm from the sample. The polymerization rate (R_p) was determined below 10% conversion where R_p is almost independent of the conversion.

2.5. Photo-DSC

The photopolymerization of TMPTA was carried out by DSC 6200 (Seiko Instrument Inc) photo-DSC with incident light of 365 nm. Approximately 1.0 mg sample mixture was placed in the aluminum DSC pans.

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 conversion of the vinyl groups (C) or the extent of reaction could be determined according to:

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

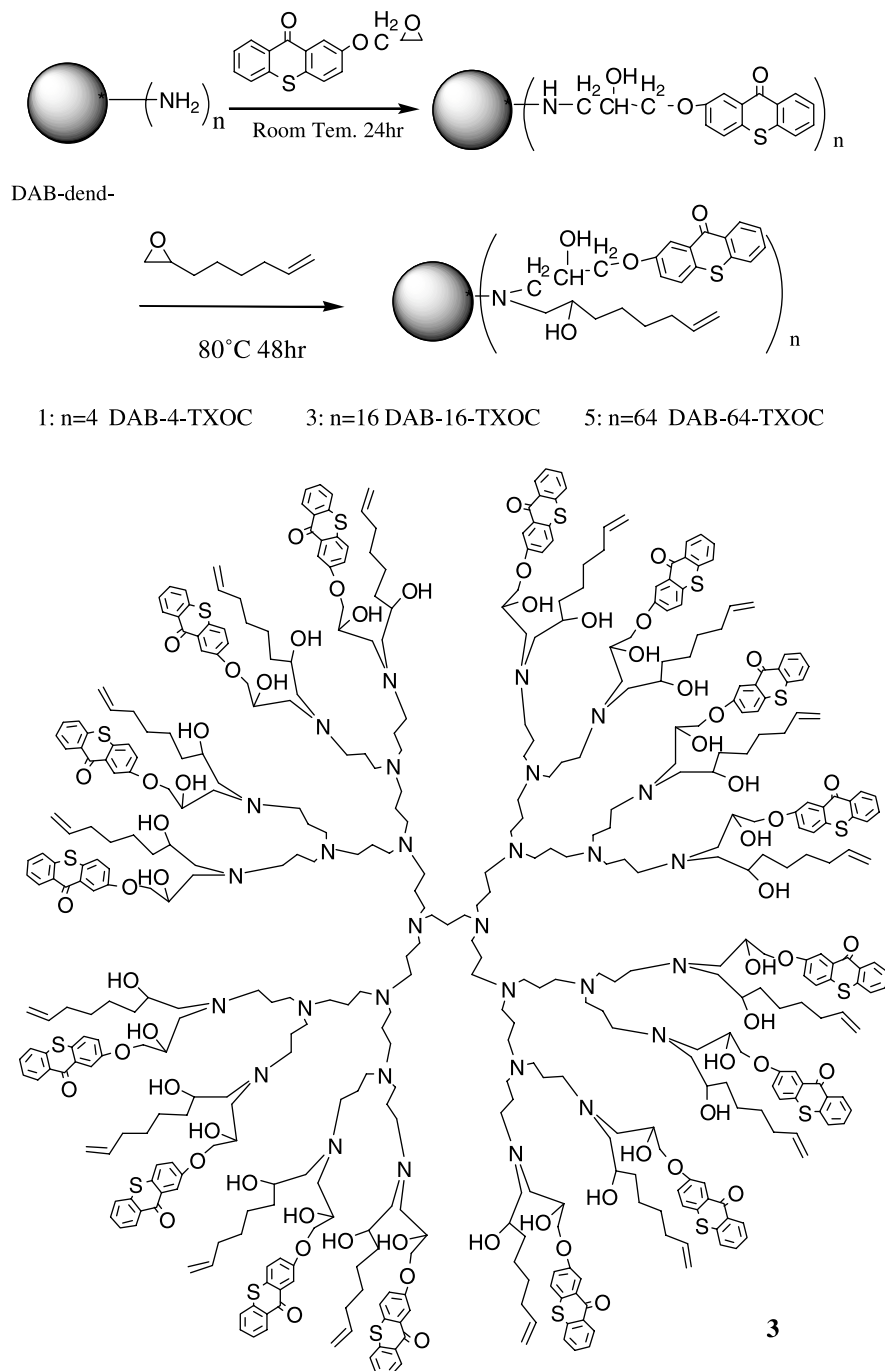
where ΔH_t is the reaction heat evolved at time t, and $\Delta H_0^{\text{theor}}$ is the theoretical heat for complete conversion. $\Delta H_0^{\text{theor}} = 86$ kJ/mol for an acrylic double bond [24]. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:

