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Novel chemical-bonded polymerizable sulfur-containing photoinitiators comprising the structure of planar *N*-phenylmaleimide and benzophenone for photopolymerization

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Abstract

As a continuation of the research on chemical-bonded photoinitiators comprising the structure of planar *N*-phenylmaleimide (NPMI) and benzophenone (BP), three novel polymerizable sulfur-containing photoinitiator MTPBP, CMTPBP and BMTPBP were synthesized by introducing NPMI group into benzophenone (BP). BP was selected as the reference to evaluate their photoefficiency. These novel photoinitiators possess greatly red-shifted UV maximal absorption, and their fluorescence emission varies. Three representative types of different functionality monomers, methyl methacrylate (MMA), 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA), initiated by the three novel photoinitiators were studied through dilatometer and photo-DSC using unsaturated tertiary amine *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) as the coinitiator. The results show surprising high efficiency of these chemical-bonded photoinitiators towards different monomers in contrast to BP, and they can initiate photopolymerization without the coinitiator because of the photolysis at C–S bond. The results also verify that the higher viscosity of monomers and the larger molecular size of the photoinitiators may restrict the bimolecular H-abstraction reaction.

Keywords: Polymerizable photoinitiator; Sulfur-containing initiator; N-substituted maleimide

1. Introduction

Photopolymerization science and technology is very important due to their extensive applications in the manufacture of printed circuits, encapsulation of electronic components, decorative coating, surface coating, etc. [1–6]. A crucial component in all photopolymerization systems is the photoinitiator, which absorbs light and generates active radicals to initiate the polymerization [7]. Many reaserch groups have focused on the photoinitiator systems, concerning novel photoinitiators [8]. The most studied photoinitiator systems are those in which radicals are formed by a bimolecular process consisting of an excited chromophore, such as benzophenone (BP), thioxanthone (TX), benzil, and quinone, etc. [9–11], and an amine as a coinitiator (type α photoinitiators). The performance of such system is related to high absorptivity, high photoefficiency and low odour [9]. However, only a small amount of conventional photoinitiators is actually consumed during the polymerization process, which results in undesirable effects in the post-cured material. To overcome such problems, a possible way is to develop polymerizable and polymeric photoinitiators [1,10,12–19].

Yamada firstly reported that N-substituted maleimides (MIs) could readily polymerize through a free-radical polymerization process upon exposure to light in 1968 [20]. Recently, much significant work has been done dealing with the use of MIs as photoinitiators [7,21–31], because of their ability both as photoiniatiator and polymerizable monomer, i.e. they may participate in producing radical species and also be consumed by the free-radical chain processes that they initiate (Scheme 1) [32]. Meanwhile, it is well known that the copolymerization of MIs with various vinyl monomers has been examined to improve the thermal properties of the polymers [33]. Unfortunately, the initiation rates of these systems are usually not high [29,32,33]. According to the research by Holye [32], *N*-aliphatic, alkyl, or twisted *N*-aryl MIs all initiate polymerization in the presence of transferable hydrogens oppositely to the planar *N*-aryl MIs. But it was

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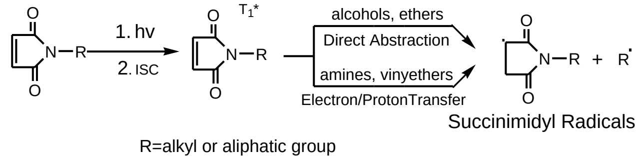
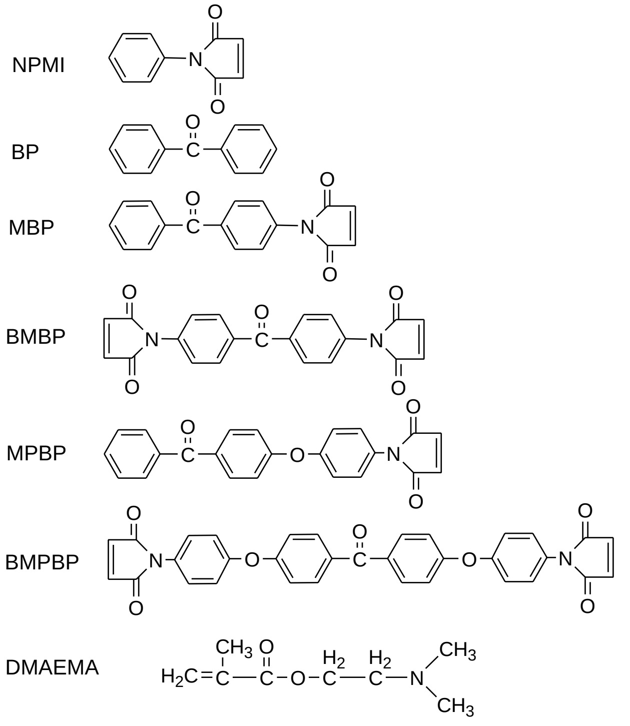


Scheme 1. Proposed initiation mechanisms for *N*-alkyl MIs and *N*-aliphatic MIs.

found that with the addition of any kind of N-substituted MIs into BP or TX system would increase their photoefficiency to a level equivalent to that of conventional cleavage photoinitiators [25,32,34,35].

