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ARTICLE

Novel Highly Efficient Macrophotoinitiator Comprising Benzophenone, Coinitiator Amine, and Thio Moieties for Photopolymerization

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ABSTRACT: To investigate the photoefficiency differences between the macrophotoinitiator and the polymerizable photoinitiator, a novel thio-containing macrophotoinitiator P(MTPBP-*co*-DMAEMA) bearing side-chain benzophenone and coinitiator amine was synthesized through free radical copolymerization of a polymerizable photoinitiator 4-[(4-maleimido)thiophenyl]benzophenone (MTPBP) and an unsaturated coinitiator amine *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA). To determine the influences of coinitiator amine on photopolymerization, a macroamine P(DMAEMA) was also synthesized through homopolymerization of DMAEMA for comparison. FT-IR, ^{1}H NMR, and gel permeation chromatography (GPC) analyses confirmed the structures of the two polymers. The UV−vis spectra of macrophotoinitiator P(MTPBP-*co*-DMAEMA) and polymerizable photoinitiator MTPBP are similar, and both exhibit high red-shifted maximum of absorption compared with benzophenone. Photopolymerization of 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA), initiated by benzophenone/DMAEMA, MTPBP/DMAEMA, MTPBP/P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems, was studied by differential scanning photocalorimetry (photo-DSC). The results indicate that P(MTPBP-*co*-DMAEMA) is most efficient for the polymerization of both HDDA and TMPTA. As for the photopolymerization of HDDA, the final conversion runs up to 98%. However, the photoefficiency of the MTPBP/P(DMAEMA) system, with macroamine as coinitiator, is unsatisfactory.

Introduction

Conventional low-molecular-weight photoinitiators, because of the inherent disadvantages, such as odor, yellowing, poor compatibility with the UV-curable resin and migration, will usually lead to many undesirable effects in the postcured materials. In typical, only a small amount of the photoinitiator is actually consumed in the polymerization process, and the photoactive residues located in the macromolecular network can lead to premature photodegradation and yellowing. To overcome these disadvantages and attain high photoefficiency, macrophotoinitiators have recently drawn remarkable interest.[1−12] Compared with their low-molecular-weight analogues, macrophotoinitiators, because of the unique properties of macromolecular chain, can improve the compatibility in the formulation in many cases and limit the migration in the postcured materials, which is favorable for the synthesis of environmentally friendly products.[13−19] Many macrophotoinitiators are based on benzophenone derivatives,[20−24] and their photoefficiency greatly depends on the amine radicals generated by the hydrogen abstraction reaction between the triplet benzophenone moieties and the coinitiator amine.[17,25−28] Macrophotoinitiators containing thio functionalities, because of increased photoefficiency from the photolysis reaction of the C−S bond, have become very attractive for the application in the UV-curing system and have recently been studied in our lab.[21,22,29]

We previously synthesized a series of polymerizable photoinitiators containing maleimides and thio group and proposed the concept of a chemically bonded photoinitiator composed of benzophenone and maleimides.[30−32] The results indicate that the chemically bonded maleimides can dramatically promote the photoefficiency of benzophenone derivatives, especially for 4-[(4-maleimido)thiophenyl]benzophenone (MTPBP). In the photocuring process, MTPBP will participate in the copolymerization with the unsaturated resin, resulting in the disappearance of its double bond. It is therefore difficult to evaluate the contribution of maleimide to photoefficiency because it will be converted to fumarimide. Meanwhile, the polymerizable photoinitiator, of course, will be converted to macrophotoinitiator. Therefore, compared with MTPBP, its macromolecular counterpart may have a more important influence on photopolymerization, and it may be very valuable to investigate the photoefficiency differences between them. However, to the best of our knowledge, research on the photoefficiency between macrophotoinitiators and its relevant polymerizable photoinitiators has seldom been reported.[33,34]

Considering the advantages of the macrophotoinitiator and to determine the differences in photoefficiency between the macrophotoinitiator and its low-molecular-weight polymerizable counterpart, we introduce the polymerizable photoinitiator MTPBP and an unsaturated coinitiator amine *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) into the macromolecular chain through free radical copolymerization. Therefore, we obtained a macrophotoinitiator P(MTPBP-*co*-DMAEMA) with a side-chain benzophenone, thio group, and coinitiator amine in the same macromolecule. Similar to MTPBP, the unsaturated coinitiator DMAEMA will also be converted to a macromolecule in the photocuring process through homopolymerization or copolymerization with the photocurable resin or MTPBP. Therefore, we synthesized a macroamine P(DMAEMA), through

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homopolymerization of DMAEMA, to further reveal the influence of coinitiator amine on photopolymerization. UV−vis spectra were studied to investigate the photochemical behavior of the macrophotoinitiator with benzophenone and MTPBP as references. The photopolymerization of two monomers with different functionality, that is, difunctional monomer 1,6-hexanediol diacrylate (HDDA) and trifunctional monomer trimethylolpropane triacrylate (TMPTA), initiated by benzophenone/DMAEMA, MTPBP/DMAEMA, MTPBP/P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems was studied by differential scanning photocalorimetry (photo-DSC).