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

3. Results and discussion

Three kinds of copolymeric dendritic macrophotoinitiators DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC were synthesized according to Scheme 1. Because of different reactivity of epoxy group to primary and second amine group ($-\text{NH}_2$ and $-\text{NH}$), the thioxanthone and octane moieties can be introduced into periphery of PPI through two steps. We can introduce the thioxanthone moieties into periphery of PPI at room temperature to synthesize DAB-*n*-TX (According to Ref. [22]), and then introduced 1,2-epoxy-7-octene into DAB-*n*-TX

through the reaction between the epoxy group and $-\text{NH}$ group to synthesize DAB-*n*-TX-OC. Compared with DAB-*n*-TX, the occurrence of signals related to $\text{CH}=\text{CH}_2$ and the disappearance of signals related to $-\text{CH}_2-\text{NH}$ in NMR spectra of DAB-*n*-TX-OC, were considered as the evidence of the introduction of 1,2-epoxy-7-octene into DAB-*n*-TX. The component of DAB-*n*-TX-OC were determined by the elemental analysis data (nitrogen content/sulfur content) and ^1H NMR spectra (signal related to benzene ring/signal related to $-\text{NCH}_2$ /signal related to $-\text{CH}=\text{CH}_2$). The results show that the TX moieties/OC moieties/the peripheral amino groups is 1:1:1 in



Scheme 1.

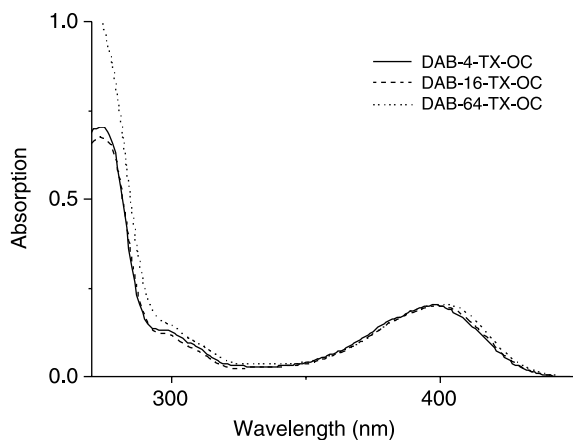


Fig. 1. UV-vis absorption spectra of DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC in ethanol solution (concentration = 5×10^{-5} mol L $^{-1}$ in terms of thioxanthone moieties).

DAB-4-TX-OC and DAB-16-TX-OC, and about 0.9:1:1 in DAB-64-TX-OC.

Fig. 1 shows UV-vis spectra of DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC in ethanol solution, which exhibit the usual characteristic absorption of TX derivatives [15]. The maximums of absorption (λ_{\max}) are found to be 399, 400 and 402 nm, respectively, and red-shift slightly with the increase of PPI's generation. Although the fluorescence emission of these dendritic photoinitiators has a similar maximum at 460 nm, the intensity obviously decreases with the increase of PPI's generation according to Fig. 2. This indicates that the excited singlet state of TX is most efficiently quenched by coinitiator amine in DAB-64-TX-OC, and the energy transfer between the excited state of TX and amine is the most effective in this system. With the increase of PPI' generation, the polymeric and dendritic effect become more obvious [25–28], and the TX moieties are surrounded by coinitiator amine of higher concentration, which leads to higher efficiency in quenching of the excited state of TX and higher polar microenvironment of TX. Consequently, the absorption maximum red-shifts and the fluorescent emission decreases with the increase of PPI' generation. Fig. 3 shows