In our previous work [36–38], taking into account that there might be significant interaction between MIs and BPs to enhance both of the their photoefficiency, we built the new concept of chemical-bonded photoinitiators comprising the structure of MIs and type α photoinitiators, and synthesized four polymerizable BP derivatives containing planar *N*-phenylmaleimide (NPMI) group in the same molecule (Scheme 2). The results showed these chemical-bonded photoinitiators were more efficient than BP when used in the photopolymerization of 1,6-hexanediol diacrylate (HDDA) using *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) as the coinitiator. Aside from the mutual influence between BP and NPMI in their chemical-bonded structures as in their physical mixtures, the introduction of C–S bond in their molecule instead of C–O bond will undergo photolysis reaction [12,38,39], which may further enhance their photoefficiency. In this context, three kinds of novel polymerizable sulfur-containing photoinitiators comprising the structure of planar NPMI were synthesized to further investigate such effect. BP, the most commercially used photoinitiator, was selected as the reference to evaluate their photoefficiency. UV–vis and fluorescence spectra were used to investigate their photochemical behavior. In order to reveal their efficiency towards different functionality monomers, three representative types of monomers, methyl methacrylate (MMA), 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA), were chosen to be studied through dilatometer and photo-DSC using DMAEMA as the coinitiator. At least two advantages may be expected for such system: one is that all the chemical-bonded photoinitiators and DMAEMA may participate in the photopolymerization, which will greatly reduce the migration of the species; the other is that they may exhibit high efficiency due to the mutual influence between NPMI and BP as in their physical mixtures and the photolysis reaction at C–S bond.



Scheme 2. Photoinitiators comprising the structure of planar NPMI and BP with the coinitiator of DMAEMA.

2. Experimental

2.1. Materials

4-Aminothiophenol, maleic anhydride, acetic anhydride, anhydrous potassium hydroxide, *N*-methyl-2-pyrrolidone (NMP), methyl methacrylate (MMA) (from Medicine Group of China), 4-chlorobenzophenone, 4,4′-dichlorobenzophenone (from Changzhou High-Tech Chemical Company), *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) (from Shanghai Well Tone Material Company), 1,6-hexanediol diacrylate (HDDA) (from Kewang Chemical Reagent Company), trimethylolpropane triacrylate (TMPTA) (from Nantong Litian Chemical Company) were used as received. MMA was washed with 5 wt% aqueous NaOH solution, dried over Na_2CO_3 and distilled. Other chemicals are of analytical grade except as noted.

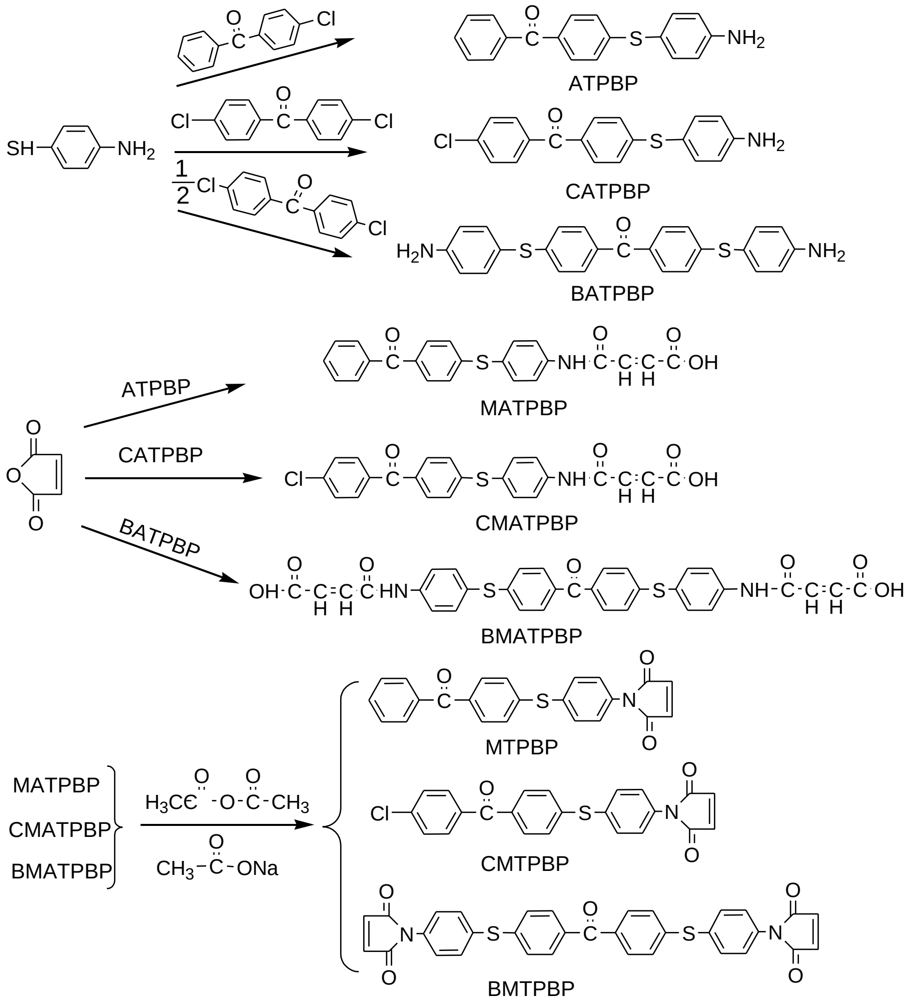
2.2. Synthesis

2.2.1. Synthesis of 4-[(4-maleimido)thiophenyl]benzophenone (MTPBP)

MTPBP was synthesized according to our previous work [38] through three steps as shown in Scheme 3 and recrystallized from methanol with the yield of 77.3%.

