Macromolecules **2007,** *40,* 2344−2351

Novel Photosensitive Thio-Containing Polyurethane as Macrophotoinitiator Comprising Side-Chain Benzophenone and Co-Initiator Amine for Photopolymerization

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Received July 7, 2006; Revised Manuscript Received January 25, 2007

ABSTRACT: A novel thio-containing polyurethane (PU) as macrophotoinitiator (PUIA) was synthesized through polycondensation of 3,5-diamino-4′-thiophenylbenzophenone (DATBP), hexamethylene-1, 6-diissocyanate (HDI), and *N*-methyldiethanolamine (MDEA). The beznophenone and co-initiator amine structures were successfully introduced into the backbones of PUIA. A macrophotoinitiator without co-initiator amine in polymer chain (PUI) and a macroamine (PUA) were also synthesized for comparison. FT−IR, ^{1}H NMR and GPC analyses confirmed the structures of all polymers. The UV−vis spectra of PUIA and PUI are similar and both exhibit the maximal absorption near 320 nm. ESR spectra indicate PUIA can efficiently generate free radicals. The photopolymerization of trimethylolpropane triacrylate (TMPTA) and PU prepolymer, initiated by PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA, was studied by photo-DSC. The results show that PUIA is the most efficient photoinitiator for both TMPTA and PU prepolymer. As for the polymerization of PU prepolymer, the final conversion is higher than 97%.

Introduction

Photoinitiated free radical polymerization finds extensive applications in the manufacture of printed circuits, encapsulation of electronic components, coatings, printing inks, and so forth.[1−4] This technology is based on the efficient photoinitiator systems. Compared with low molecular weight analogues, macrophotoinitiators have obtained much attention recently due to several advantages, such as low odor, nontoxicity, and compatibility improvement with formulation components.[5−16] Through introducing the photoinitiator chromophore into polymers, a large amount of macrophotoinitiators has been synthesized. These macrophotoinitiators have been classed as belonging either to photofragmenting (type I) or to hydrogen-abstracting chromophores (type II) system.[9] Most of type II macrophotoinitiators are based on benzophenone,[16−18] probably because of its relatively low cost.

Through free radical copolymerization of derivatives of chromophoric groups and the other monomers, many kinds of macrophotoinitiators were synthesized.[6,9,17,19−21] However, few of macrophotoinitiators were synthesized by polycondensation.[5,22−24] To our knowledge, macrophotoinitiator containing side-chain benzophenone synthesized by polycondensation has seldom been reported before.

Recently, much significant work has been reported about aromatic ketone systems containing thio functionalities.[8,25−28] Aside from the hydrogen-abstraction reaction, these photoinitiators may also undergo photolysis reactions at the C−S bond, resulting in the promotion of their photoefficiency.[27] However, there are few studies on thio-containing macrophotoinitiators,[29] especially through the polycondensation method. From the viewpoint of their applications, UV radiation is a well-accepted technology for the fast curing of polymeric materials.[30] Among them, UV-curable coating is one of the substitutes for the conventional solvent-based coating,[31] because of the possibility to reduce environmental pollution. Because of its unique properties in many cases, polyurethane (PU) probably is one of the most widely used UV-curable coatings. Therefore, it may be very valuable to synthesize PU type macrophotoinitiators to initiate PU prepolymers. These macrophotoinitiators can work both as efficient macrophotoinitiators and functional prepolymers due to the residual hydroxyl or amino group. For example, if they are further introduced into another UV-curable backebone as prepolymers, they may undergo self-initiation upon UV irradiation. Moreover, this PU type photoinitiator may also have good compatibility to PU-based photocuring systems.

In this context, taking into account of the advantages of macrophotoinitiators and their applications in UV-curable systems, we provide a new idea to achieve functional PU type macrophotoinitiators. Through polycondensation of a novel diamine monomer of 3,5-diamino-4′-thiophenylbenzophenone (DATBP), hexamethylene-1,6-diissocyanate (HDI), and *N*-methyldiethanolamine (MDEA), we obtained a PU type macrophotoinitiator containing side-chain benzophenone, thio group and tertiary amine in the same macromolecule (PUIA). UV−vis and ESR spectra were studied to investigate their photochemical behavior. Two representative types of monomer with different functionality, a trifunctional trimethylolpropane triacrylate (TMPTA) and a difunctional PU prepolymer, were chosen to be initiated by PUIA through differential scanning photocalorimetry (photo-DSC). In order to investigate the influences of co-initiator amine on the photopolymerizaton, macrophotoinitiator without co-initiator amine in polymer chain