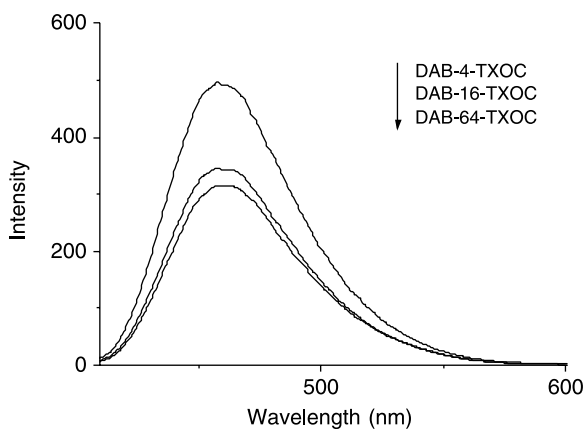


Fig. 2. Fluorescence spectra (concentration = 2×10^{-5} mol L $^{-1}$ in terms of thioxanthone moieties, $\lambda_{\text{ex}} = 400$ nm) for DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC in ethanol solution.

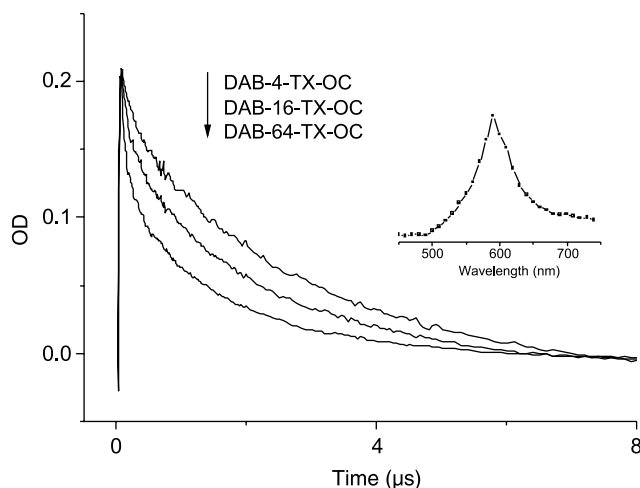


Fig. 3. Triplet decay of DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC, monitored at 600 nm, in ethanol solution (concentration = 5×10^{-4} mol L $^{-1}$ in terms of thioxanthone moieties); insert, transient absorption spectra obtained from 355 nm laser flash photolysis of DAB-64-TX-OC.

the triplet decay of three copolymeric dendritic photoinitiators in ethanol solution. The maximum of absorption is at about 600 nm, which is similar to the triplet-triplet absorption of other TX derivatives. From DAB-4-TX-OC to DAB-64-TX-OC, the lifetime of triplet state (τ) decreases, which shows that the triplet state of TX was quenched by amine more and more efficiently. This is in good agreement with the UV-vis and fluorescence measurement.

By the incident light, TX moieties of ground state can be excited. The excited state can then transfer energy to coinitiator amine to produce two kinds of radicals: one from TX (ketyl-type radical) and the other from amine (amine radicals). The photopolymerization of vinyl monomers is usually initiated by the amine radicals and the ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron [29]. Therefore,

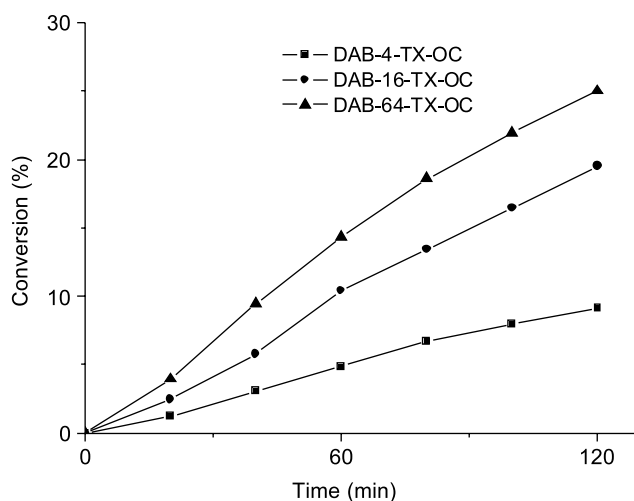


Fig. 4. Conversion versus time curves for the polymerization of MMA in DMF solution, photoinitiated by DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC at 30 °C. The photoinitiator concentration is 0.001 M in terms of thioxanthone moieties and [MMA] is 3 M.