2.2.2. Synthesis of 4-chloro-4′-[(4-maleimido)thiophenyl] benzophenone (CMTPBP)

In a three-necked flask equipped with a nitrogen pad and a Dean–Stark trap, a mixture of 2.50 g (0.0200 mol) 4-aminothiophenol, 5.02 g (0.0200 mol) 4,4′-dichlorobenzophenone, 1.40 g (0.0250 mol) KOH were dissolved in a mixed solvent of 25 mL toluene and 25 mL NMP. The mixture was heated at 130–135 °C for 3 h, which stripped 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 filtrated to remove most of the salt and then precipitated by pouring the solution slowly into the mixture of 45 mL concentrated



Scheme 3. Synthesis routes for novel polymerizable sulfur-containing photoinitiators.

hydrochloric acid and 150 mL ice water. The precipitate was filtered out, and then washed twice with water and petroleumether, respectively. The crude product was recrystallized from mixed solvent of water, concentrated hydrochloric acid, ethanol and isopropanol, and dried under vacuum at 50 °C for 48 h to yield 3.27 g yellow to cream-colored hydrochloride of 4-chloro-4′-[(4-amino)thiophenyl]benzophenone (CATPBP). Yield: 43.5%.

Mp: 107–109 °C. EIMS (70 eV) *m/e*: 339, 250, 228, 215, 200, 167, 151, 139, 124, 111, 93, 80, 75, 65, 50, 44. ^{1}H NMR ([-d_6] DMSO, 400 MHz): $\delta = 7.73$–7.69 (2H, aromatic), 7.66–7.58 (4H, aromatic), 7.40–7.38 (2H, aromatic), 7.20–7.18 (2H, aromatic), 7.01–6.99 (2H, aromatic), 4.24 (2H, NH_2). ^{13}C NMR ([-d_6] DMSO, 400 MHz): 194.3, 144.2, 138.2, 136.3, 135.6, 134.7, 132.2, 132.1, 131.4, 129.5, 129.4, 127.8, 123.5. FT-IR (KBr): 3406 (NH), 1646 (C=O), 1588 (C=C), 1083 (C–S). Elemental analysis, calculated for $C_{19}H_{15}Cl_2NOS$: C 60.64, H 4.02, N 3.72, S 8.52. Found: C 60.84, H 4.21, N 3.43, S 7.53.

3.01 g (0.0080 mol) CATPBP hydrochloride was dissolved in 80 mL saturated sodium acetate under mechanical stirring for 2 h, then the precipitate was filtered out and washed twice with water to remove the hydrochloric acid. In a three-necked flask provided with a reflux condenser, the filtrate was dissolved in 30 mL acetone. Under mechanical stirring, a solution of 0.89 g (0.0091 mol) maleic anhydride in 10 mL acetone was added dropwise through a dropping funnel in 10 min and stirred at room temperature for additional 2 h. The mixture was poured into 150 mL ice water to precipitate yellow product. The precipitate was obtained by filtration and washed twice with water and petroleumether, respectively, and dried in vacuum to yield 2.80 g yellow 4-chloro-4′-[(4-maleic acid)-thiophenyl]benzophenone (CMATPBP), which was used in the next step without purification. Yield: 80.1%.

Mp: 153–155 °C. ^{1}H NMR ([-d_6] DMSO, 400 MHz): $\delta =$ 12.90 (1H, COOH), 10.54 (1H, NH), 7.76–7.69 (4H, aromatic), 7.67–7.57 (4H, aromatic), 7.54–7.52 (2H, aromatic), 7.22–7.20 (2H, aromatic), 6.49–6.47 (1H, –CH=), 6.31–6.29 (1H, –CH=). FT-IR (KBr): 3480 (NH), 3294 (COOH), 1717 (C=O of $-\mathrm{HN}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$), 1646 ($\mathrm{Ar}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{Ar}$), 1634 (C=O of COOH), 1589 (CH=CH), 1084 (C–S).

A mixture of 2.19 g (0.0050 mol) CMATPBP, 0.41 g (0.0050 mol) anhydrous sodium acetate and 15 mL acetic anhydride (0.0531 mol) was heated at 95–100 °C for 30 min under stirring. After cooling to room temperature, the reaction mixture was poured into a breaker filled with 60 mL cold water, then dumped the upper transparent liquid. Additional

80 mL ice water was added with vigorous stirring for 1 h. The precipitate was obtained by filtration, washed with water and petroleum ether. The product was dried under vacuum and recrystallized from ethanol to yield 1.25 g yellow CMTPBP. Yield: 59.1%.

Mp: 67–68 °C. ESIMS (70 eV) *m*/*e*: 420/423 (M + 1). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.73–7.67$ (4H, aromatic), 7.58–7.55 (2H, aromatic), 7.48–7.41 (4H, aromatic), 7.32–7.30 (2H, aromatic), 6.88–6.87 (2H, CH=CH). ^{13}C NMR ($CDCl_3$, 400 MHz): 194.6, 169.4, 143.5, 139.1, 137.0, 136.1, 134.6, 134.1, 132.6, 131.7, 131.5, 131.0, 128.9, 128.4, 127.0. FT-IR (KBr): 1716 ($-N-\overset{O}{\overset{\|}{O}}-$), 1652 ($Ar-\overset{O}{\overset{\|}{C}}-Ar$), 1588 (CH=CH), 1082 (C–S). Elemental analysis, calculated for $C_{23}H_{14}ClNO_3S$: C 65.79, H 3.36, N 3.34, S 7.64. Found: C 65.54, H 3.49, N 3.23, S 7.58.