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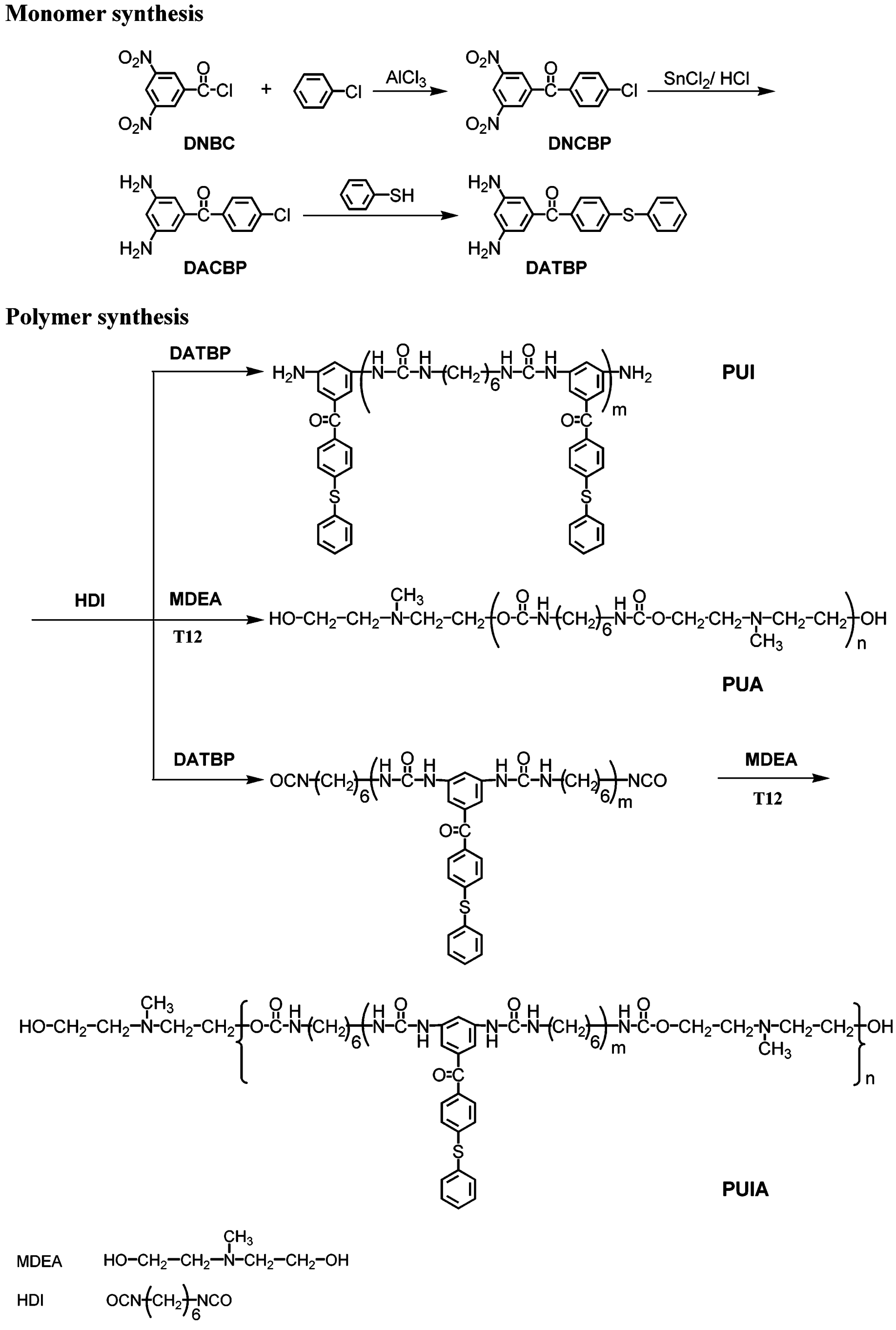
10.1021/ma0615304 CCC: \$37.00

Scheme 1. Synthesis Routes for Macrophotoinitiators



(PUI) and macroamine (PUA) were also synthesized for comparison.

Experimental Section

Materials. Chlorobenzene, anhydrous aluminum chloride, stannous chloride, concentrated hydrochloric acid, *N*-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF), N, *N*-dimethylformamide (DMF), anhydrous potassium hydroxide (KOH), dibutyltindilaurate (T12), (from Medicine Group of China), 3,5-dinitrobenzoyl chloride (DNBC) (from Taixing Summy Fine Chemical Company), thiophenol (from Zhejiang Shou&Fu Chemical Company), hexamethylene-1,6-diissocyanate (HDI) (from Fluka), PU prepolymer (UA-4200, CAS No. 199875-93-9, from Shin-Nakamura Chemical Co. Ltd), *N*-methyldiethanolamine (MDEA) (from Kewang Chemical Reagent Company), trimethylolpropane triacrylate (TMPTA) (from Nantong Litian Chemical Company) were used as received. Other chemicals are of analytical grade except as noted.

Monomer Preparation. Synthesis of 3,5-Dinitro-4′-chlorobenzophenone (DNCBP). DNBC (23 g, 0.10 mol) and $AlCl_3$ (17.4 g, 0.13 mol) were added into a three-necked flask with magnetic stirring under an ice−water bath, and then 12 mL of chlorobenzene was added dropwise by a constant pressure funnel in 30 min. After the addition was complete, the mixture was further reacted for 1 h. Then the mixture was slowly heated to 70 °C under reduced pressure. When there was no gas emitted, it was cooled to room temperature before being poured into 1 L of an ice−water solution of 4 M HCl aqueous solution. The precipitate was filtered and washed with a large amount of water. The crude product was recrystallized from mixed solvent of chloroform and cyclohexane, and dried under vacuum at 50 °C for 48 h to yield 20.5 g of white DNCBP. Yield: 67.0%.

Mp: 171.6 °C (DSC in N_2). EIMS (70 eV) *m*/*e*: 305. ^{1}H NMR ([-d_6] DMSO, 400 MHz): δ = 9.03−9.02 (1H, aromatic), 8.77−8.76 (2H, aromatic), 7.86−7.84(2H, aromatic), 7.68−7.65 (2H,

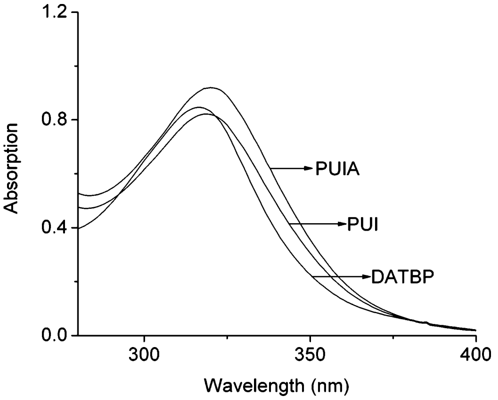


Figure 1. UV−vis absorption spectra of PUIA, PUI, and DATBP in chloroform solution. (The concentration is 5 × 10^{-5} M in term of benzophenone moieties).