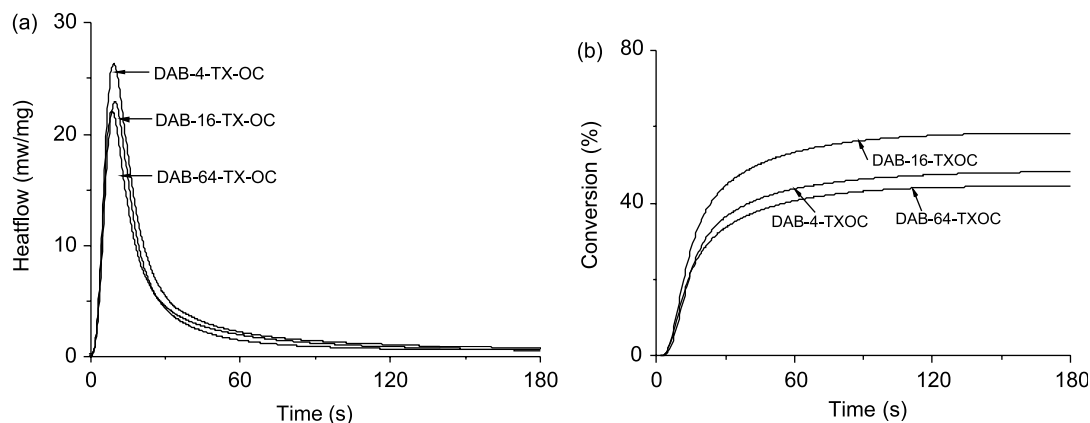


Fig. 5. (a) Photo-DSC profiles; (b) conversion versus time, for photopolymerization of TMPTA initiated by DAB-4-TX-OC, DAB-16-TX-OC and DAB-64-TX-OC, cured at 25 °C by UV light with an intensity of 50 mW/cm² ([PI]=0.01 M).

the energy transfer between the excited state of TX and amine is very associative with the number of radicals, which determines the photopolymerization rate. The photochemical properties of DAB-*n*-TX-OC systems are clearly reflected in the photopolymerization of low viscosity systems, such as MMA. Fig. 4 is conversion versus time for photopolymerization of MMA initiated by DAB-*n*-TX-OC. From DAB-4-TX-OC to DAB-64-TX-OC, the conversion and polymerization rate increase. This can be ascribed to more efficient quenching of TX excited state by amine to generate more radicals with the increase of PPI's generation.

The photo-DSC profiles of the polymerization of TMPTA for these three copolymeric dendritic systems are shown in Fig. 5(a). This polymerization behavior is controlled by diffusion and similar to other multifunctional monomers [30–34]. Fig. 5(b) shows the conversion versus time profile. It is found that DAB-16-TX-OC has the highest efficiency in the photopolymerization of TMPTA, which is different from the photopolymerization of MMA. This may be ascribed to the different structure between TMPTA and MMA. Compared with the photopolymerization of MMA in DMF solution, the bulk photopolymerization of TMPTA become diffusion-controlled [30,31] and the mobility of radicals is very important to polymerization, due to the high crosslinking density and viscosity of multifunctional monomer TMPTA. As to DAB-4-TX-OC and DAB-16-TX-OC, the mobility of DAB-64-TX-OC maybe restricted, which leads to the lowest conversion rate although the energy transfer is the most effective in DAB-64-TX-OC. Because the volumes of both DAB-4-TX-OC and DAB-16-TX-OC are small, the number of radicals may determine the polymerization rate in these two systems. Therefore, the polymerization rate for DAB-16-TX-OC is greater, which leads to the higher conversion due to the free volume effect [34].

4. Conclusions

In this article, we synthesized three kinds of copolymeric dendritic photoinitiator by introducing TX and OC moieties into the periphery of PPI, and studied the photopolymerization

of monofunctional monomer MMA and trifunctional monomer TMPTA initiated by the three macrophotoinitiators through dilatometer and photo-DSC. With the increase of PPI's generation, the fluorescence emission intensity and the lifetime of the triplet state for TX decreases. Photopolymerization results show that different photoinitiators exhibit different behavior towards different monomers: DAB-64-TX-OC is the most efficient for MMA, and DAB-16-TX-OC is the most efficient for TMPTA.