2.2.3. *Synthesis of 4,4′-bis[(4-maleimido)thiophenyl] benzophenone (BMTPBP)*

A mixture of 5.02 g (0.0200 mol) 4,4′-dichlorobenzophenone, 5.00 g (0.0400 mol) 4-aminothiophenol, 2.80 g (0.0500 mol) KOH were dissolved in a mixed solvent of 25 mL toluene and 35 mL NMP. Work-up was similar to that given for CATPBP. The crude product was recrystallized from mixed solvent of water, concentrated hydrochloric acid, ethanol and isopropanol, and dried under vacuum at 50 °C for 48 h to yield 6.42 g yellow to cream-colored hydrochloride of 4,4′-bis[(4-amino)thiophenyl]benzophenone (BATPBP). Yield: 62.9%.

Mp: 135–137 °C. ESIMS (70 eV) *m*/*e*: 429 (M + 1), 256, 236, 215, 197. ^{1}H NMR ([-d_6] DMSO, 400 MHz): $\delta = 7.66–7.63$ (4H, aromatic), 7.50–7.47 (4H, aromatic), 7.26–7.24 (8H, aromatic). ^{13}C NMR ([-d_6] DMSO, 400 MHz): 194.4, 143.0, 135.3, 135.1, 134.6, 131.3, 130.8, 128.4, 124.9. FT-IR (KBr): 3420 (NH), 1655 (C=O), 1589 (C=C), 1084 (C–S). Elemental analysis, calculated for $C_{19}H_{16}ClNOS$: C 59.87, H 4.42, N 5.59, S 12.79. Found: C 57.69, H 4.68, N 5.15, S 12.35.

5.01 g (0.0100 mol) BATPBP hydrochloride was dissolved in 150 mL saturated sodium acetate under mechanical stirring for 2 h, and then the precipitate was filtered out and washed twice with water. In a three-necked flask provided with a reflux condenser, the filtrate was dissolved in 60 mL acetone. A solution of 2.30 g (0.0235 mol) maleic anhydride in 15 mL acetone was added dropwise in 30 min. Work-up was similar to that given for CMATPBP to yield 5.70 g yellow 4,4′-bis[(4-maleic acid) thiophenyl]benzophenone (BMATPBP). Yield: 91.3%.

Mp: 189–191 °C. ^{1}H NMR ([-d_6] DMSO, 400 MHz): $\delta =$ 12.90 (2H, COOH), 10.54 (2H, NH), 7.75–7.73 (4H, aromatic), 7.62–7.60 (4H, aromatic), 7.53–7.50 (4H, aromatic), 7.19–7.17 (4H, aromatic), 6.49–6.46 (2H, –CH=), 6.31–6.28 (2H, –CH=). FT-IR (KBr): 3445 (NH), 3315 (COOH), 1727 (C=O of $-HN-\overset{O}{\overset{\|}{C}}-$), 1656 ($Ar-\overset{O}{\overset{\|}{C}}-Ar$), 1623 (C=O of COOH), 1589 (CH=CH), 1084 (C–S).

4.16 g BMATPBP (0.0067 mol), 0.56 g (0.0068 mol) anhydrous sodium acetate and 30 mL (0.3186 mol) acetic anhydride were added into a three-necked flask. Work-up was similar to that given for CMTPBP. The product was recrystallized from mixed solvent of methanol and chloroform to yield 2.40 g yellow 4,4′-bis[(4-maleimido) thiophenyl]benzophenone (BMTPBP). Yield: 61.2%.

Mp: 98–100 °C. ESIMS (70 eV) *m*/*e*: 589/591 (M + 1), 551/553, 537/539, 464, 452, 432. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.70–7.68$ (4H, aromatic), 7.57–7.56 (4H, aromatic), 7.41–7.39 (4H, aromatic), 7.33–7.31 (4H, aromatic), 6.88 (4H, CH=CH). ^{13}C NMR ($CDCl_3$, 400 MHz): 195.0, 169.4, 143.0, 135.5, 134.6, 133.9, 132.8, 131.6, 131.0, 128.5, 126.9. FT-IR (KBr): 1715 ($-N-\overset{O}{\overset{\|}{O}}-$), 1651 ($Ar-\overset{O}{\overset{\|}{C}}-Ar$), 1588 (CH=CH), 1081 (C–S). Elemental analysis, calculated for $C_{23}H_{15}NO_3S$: C 67.33, H 3.42, N 4.76, S 10.89. Found: C 66.67, H 3.68, N 4.58, S 10.79.

2.3. *Measurement*

2.3.1. *Physicochemical measurements*

^{1}H NMR spectra were recorded on a mercury plus 400 MHz spectrometer with DMSO-d_6 or $CDCl_3$ as solvent.

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

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

Elemental analysis was conducted on an Elementary Varioel apparatus.

UV–vis spectra were recorded in chloroform solution by a Perkin–Elmer Lambda 20 UV–vis spectrophotometer.

Fluorescence spectra were recorded in chloroform solution by a Perkin–Elmer LS50B luminescence spectrophotometer.

2.3.2. *Photopolymerization*

Photopolymerization of MMA was performed dilatometerically in a recording dilatometer by irradiating about 12 mL of 4.0 M MMA solution in DMF at 40 °C. The concentration of photoinitiator is 0.002 M and [DMAEMA] is 0.008 M. The light source was a high-pressure Hg lamp (400 W), set at a distance of 30 cm from the sample. The polymerization rate (R_p) was determined below 10% conversion where R_p is almost independent of the conversion.