Table 1. Absorption Properties of PUIA, PUI, and DATBP in Chloroform Solution

photoinitiator[a]	λ_{max} (nm)	$\epsilon \times 10^{-4}$ (L $mol^{-1}cm^{-1}$)
PUIA	320	1.808
PUI	319	1.643
DTABP	316	1.588

[a] The photoinitiator concentration is 5 × 10^{-5} M in terms of benzophenone moieties.

aromatic). FT−IR (KBr, cm^{-1}): 1344 (NO_2), 1668 (C═O), 728 (Cl). Anal. Calcd for $C_{13}H_7ClN_2O_5$: C, 50.92; H, 2.30; Cl, 11.56; N, 9.14. Found: C, 50.92; H, 2.26; Cl, 11.57; N, 9.07.

Synthesis of 3,5-Diamino-4′-chlorobenzophenone (DACBP). A suspension of 30.6 g (0.10 mol) of DNCBP and 120 mL of THF in a three-necked flask was heated to reflux with magnetic stirring under a nitrogen atmosphere. A solution of 135 g (0.60 mol) of $SnCl_2{\cdot}2H_2O$ in 135 mL of concentrated hydrochloric acid was added dropwise over 1.5 h. After the addition was completed, the mixture was further refluxed for 8 h, and then cooled to room temperature. The mixture was condensed under reduced pressure to remove most of the solvent before pouring it into 600 mL of 3 N HCl aqueous solution. The solution was then filtered to remove the undissolved substance, and ammonia water was added dropwise to the filtrate until the pH value is over 7. The precipitate was collected by filtration and washed with a large amount of water. The crude product was recrystallized from mixed solvent of water and 2-propanol, and dried under vacuum at 50 °C for 48 h to yield 14.1 g of yellow DACBP. Yield: 57.2%.

Mp: 159.6 °C (DSC in N_2). EIMS (70 eV) *m*/*e*: 246. ^{1}H NMR ([-d_6] DMSO, 400 MHz): δ = 7.67−7.65 (2H, aromatic), 7.58−7.56 (2H, aromatic), 6.11−6.10 (2H, aromatic), 6.04−6.03 (1H, aromatic), 5.04 (4H, NH_2). FT−IR (KBr, cm^{-1}): 3218, 3342 (NH_2), 1644 (C═O), 758 (Cl). Anal. Calcd for $C_{13}H_{11}ClN_2O$: C, 63.29; H, 4.49; Cl, 14.37; N, 11.36. Found: C, 63.18; H, 4.52; Cl, 14.45; N, 11.28.

Synthesis of 3,5-Diamino-4′-thiophenylbenzophenone (DATBP). A three-necked round-bottom flask containing 11.0 g (0.10 mol) of thiophenol, 24.60 g (0.10 mol) of DACBP, 6.72 g (0.11 mol) of KOH, 15 mL of toluene and 40 mL of *N*-methyl-2-pyrrolidone (NMP) was equipped with a nitrogen pad and a Dean−Stark trap. The mixture was heated at 130 °C for 3 h to strip off most of toluene to dehydrate the system, and then the temperature was kept at 170−175 °C for additional 3 h. After cooled down to ambient temperature, the resultant viscous solution was filtered to remove most of the salt before being poured into 600 mL of 3 N HCl aqueous solution. The solution was filtered again to remove the undissolved substance, and then ammonia water was added dropwise to the filtrate until the pH value is over 7. The precipitate was collected by filtration and washed with a large amount of water. The crude product was recrystallized from mixed solvent of water and ethanol, and dried under vacuum at 50 °C for 48 h to yield 18.20 g DATBP. Yield: 56.8%.

Mp: 159.8 °C (DSC in N_2). EIMS (70 eV) *m*/*e*: 320. ^{1}H NMR ([-d_6] DMSO, 400 MHz): δ = 7.62−7.60 (2H, aromatic), 7.52−7.44 (5H, aromatic), 7.26−7.24 (2H, aromatic), 6.30−6.29 (2H, aromatic), 6.22−6.21 (1H, aromatic), 6.08−6.04 (4H, NH_2). FT−IR (KBr, cm^{-1}): 3362 (NH_2), 1642 (C═O), 1080 (C−S). Anal. Calcd for $C_{19}H_{16}N_2OS$: C, 71.22; H, 5.03; N, 8.74; S, 10.01. Found: C, 71.42; H, 5.14; N, 8.68; S, 9.97.

Polymer Preparation. Synthesis of Macrophotoinitiator Containing Side-Chain Benzophenone (PUI). In a three-necked flask containing 0.908 g (5.40 mmol) of HDI and 10 mL of DMF was equipped with magnetic stirring under nitrogen atmosphere, a solution of 1.922 g (6.00 mmol) of DATBP in 10 mL of DMF was added dropwise through a dropping funnel in 10 min. The mixture was stirred at room temperature for 1 h and then it was heated at 50 °C for additional 1 h. After the reaction had cooled down to ambient temperature, the resultant solution was poured into 10-fold diluted aqueous solution of ammonia water. The solution was filtered to give yellow product, which was dried in vacuo to obtain macrophotoinitiator (PUI).

PUI: $M_n = 8.6 \times 10^3$, $M_w/M_n = 1.65$ (determined by GPC using DMF as eluent). ^{1}H NMR ([-d_6] DMSO, 400 MHz): δ = 8.66 (4H, NH), 7.72 (2H, aromatic), 7.65−7.45 (5H, aromatic), 7.34 (2H, aromatic), 7.25 (2H, aromatic), 6.10 (1H, aromatic), 3.02 (4H, CH_2), 1.37−1.26 (8H, CH_2). FT−IR (KBr cm^{-1}): 3358 (N−H), 2928, 2858 (CH_2), 1690 (C═O of −HN−C(═O)−), 1650 (C═O of Ar−C(═O)−Ar), 1080 (C−S).