Acknowledgements

The authors express their gratitude to the Ministry of Science and Technology of China (NO: 2004AA33H010), Ministry of Education of China (Kuashiji Scholar Project) and the Science and Technology Commission of Shanghai Municipal Government for their financial support.

References

- [1] Fouassier JP. Photoinitiation, photopolymerization, and photocuring fundamentals and applications. New York: Hanser; 1995.
- [2] Decker C. Prog Polym Sci 1996;21:593.
- [3] Przyjazna B, Kucybala Z, Paczkowski J. Polymer 2004;45:2559.
- [4] Grotzinger C, Burget D, Jacques P, Fouassier JP. Polymer 2003;44:3671.
- [5] Dursun C, Degirmenci M, Yagci Y, Jockusch S. Polymer 2003;44:7389.
- [6] Angiolini L, Caretti D, Salatelli E. Macromol Chem Phys 2000;201:2646.
- [7] Corrales T, Catalina F, Peinado C, Allen NS. J Photochem Photobiol A: Chem 2003;159:103.
- [8] Sarker AM, Sawabe K, Strehmel B, Kaneko Y, Neckers DC. Macromolecules 1999;32:5203.
- [9] Angiolini L, Caretti D, Corell E, Carlini C, Rolla PA. J Appl Polym Sci 1997;64:2247.
- [10] Ajayaghosh A. Polymer 1995;36:2049.
- [11] Degirmenci M, Hizal G, Yagci Y. Macromolecules 2002;36:8265.
- [12] Angiolini L, Caretti D, Carlini C, Corell E. Polymer 1999;40:7197.
- [13] Castelvetro V, Molesti M, Rolla P. Macromol Chem Phys 2002;203:1486.
- [14] Encinas MV, Rufs AM, Corrales T, Allen NS. Polymer 2002;43:3909.
- [15] Yang JW, Zeng ZH, Chen YL. J Polym Sci, Part A: Polym Chem 1998;36:2563.
- [16] Robert L. J Polym Sci, Part A: Polym Chem 2002;40:1504.
- [17] Corrales T, Catalina F, Allen NS, Peinado C. J Photochem Photobiol A: Chem 2005;169:95.
- [18] Schenning APHJ, Peeters E, Meijer EW. J Am Chem Soc 2000;122:4489.

- [19] Tsuda K, Dol GC, Gensh T, Hofkens J, Latterini L, Weener JW, et al. *J Am Chem Soc* 2000;122:3445.
- [20] Salmon A, Jutzi P. *J Organomet Chem* 2001;637:595.
- [21] Angiolini L, Caretti D, Carlini C. *J Appl Polym Sci* 1994;51:133.
- [22] Jiang XS, Yin J. *Macromolecules* 2004;37:7850.
- [23] Jiang XS, Yin J. *J Appl Polym Sci* 2004;94:2395.
- [24] Andrejewska E, Andrzejewski M. *J Polym Sci, Part A: Polym Chem* 1998;36:665.
- [25] Vogtle F, Gorka M, Hesse R, Ceroni P, Maestri M, Balzani V. *Photochem Photobiol Sci* 2002;1:45.
- [26] Pistolis G, Malliaris A. *Langmuir* 2002;18:246.
- [27] Michels JJ, Baars MWPL, Meijer EW, Huskens J, Reinhoudt DN. *J Chem Soc, Perkin Trans 2* 2000;1914.
- [28] Baars MWPL, Kleppinger R, Koch MHJ, Yeu SL, Meijer EW. *Angew Chem Int Ed* 2000;39:1285.
- [29] Anderson DG, Davidson RS, Elvery JJ. *Polymer* 1996;37:2477.
- [30] Cook WD. *Polymer* 1992;33:2152.
- [31] Cook WD. *Polymer* 1992;33:600.
- [32] Anseth KS, Wang CM, Bowman CN. *Polymer* 1994;35:3243.
- [33] Lecamp L, Youssef B, Bunel C. *Polymer* 1999;40:1403.
- [34] Yu Q, Nauman S, Santerre JP, Zhu S. *J Appl Polym Sci* 2001;82:1107.