2.3.3. *Photocalorimetry (photo-DSC)*

Photopolymerization of HDDA and TMPTA was carried out by DSC 6200 (Seiko Instrument Inc.) photo-DSC with a high-pressure Hg lamp. The intensity of the light was measured by an Ultraviolet Radiometer (UIT-101). Approximately, 1.2 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 (only a trace of polymerizable photoinitiator system was used compared with HDDA or TMPTA, which can be omitted here). 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

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

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 [40]. The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:

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

3. Results and discussion

3.1. Synthesis

Chemical-bonded polymerizable photoinitiators comprising the structure of plannar *N*-phenylmaleimide and benzophenone were synthesized by three steps according to Scheme 3, and their structures were confirmed by spectroscopic and elemental analysis. ATPBP, CATPBP and BATPBP were synthesized through nucleophilic substitution reaction of 4-aminothiophenol with corresponding 4-chlorobenzophenone or 4,4′-dichlorobenzophenone under alkali condition, and toluene was used to dehydrate the system. By changing the molar ratio of 4,4′-dichlorobenzophenone and 4-aminothiophenol, CATPBP and BATPBP can be well acquired. Because the amino group is unstable and easy to be oxidized in air, ATPBP, CATPBP and BATPBP were all converted to their hydrochloride salts and purified through recrystallization. All the hydrochloride salts were used through pouring into weak alkali to remove the hydrochloric acid in the next step. *N*-arylmaleimide derivatives were synthesized from maleic anhydride and amine through the usual routes of two steps [41], which are particularly attractive due to ease of synthesis and obtaining high purity products.

3.2. UV–vis and fluorescence spectra

UV absorption spectra of MTPBP, CMTPBP and BMTPBP were measured in chloroform as the solvent using BP as the reference. Their maximal absorption($\lambda_{\max}$) and the logarithmic values of molar extinction coefficient at $\lambda_{\max}$ (log ε)are summarized in Table 1. The longest wavelength absorption maximal for the compounds are important in terms of their photochemical activity.

Table 1
Absorption properties of BP, MTPBP, CMTPBP and BMTPBP in chloroform solution

Photoinitiator[a]	Chloroform	
	$\lambda_{\max}$ (nm)	log ε (mol^{-1} cm^{-1} L)
BP	254	4.286
MTPBP	263	4.166
	316	4.169
CMTPBP	263	4.383
	321	4.293
BMTPBP	327	4.480

[a] The photoinitiator concentration is 5×10^{-5} M.

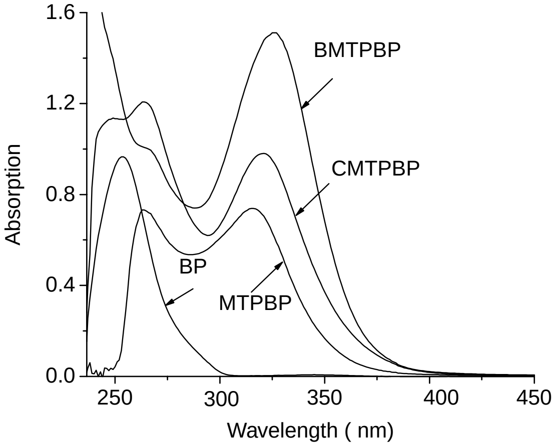


Fig. 1. UV–vis absorption spectra of BP, MTPBP, CMTPBP and BMTPBP in chloroform solution with the concentration of 5×10^{-5} M.

The three polymerizable initiators exhibit markedly different maximal absorption from BP, which are significantly red shifted as can be seen from Table 1 and Fig. 1. Transitions of BPs in the region of 250–300 nm are well known to belong to the main benzenoid π–π* type transitions [42]. The important n–π* type transitions are usually found between 300 and 350 nm because of the spin forbidden transition. The important consequence is that the molar extinction coefficient of n–π* transitions are considerately weaker than that of π–π* type transitions. The introduction of thiophenyl groups markedly red shifts their main absorption maximum to above 300 nm due to increased electron donation via the sulfur atom. This would certainly account for their increased photochemical activity during the photopolymerization.

Fig. 2 shows the fluorescence emission spectra of these chemical-bonded photoinitiators. Luminescence analysis of MTPBP and BMTPBP indicated weak fluorescence with a maximum around 360 nm, but the emission intensity of MTPBP is slightly stronger than BMTPBP. As for

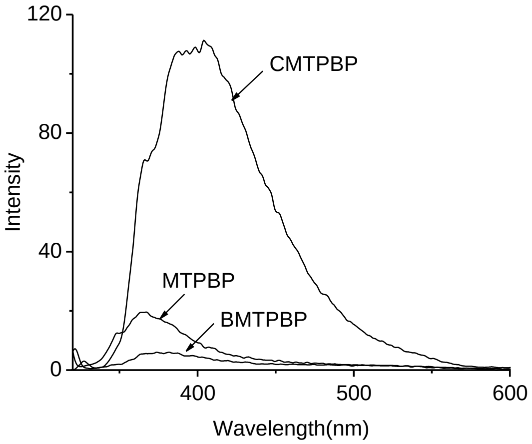


Fig. 2. Fluorescence emission spectra of BP, MTPBP, CMTPBP and BMTPBP in chloroform solution with the concentration of 5×10^{-5} M: (a) MTPBP, $\lambda_{ex}=317$ nm; (b) CMTPBP, $\lambda_{ex}=321$ nm; (c) BMTPBP, $\lambda_{ex}=327$ nm.

benzophenone itself, this suggests that there is a high rate of intersystem crossing from the singlet state to the triplet state. This result is quite consistent with our previous study [36]. Notably, the chlorine atom in CMTPBP greatly enhances its emission intensity and red shifts its maximal absorption, which is similar to other chlorine-containing BP derivatives [43]. Such differences will affect their behaviors eventually.