Synthesis of Macroamine (PUA). A solution of 1.430 g (12.00 mmol) of MDEA, 1.816 g (10.80 mmol) of HDI and a drop of T12 in 15 mL of DMF were added in a three-necked flask with magnetic stirring under nitrogen atmosphere. The mixture was heated at 60 °C for 5 h and then poured into 10-fold diluted aqueous solution of ammonia water. The precipitate was collected by filtration and washed twice with water and dried in vacuo to obtain white polyurethane containing tertiary amine (PUA).

PUA: $M_n = 7.0 \times 10^3$, $M_w/M_n = 1.24$ (determined by GPC using DMF as eluent). ^{1}H NMR ([-d_6] DMSO, 400 MHz): δ = 7.05 (2H, NH), 3.97−3.96 (4H, CH_2), 2.92−2.90 (4H, CH_2), 2.54−2.51 (3H, NCH_3), 2.49−2.47 (2H, CH_2), 1.33 (4H, CH_2), 1.91(4H, CH_2). FT−IR (KBr, cm^{-1}): 3330 (NH), 2938, 2858 (CH_2), 1686 (C═O of −HN−C(═O)−), 1050 (N−C).

Synthesis of Macrophotoinitiator Containing Side-Chain Benzophenone and Co-Initiator Amine (PUIA). A three-necked flask containing 1.009 g (6.00 mmol) of HDI and 10 mL of DMF was equipped with magnetic stirring under nitrogen atmosphere, a solution of 0.961 g (3.00 mmol) of DATBP in 10 mL of DMF was added dropwise through a dropping funnel in 10 min and stirred at room temperature for 1 h, and then the mixture was heated at 50 °C for additional 1 h. After the reaction had cooled down to ambient temperature, a solution of 0.536 g (4.5 mmol) MDEA in 5 mL of DMF was added. The mixture was kept at 60 °C for 5 h. The resultant solution was poured into 10-fold diluted aqueous solution of ammonia water. The solution was filtered to give yellow product, which was dried in vacuo to obtain macrophotoinitiator containing co-initiator amine.

PUIA: $M_n = 5.1 \times 10^3$, $M_w/M_n = 1.35$ (determined by GPC using DMF as eluent). ^{1}H NMR ([-d_6] DMSO, 400 MHz): δ = 8.53 (4H, NH), 7.67−7.63 (2H, aromatic), 7.52 (2H, aromatic), 7.45 (2H, aromatic), 7.33 (1H, aromatic), 7.25−7.24 (2H, aromatic), 7.08−7.07 (2H, aromatic), 6.10−6.08 (1H, aromatic), 3.95 (4H, CH_2), 3.02−2.84 (8H, CH_2), 2.52−2.48 (3H, NCH_3), 2.41−2.39 (4H, CH_2), 1.35−1.19 (12H, CH_2). FT−IR (KBr, cm^{-1}): 3344 (NH), 2928, 2854 (CH_2), 1700 (C═O of −HN−C(═O)−), 1652 (C═O of Ar−C(═O)−Ar), 1078 (C−S). Anal. Calcd for PUIA: C, 61.09; H, 7.18; N, 12.57; S, 3.84. Found: C, 61.12; H, 7.09; N, 12.51; S, 3.82.

Measurements. Physicochemical Measurements. Molecular weights were determined by gel permeation chromatography (GPC) on a Perkin-Elmer Series 200 apparatus on the basis of linear polystyrene (PS) standards. DMF was used as eluent.

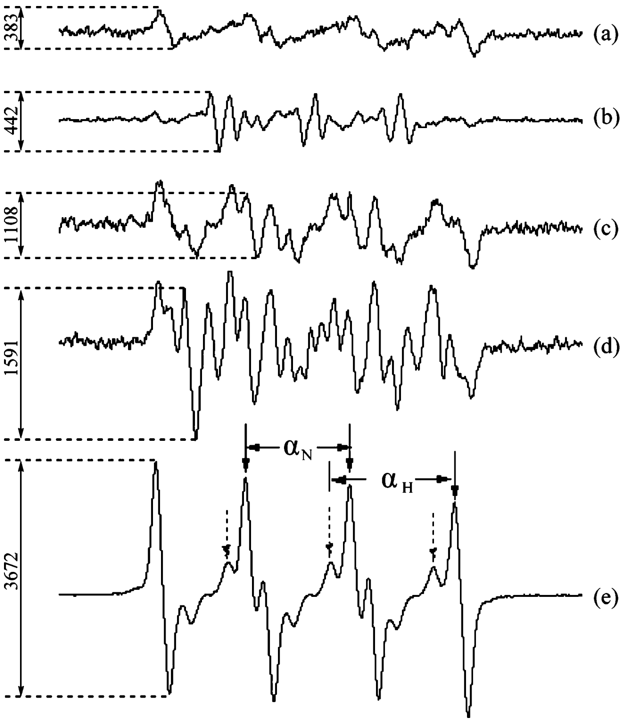


Figure 2. ESR spectra of (a) DATBP/MDEA, (b) DATBP/PUA, (C) PUI/PUA, (d) PUI/MDEA, and (e) PUIA in dichloromethane, irradiated for 5 min.

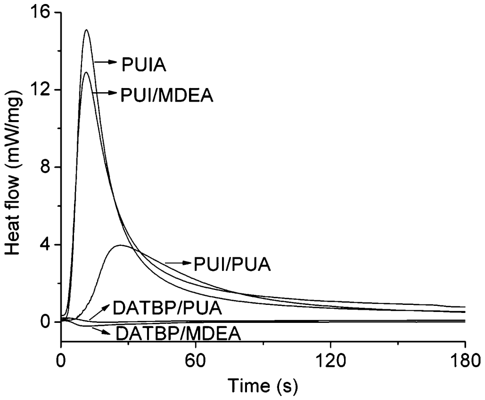


Figure 3. Photo-DSC profiles for polymerization of TMPTA initiated by PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA systems, cured at 25 °C by UV light with an intensity of 50 mW/cm^2 (the photoinitiator concentration is 0.02 M in terms of benzophenone moieties).

^{1}H NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with DMSO-d_6 as the solvent.

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

Elemental analysis was conducted on an Elementar Varioel apparatus.

Mass spectra were recorded on a HP5989A mass spectrometer at 70 eV.

UV−vis spectra were recorded in ethanol solution by Perkin-Elmer Lambda 20 UV−vis spectrophotometer.

Electron spin resonance (ESR) experiments were carried out with a Bruker EMX EPR spectrometer at 9.77 GHz with a modulation frequency of 100 kHz with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) as radical capturing agent. A high-pressure mercury lamp was used for irradiation in the ESR spectrometer cavity. The concentration of photoinitiators dissolved in dichloromethane were 1×10^{-3} M. 0.5 mL of each sample was transformed into a quartz ESR tube and then purged with nitrogen to remove oxygen.

Photocalorimetry (Photo-DSC). The photopolymerization of TMPTA was carried out by DSC 6200 (Seiko Instrument Inc) photo-DSC according to reference.[7] An approximately 2 mg sample mixture was placed in the aluminum DSC pans.

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 $\Delta H_o^{\text{theor}}$ is the theoretical heat for complete conversion. $\Delta H_o^{\text{theor}} = 86$ kJ/mol for an acrylic double bond.[32] The rate of polymerization (R_p) is directly related to the heat flow (d*H*/d*t*) by the following equation:

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

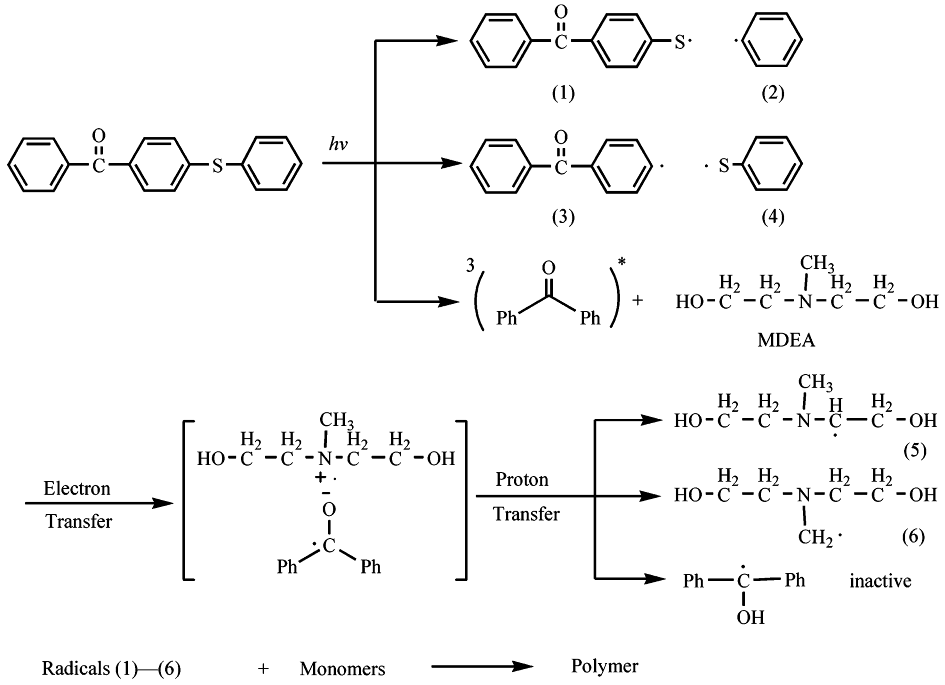
Results and Discussion

Monomer Synthesis. To achieve macrophotoinitiator with both high photoefficiency and good organosolubility, we intentionally designed a thio-containing diamine with benzophenone structure, DATBP. The monomer was synthesized through three steps as shown in Scheme 1, DNCBP was prepared by Friedel−Crafts acylation of DNBC with chlorobenzene under the catalyst of anhydrous aluminum chloride, which was then reduced with SnCl$_2$/HCl in THF to afford DACBP. DATBP was synthesized through nucleophilic substitution reaction of thiophenol with DACBP in one step by using toluene to dehydrate the system. Their structures were characterized by ^{1}H NMR and FT−IR spectra, and further confirmed by mass spectra and elemental analysis.

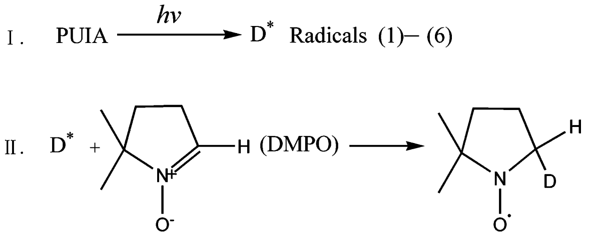
Polymer Synthesis. The purpose of this paper is to provide a new idea to achieve functional PU type macrophotoinitiators. Through the polycondensation, a novel PU containing functional hydroxyl group was successfully achieved; that is, this PU can work both as an efficient macrophotoinitiator and as a prepolymer. As macrophotoinitiators, they may greatly reduce the migration of active species. Meanwhile, as prepolymers, they can further react with other monomers. For example, if these prepolymers were used to synthesize even higher molecular weight PUs applied in UV-curable systems, they may undergo self-initiation process upon UV light without addition of any photoinitiators. This is a facile way to obtain environmental-friendly polymeric materials.