3.3. Photopolymerization of MMA

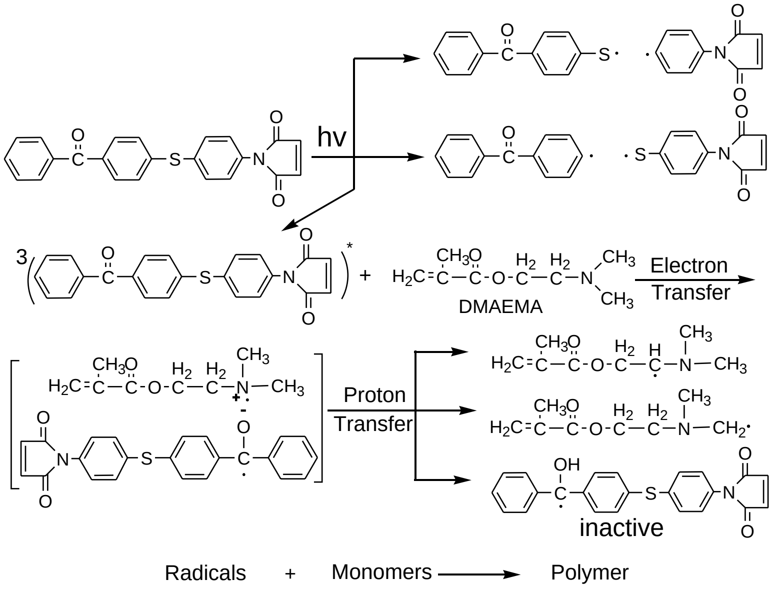
Planar NPMI in these chemical-bonded photoinitiators does not generate radicals and initiate photopolymerization as *N*-alkyl or twisted *N*-aromatic MIs do [32,37,38]. The photopolymerization initiated by MTPBP, CMTPBP and BMTPBP should be addressed to the structure of BP and the photolysis reaction at the C–S bond as other sulfur-containing BP derivatives shown in Scheme 4 [12,39,43,44]. In the presence of DMAEMA, such system produced free radicals by electron transfer from DMAEMA to excited triplet-state BP, followed by proton transfer, leading to the formation of a radical produced from a carbonyl compound (ketyl-type radical) and another radical derived from DMAEMA [45,46]. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron in comparison with amine radicals [9], from which we can know that the quantity and the activity of active amine radicals with those radicals caused by the photolysis reactions at C–S bond will determine the photopolymerization rate greatly. Because of the stronger electron-donating ability of the ethyl groups relative to the methyl groups, the excited triplet BPs may abstract hydrogen mainly from the methylene groups but not from the methyl groups of dimethylamino groups of DMAEMA [47].

Conversion of MMA vs time for these chemical-bonded photoinitiators is shown in Fig. 3. They all exhibit higher photochemical activity than BP with the coinitiator of DMAEMA, among which MTPBP is the most efficient. Because of the photolysis at the C–S bond, MTPBP, CMTPBP and BMTPBP can also initiate the photopolymerization without the coinitiator, which possess a very long induction period, indicative of low efficiency as other sulfur-containing benzophenone photoinitiators [39,43,44] as can be seen from Table 2.

The high efficiency of the chemical-bonded photoinitiators with the coinitiator in comparison with BP may be mainly addressed to two reasons: one is the red-shifted maximal absorption to BP; the other might be the efficient energy transfer from the triplet of BP group to the maleimide group and the efficient electron transfer from the DMAEMA to the excited triplet state maleimide group as in their physical mixtures of NPMI and BP [22,34]. The high photoinitiation efficiency of MTPBP may be ascribed to its smaller molecular size in contrast to BMTPBP (because the larger molecular size may limit its mobility and restrict bimolecular H-abstraction reaction) and the accelerated rate of intersystem crossing from the singlet state to the triplet state in contrast to CMTPBP, which can be seen from the fluorescence spectra.

3.4. Photopolymerization of HDDA

Figs. 4 and 5 and Table 3 exhibit the photo-DSC profiles of HDDA initiated by these photoinitiators. Compared with the polymerization of MMA, they behave significantly higher efficiency than BP with the existence of DMAEMA, and their polymerization behavior appears similar to other multifunctional monomers [48,49]. Photopolymerization of multifunctional monomers exhibits auto-acceleration induced behavior by controlled propagation and termination. However, the increased cross-linking level may limit the mobility of the



Scheme 4. Proposed initiation mechanism for the system of the polymerizable photoinitiators and DMAEMA.

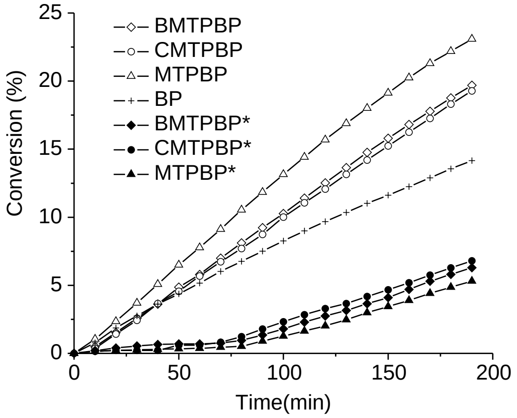


Fig. 3. Conversion vs time curves for the polymerization of MMA in DMF solution photoinitiated by BP, MTPBP, CMTPBP, and BMTPBP (the photoinitiator concentration is 2 mM, DMAEMA concentration is 8 mM and [MMA] is 4 M, *without DMAEMA).