All polymers were synthesized by polycondensation according to Scheme 1. By controlling the molar ratio of isocyanate group (NCO)/amino group (NH$_2$) or hydroxyl group (OH), NH$_2$-terminated macrophotoinitiators containing side-chain benzophenone (PUI) and OH-terminated macroamine (PUA) were synthesized through the polycondensation of HDI with DATBP and MDEA, respectively. PUIA was synthesized through two steps: At first, the NCO-terminated polymer was synthesized through polycondensation of DATBP and HDI by controlling the molar ratio of NCO/NH$_2$, and then through a chain-extending reaction of NCO-terminated polymer with MDEA, co-initiator amine was successfully incorporated into the macromolecular backbone. FT−IR, ^{1}H NMR, GPC spectra, and elemental analysis confirmed the structures of all polymers. The appearance of signals related to the urethano and urea group in IR and ^{1}H NMR spectra of polymers, was considered as evidence of completion of reaction, which is also shown by the molecular

Scheme 2. Proposed Initiation Mechanisms for the Macrophotoinitiatiors and MDEA.



Scheme 3. Mechanisms for the Radicals Trapped by DMPO



weight of polymers determined by GPC. Furthermore, the elemental analyses of PUIA indicate that the ratio of photosensitive groups to amine co-initiators in the final polymers is consistent with their feeding ratio.

UV−Vis Spectra. UV−vis spectra of PUIA, PUI, and DATBP in chloroform are shown in Figure 1. Their maximum absorption (λ_{max}) and the values of molar extinction coefficient at $\lambda_{max}(\epsilon)$ are summarized in Table 1. Transitions of BPs in the region of 250−300 nm are well-known to belong to the main benzenoid $\pi-\pi^*$ type transitions.[33] These macrophotoinitiators exhibit significantly red-shifted maximal absorption near 320 nm, which may be addressed to the electron donation via the thiophenyl. As should be pointed out, the maximal absorption is important in terms of their photochemical activity. Meanwhile, they possess an absorption similar to DATBP, which shows that the macromolecular structure has no significant influence on the UV−vis absorption of benzophenone moieties in macrophotoinitiators.

ESR Spectroscopy. In order to investigate the mechanism of photoinitiation, ESR studies of PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA were carried out in dichloromethane using DMPO as radical trapper as shown in Figure 2. The mechanism of radicals trapped by DMPO was shown in Scheme 3. As shown in Figure 2e, ESR signals usually have six-line hyperfine splitting, which is explained by a triplet with α-nitrogen and a further split into a doublet with a β-proton.[5] Due to the stronger electron-donating ability of the methylene groups relative to the methyl groups in MDEA moieties, the excited triplet BP moieties may abstract hydrogen mainly from the methylene groups of MDEA moieties instead of methyl groups.[34] Therefore, radical **5** (depicted in Scheme 2) marked in Figure 2e is the main radical.

Compared with those for the macrophotoinitiators systems, the signal intensities of DATBP/MDEA and DATBP/PUA are very weak, which indicates that few free radicals were generated, and their concentrations are very low. It should be noted that the bimolecular hydrogen-abstraction reaction belongs to the nucleophilic substitution reaction. Because of the electron-donating ability of the amino group and the thiophenyl group that directly links to benzophenone structure in DATBP, the electropositivity of the carbon atom of the carbonyl group will decrease, which is certainly unfavorable for the hydrogen-abstraction reaction. As a result, it is difficult for DATBP/MDEA or DATBP/PUA systems to generate active radicals. Moreover, due to the good mobility of both low molecular weight photoinitiator and co-initiator amine, free radicals generated in these systems may be easily recombined together. Therefore, most of them might be easily quenched, resulting in low signal intensity in ESR spectrum. On the contrary, when DATBP was introduced into PUI or PUIA by the polycondensation with HDI, the amino groups were converted to urea groups. The electrophilic effect of urea groups would increase the electropositivity of carbon atom in carbonyl group, which is favorable for the hydrogen-abstraction reaction. Therefore, the macrophotoinitiators system may produce a much higher concentration of free radical than DATBP/MDEA and DATBP/PUA system. Compared with PUI/MDEA and PUI/PUA, the signal intensity of PUIA is much higher, which may be ascribed to the more efficient energy transfer along polymer chain in PUIA than the intermolecular reactions in PUI/MDEA and PUI/PUA systems. As a result, the bimolecular hydrogen-abstraction reaction rate of PUIA is much higher than the other two, resulting in high concentration of active species.

Photopolymerization of TMPTA. The photo-DSC profiles of the polymerization of TMPTA for PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA are shown in Figure 3. Their polymerization behaviors appear similar to other multifunctional monomers.[35−39] Figure 4a shows that the