Table 2
Photopolymerization of MMA initiated by BP, MTPBP, CMTPBP and BMTPBP (the photoinitiator concentration is 2 mM, [DMAEMA] is 8 mM and [MMA] is 4 M)

Photoinitiator	R_p (mol L^{-1} s^{-1})$\times 10^5$	Final conversion (%)
BP	5.92	14.16
MTPBP	10.02	23.09
MTPBP[a]	2.26	5.31
CMTPBP	8.38	19.28
CMTPBP[a]	2.43	6.80
BMTPBP	8.55	19.69
BMTPBP[a]	2.36	6.30

[a] Without DMAEMA.

monomers. As the mobility of the reaction system is further reduced, the reactive species become trapped and the reaction eventually stops [9].

With the coinitiator, the three chemical-bonded photoinitiators behave almost similar photochemical efficiency, and their maximal initiating rates (R_{pmax}) are almost four times of that of BP as shown in Table 3, and the final conversion is also dramatically higher than BP system. This result may be addressed to the same reason as discussed in the photopolymerization of MMA. As should be pointed out, the photopolymerization of multifunctional monomers exhibits auto-acceleration induced behavior by controlled propagation and termination, and the viscosity of the monomers will greatly affect the bimolecular H-abstraction reaction. The cross-linking of HDDA studied by photo-DSC is a very rapid process, in which gelation often occurs at an early stage of the reaction. The formation of such gel structure may restrict the diffusion and mobility of radicals [9], resulting in a very short time to reach the R_{pmax} in contrast to MMA.

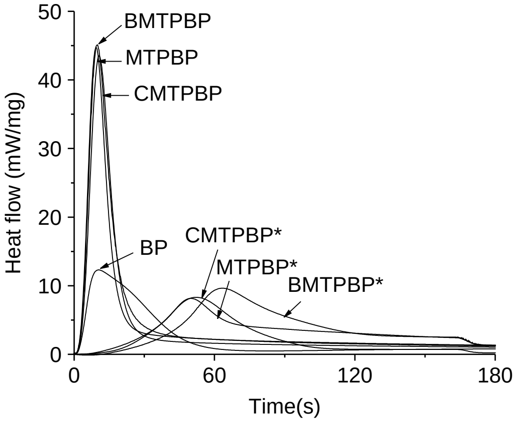


Fig. 4. Photo-DSC profiles for polymerization of HDDA initiated by BP, MTPBP, CMTPBP, and BMTPBP, cured at 25 °C by UV light with an intensity of 55 mW/cm^2 (the photoinitiator concentration is 0.04 M and [DMAEMA] is 0.16 M, *without DMAEMA).

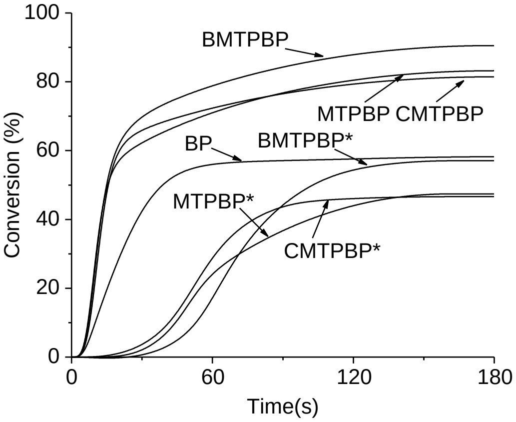


Fig. 5. Conversion vs time for polymerization of HDDA for BP, MTPBP, CMTPBP, and BMTPBP systems, cured at 25 °C by UV light with an intensity of 55 mW/cm^2 (the photoinitiator concentration is 0.04 M and [DMAEMA] is 0.16 M, *without DMAEMA).

From Figs. 3 and 4, the difference in their photoefficiency between the chemical-bonded one and BP is much stronger than in MMA. This may be mainly addressed to the reasons below: firstly, the concentration of photoinitiators is relatively much higher than that in MMA; secondly, photopolymerization of HDDA would certainly exhibit auto-acceleration induced behavior, leading to the cross-linking in a very rapid process by Photo-DSC in contrast to the photopolymerization of MMA.

MTPBP, CMTPBP and BMTPBP can also initiate the photopolymerization without the coinitiator, among which

Table 3
Photopolymerization of HDDA initiated by BP, MTPBP, CMTPBP and BMTPBP, cured at 25 °C by UV light with an intensity of 55 mW/cm^2 (the photoinitiator concentration is 0.04 M and [DMAEMA] is 0.16 M)

Photoinitiator	$R_{pmax}\times 10^2$ (s^{-1})	Final conversion (%)	T_{max} (s)
BP	1.989	58.22	10.4
MTPBP	7.250	83.21	9.4
MTPBP[a]	1.204	47.43	50.0
CMTPBP	7.054	81.44	10.6
CMTPBP[a]	1.313	46.62	52.2
BMTPBP	7.293	90.52	9.8
BMTPBP[a]	1.411	57.05	63.4

[a] Without DMAEMA.