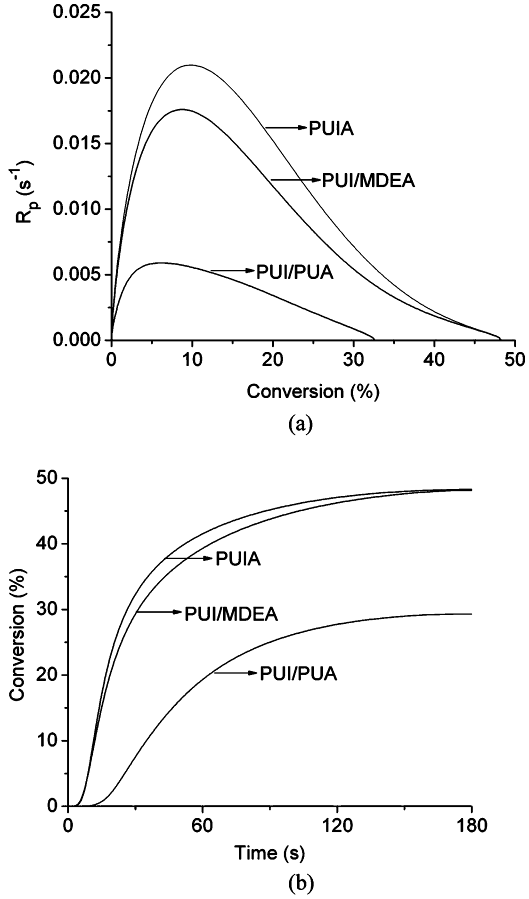


Figure 4. (a) Rate vs conversion. (b) Conversion vs time for polymerization of TMPTA for PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA systems, cured at 25 °C by UV light with an intensity of 50 mW/cm^2 (The photoinitiator concentration is 0.02 M in terms of benzophenone moieties).

Table 2. Photopolymerization of TMPTA Initiated by PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA and Cured at 25 °C by UV Light with an Intensity of 50 mW/cm^2

photoinitiator[a]	$R_{p,\max} \times 10^2$ (s^{-1})[b]	final convn (%)	$H_{\max}$ (mW/mg)[c]	$T_{\max}$ (s)[d]
PUIA	2.098	48.27	14.24	11.2
PUI/MDEA	1.760	48.13	12.91	11.1
PUI/PUA	0.590	32.56	4.35	26.0
DATBP/MDEA				
DATBP/PUA				

[a] The photoinitiator concentration is 0.02 M in term of benzophenone moieties and [BP moieties]: [MDEA moieties] = 1:1.5. [b] $R_{p,\max}$: The maximal polymerization rate. [c] $H_{\max}$: The maximal heat flow. [d] $T_{\max}$: Time to reach maximal heat flow.

conversion corresponding to the maximal of polymerization ($R_{p,\max}$) is dependent on photoinitiaitor. The data for $R_{p,\max}$ and final conversion of polymerization of TMPTA are summarized in Table 2. Under the incident light, aside from the bimolecular hydrogen-abstraction reaction, the photolysis reaction would take place at the C−S bond to form radicals **1**−**4**.[8,26] Therefore, the photopolymerization of vinyl monomers is mainly initiated by radicals **1**−**6** as shown in Scheme 2.

From Figures 3 and 4 and Table 2, PUIA is the most efficient photoinitiator for the polymerization of TMPTA. This result may be addressed to its macromolecular structure, which favors the possibility of energy transfer and hydrogen-abstraction between excited-state of BP and MDEA moieties along the polymer chain, resulting in lots of active species be generated in the photoinitiator system. This result is consistent with the

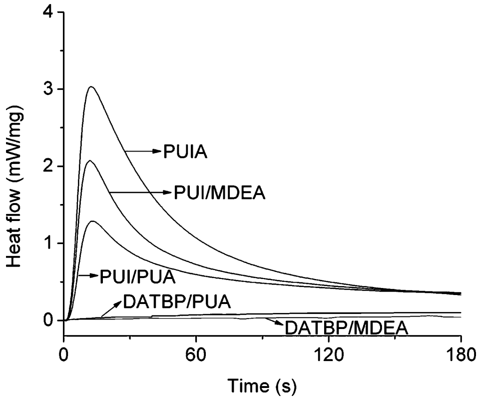
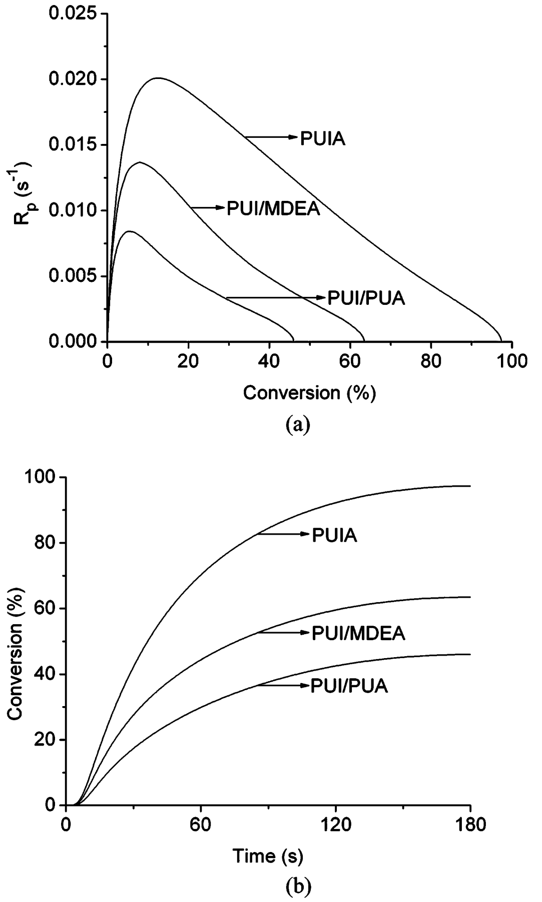


Figure 5. Photo-DSC profiles for polymerization of PU prepolymer initiated by PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA systems, cured at 25 °C by UV light with an intensity of 50 mW/cm^2 (the photoinitiator concentration is 0.02 M in terms of benzophenone moieties).