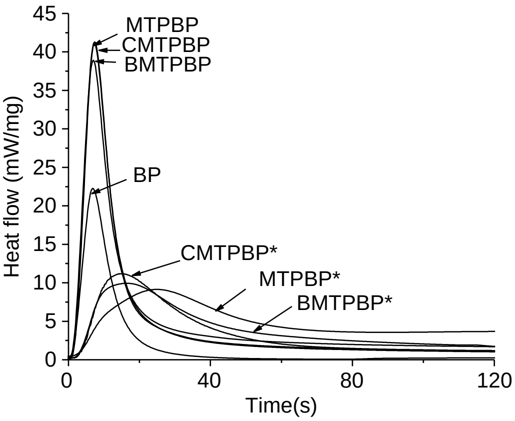


Fig. 6. Photo-DSC profiles for polymerization of TMPTA initiated by BP, MTPBP, CMTPBP, and BMTPBP, cured at 25 °C by UV light with an intensity of 55 mW/cm^2 (the photoinitiator concentration is 0.04 M and [DMAEMA] is 0.16 M, *without DMAEMA).

BMTPBP possesses the highest R_{pmax}. This may be caused by the existence of two C–S bonds in its molecule.

3.5. Photopolymerization of TMPTA

In order to further reveal the effect of molecular size of photoinitiators and the photolysis at C–S bond on photopolymerization, a trifunctional monomer of TMPTA was chosen to be initiated by the photoinitiators. From Figs. 6 and 7 and Table 4, although these initiators are still more efficient than BP with the existence of coinitiator, such difference in the increment of their R_{pmax} is smaller than HDDA polymerization system. As discussed before, the bimolecular H-abstraction reaction is greatly affected by the viscosity of monomers. Compared with difunctional monomer HDDA, the viscosity and the double bond content of trifunctional monomer TMPTA are much higher, which may lead to very high crosslinking density in the whole polymerization process of TMPTA [9]. When NPMI is introduced into the molecule of these chemical-bonded photoinitiators, their molecular size will be enlarged, and this may restrict the bimolecular H-abstraction reaction before the photolysis reaction at C–S bond and greatly affect their photoefficiency in such high viscosity system of TMPTA.

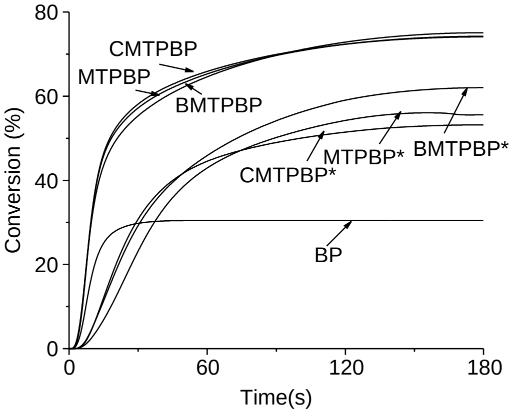


Fig. 7. Conversion vs time for polymerization of TMPTA for BP, MTPBP, CMTPBP, and BMTPBP systems, cured at 25 °C by UV light with an intensity of 55 mW/cm^2 (the photoinitiator concentration is 0.04 M and [DMAEMA] is 0.16 M, *without DMAEMA).

Table 4
Photopolymerization of TMPTA initiated by BP, MTPBP, CMTPBP and BMTPBP, cured at 25 °C by UV light with an intensity of 55 mW/cm^2 (the photoinitiator concentration is 0.04 M and [DMAEMA] is 0.16 M)

Photoinitiator	$R_{\mathrm{pmax}} \times 10^2$ (s^{-1})	Final conversion (%)	$T_{\max}$ (s)
BP	3.103	30.43	6.8
MTPBP	5.767	74.24	7.4
MTPBP[a]	1.145	55.56	25.0
CMTPBP	5.755	74.09	7.2
CMTPBP[a]	1.530	53.19	14.8
BMTPBP	5.397	75.08	7.0
BMTPBP[a]	1.350	62.03	16.4

[a] Without DMAEMA.

Interestingly, BMTPBP is slightly less efficient than MTPBP and CMTPBP although it possesses weaker fluorescence emission and larger UV maximal absorption. The higher viscosity of TMPTA and the larger molecular size of BMTPBP may lead to such result, because the bimolecular H-abstraction reaction may be restricted by higher viscosity of monomers and the lager molecular size of photoinitiators. Meanwhile, the final conversion initiated by these chemical-bonded photoinitiators without DMAEMA is higher than that of BP different from the polymerization of MMA and HDDA. From the results, we can conclude that the bimolecular H-abstraction reaction may be greatly restricted by the higher viscosity of TMPTA, and the photolysis at C–S bond here will be the mainly influencing factor on their photoefficiency.

4. Conclusions

Three kinds of highly efficient polymerizable sulfur-containing photoinitiators comprising the structure of planar NPMI and BP were synthesized, and BP was selected as the reference to evaluate their photoefficiency. The results show these photoinitiators possess greatly red-shifted UV maximal absorption, and thiophenyl group may reduce the fluorescence intensity in contrast to chlorine atom. Three representative types of monomers, monofunctional MMA, difunctional HDDA and trifunctional TMPTA, were chosen to be studied through dilatometer and photo-DSC. The results show all the photoinitiators are highly efficient using DMAEMA as the coinitiator, and they can initiate the photopolymerization without the coinitiator by the photolysis of C–S bond. The results also verify the bimolecular H-abstraction reaction is greatly affected by the viscosity of monomers and the molecular size of photoinitiators. These polymerizable photoinitiators can be consumed by the free-radical propagation or further polymerize with various vinyl monomers. There may be little difference on the copolymerizability between these polymerizable photoinitiators and NPMI because of the similarity in their structures. Copolymerization of them with DMAEMA to achieve macrophotoinitiators will be reported in our latter work. All the photoinitiators are important due to their high efficiency and the possibility in reducing the migration of the species. Synthesis of other chemical-bonded photoinitiators comprising the structure of planar NPMI and type α photoinitiators is now in progress.

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