ESR analyses as mentioned above. Moreover, the steric hindrance of the macromolecular coil could unfavor the recombination reaction between propagating radicals and macroradicals, thus strongly limiting the extent of termination and preventing a reduction of the concentration of active species. As for PUI/PUA system, due to their relatively low mobility, the intermolecular H-abstraction reaction between BP moieties of PUI and MDEA moieties of PUA is difficult to take place, resulting in a relatively longer time to reach the $R_{p,\max}(T_{\max})$ and much lower final conversion. Therefore, the co-initiator macroamine may avoid the migration of low molecules in the post-cured materials; its polymerization rate and final conversion are unsatisfactory. Compared with PUI/PUA, PUI/MDEA can efficiently initiate the polymerization of TMPTA, which may be ascribed to the much higher mobility of MDEA than that of PUA. Therefore, MDEA may be easier to diffuse into the macromolecular coil of PUI, resulting in high local concentration of co-initiator around the BP moieties in PUI/MDEA system. This would certainly favor the bimolecular hydrogen-abstraction reaction.

The major differences between PUIA and PUI/MDEA systems were that the polymerization rate of PUIA is higher than that of PUI/MDEA at early stage, but slower at later stage. At an early stage, the intramolecular hydrogen-abstraction reaction of PUIA system is more efficient than the intermolecular reaction of PUI/MDEA system, leading to more active radicals generated from PUIA system and faster polymerization rate. As the polymerization goes on, the increased cross-linking level will eventually limits the mobility of both macromolecular radicals and double bonds. Therefore, the propagation reaction may become diffusion-controlled along with radical termination.[5] In this condition, compared with PUIA system, the cross-linking density of three-dimensional gel structure formed in PUI/MDEA system may be weaker due to relatively low concentration of active species generated at the early stage. As a result, the polymerization rate of TMPTA for PUI/MDEA may decrease slowly. Thus, the polymerization rate of PUI/MDEA is faster at the later stage, resulting in a high conversion of TMPTA near that of PUIA. As should be pointed out, PUIA possesses the unique advantage that it can efficiently initiate the photopolymerization without the addition of any other low molecular weight co-initiator, which may greatly reduce the migration of small molecules in the post-cured materials. Therefore, PUIA might possess a great potential for application in UV-curable systems.



(a)

(b)

Figure 6. (a) Rate vs conversion. (b) Conversion vs time for polymerization of PU prepolymer for PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA, and DATBP/PUA systems, cured at 25 °C by UV light with an intensity of 50 mW/cm^2 (the photoinitiator concentration is 0.02 M in terms of benzophenone moieties).

Table 3. Photopolymerization of PU Prepolymer Initiated by PUIA, PUI/MDEA, PUI/PUA, DATBP/MDEA and DATBP/PUA, Cured at 25 °C by UV Light with an Intensity of 50 mW/cm^2

photoinitiator[a]	$R_{p,\,max}$ × 10^2 (s^{-1})[b]	final convn (%)	H_{max} (mW/mg)[c]	T_{max} (s)[d]
PUIA	2.008	97.33	3.03	12.4
PUI/MDEA	1.367	63.47	2.07	11.8
PUI/PUA	0.841	46.01	1.29	13.2
DATBP/MDEA				
DATBP/PUA				

[a] The photoinitiator concentration is 0.02 M in term of benzophenone moieties and [BP moieties]: [MDEA moieties] = 1:1.5. [b] $R_{p,\,max}$: The maximal polymerization rate. [c] H_{max}: The maximal heat flow. [d] T_{max}: Time to reach maximal heat flow.

However, compared with macrophotoinitiators, TMPTA cannot be photoinitiated by either DATBP/MDEA or DATBP/PUA at all, which may be related to the low concentration of free radicals in these photoinitiators system from the ESR spectroscopy. Much work is now in progress to investigate this result.

Photopolymerization of PU Prepolymer. Figures 5 and 6 and Table 3 exhibit the photo-DSC profiles of PU prepolymer initiated by these photoinitiator systems. Their behaviors are similar to that in TMPTA. Compared with trifunctional monomer TMPTA (M = 296.4), the double bond content of difunctional PU prepolymer is much lower (M_w = 1300). Therefore, the maximal heat flows (H_{max}) in PU prepolymer are much lower than that in TMPTA. Meanwhile, gelation may occur at a later stage of the reaction in PU prepolymer than that in TMPTA, resulting in relatively longer time to reach the $R_{p,max}(T_{max})$ in PU prepolymer than that in TMPTA as shown in Tables 2 and 3. However, the final conversion of PU prepolymer is much higher than that of TMPTA. This result may be addressed to the good compatibility of PU type macrophotoinitiators with PU prepolymer. As for PUIA systems, the final conversion of PU prepolymer is even higher than 97%. This result indicates that this PU type macrophotoinitiator has great potential applications in PU-based UV-curable coatings.

Conclusions

In this paper, we provide a new idea to achieve functional PU macrophotoinitiators, which can work both as efficient macrophotoinitiators and prepolymers. Through the introduction of a novel thio-containing diamine with benzophenone structure into polyurethane by polycondenation, we obtain a macrophotoinitiator containing side-chain benzophenone and co-initiator amine, PUIA. UV−vis spectra showed that the macromolecular structure has no obvious effect on the UV−vis absorption compared with the parent DATBP. ESR spectra indicate that PUIA can generate free radicals more efficient than the other photoinitiator systems. Photopolymerization of TMPTA and PU prepolymer, initiated by these macophotoinitiators, were studied through photo-DSC. The results show that PUIA can efficiently initiates the polymerization of both TMPTA and PU prepolymer. As for PU prepolymer, the final conversion is higher than 97%, which indicates that this PU type macrophotoinitiator might possess greatly applied potential in PU-based UV-curable systems. However, its low molecular weight counterpart (DATBP) cannot initiate the photopolymerization. Synthesis of other macrophotoinitiators by using other diisocyantes and co-initiator amines, together with laser flash photolysis studies, are now in progress.

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

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MA0615304