Experimental Section

Materials. 2,2′-Azo-bis-isobutyronitrile (AIBN; ≥99%), Tetrahydrofuran (THF; ≥99.9%), 1,4-dioxane (99.8%), *N*,*N*-dimethyl formamide (DMF; ≥99.5%), benzophenone (≥99.9%, Sinopharm Chemical Reagent), DMAEMA (≥99.5%, Shanghai Well Tone Material Company), HDDA (≥98%, Shanghai Kewang Chemical Reagent Company), and TMPTA (≥97%, Nantong Litian Chemical Company) were used as received. MTPBP was synthesized according to our previous work.[31] Other chemicals were of analytical grade except as noted.

Polymer Preparation. *Synthesis of Macroamine P(DMAEMA).* DMAEMA (3.144 g, 20.0 mmol), AIBN (32.84 mg, 0.2 mmol), and 1,4-dioxane (18 mL) were added to a 25 mL glass vial, which was submitted to several freeze−thaw cycles by dry ice. Then, the vial was placed under pressure to remove oxygen and was further purged with nitrogen for 5 min. After it was sealed under reduced pressure (1.3 KPa), the vial was kept at 85−90 °C for 72 h in the dark. We isolated the polymeric product by pouring the reaction mixture into a large excess of methanol; then, it was redissolved in chloroform and precipitated again with methanol. The solution was filtered to give white product, which was dried in vacuo at 50 °C for 48 h to yield 2.847 g macroamine P(DMAEMA). Yield: 90.6%. P(DMAEMA): $M_n = 295\,800$, $M_w/M_n = 1.51$ (determined by GPC using THF as eluent). ^{1}H NMR ($CDCl_3$, 400 MHz, δ): 3.96 (2H, $-CH_2-C(CH_3)-CO-O-$), 2.49 (2H, CH_2O), 2.20 (6H, CH_3), 1.98−1.58 (2H, $-O-CH_2-CH_2-$), 1.04−0.56 (3H, CH_3). FT-IR (KBr, cm^{-1}): 2947, 2821, 2770 (CH_3, CH_2), 1732 (C=O of −O−CO−), 1332 (C−N), 1270 (CO−O), 1150 (O−C−C).

Synthesis of Macrophotoinitiator P(MTPBP-co-DMAEMA). MTPBP (1.925 g, 5.0 mmol), DMAEMA (1.572 g, 10.0 mmol), AIBN (34.97 mg, 0.21 mmol), and 15 mL of DMF were added in sequence to a 25 mL glass vial. The pretreatment and reaction condition were similar to that of P(DMAEMA). The resultant solution was poured into a large excess of methanol to precipitate the polymeric product. The solution was filtered to give yellow product, which was dried in vacuo at 50 °C for 48 h to yield 1.897 g macrophotoinitiator with a side-chain benzophenone, thio moieties, and coinitiator amine in polymer chain. Yield: 54.2%. P(MTPBP-*co*-DMAEMA): $M_n = 3068$, $M_w/M_n = 1.30$ (determined by GPC using DMF as eluent). ^{1}H NMR ($CDCl_3$, δ): 7.77−7.03 (13H, aromatic), 4.32−3.80 (3H, $-CH-CH_2-$), 2.73−2.41 (2H, $-OCH_2-$), 2.41−1.50 (8H, $-CH_2-N-(CH_3)_2$), 1.41−0.40 (3H, $-C-CH_3$); FT-IR (KBr, cm^{-1}): 3472 (O···H, hydrogen bond), 2970 (CH_3, CH_2), 1714 (C=O of −N−CO− and −O−CO−), 1652 (C=O of Ar−CO−Ar), 1316 (C−N), 1284 (CO−O), 1178 (O−C−C), 1080 (C−S). Anal. Calcd: C, 66.93; H, 6.48; N, 6.00; S, 4.58. Found: C, 67.32; H, 5.65; N, 5.23; S, 7.06.

Measurements

Physicochemical Measurements. ^{1}H NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with $CDCl_3$ as solvent.

FT-IR 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.

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

Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by gel permeation chromatography (GPC) in THF or DMF solution on a Perkin-Elmer Series 200 apparatus. Monodisperse polystyrene samples were used as calibration standards.

Photocalorimetry (Photo-DSC). Photopolymerization of HDDA and TMPTA was studied by DSC 6200 (Seiko Instrument) photo-DSC with a high-pressure Hg lamp. Approximately 1.2 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 (only a small amount 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 eq 1

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

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.[35] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following eq 2

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

Results and Discussion

Polymer Synthesis. The main purpose of this article is to investigate the photoefficiency differences between the macrophotoinitiator and its low-molecular-weight polymerizable counterpart. The two polymers were synthesized through free radical polymerization or copolymerization, as shown in Scheme 1. The copolymer P(MTPBP-*co*-DMAEMA) was synthesized from the polymerizable photoinitiator MTPBP and an unsaturated coinitiator amine DMAEMA with AIBN as thermal initiator. Therefore, we obtained a macrophotoinitiator containing side-chain benzophenone, thio group, and coinitiator amine in the same macromolecule. To find out the influences of coinitiator amine on photoefficiency between polymerizable coinitiator amine and the corresponding polymeric one, we also synthesized a macroamine P(DMAEMA) from the homopolymerization of DMAEMA for comparison. Relevant synthesis and characterization data of polymers are summarized in Table 1. From the FT-IR spectra (in the Experimental Section and the Supporting Information), in addition to the absorption of carbonyl group from benzophenone moieties (Ar−CO−Ar) at 1652 cm^{-1}, the appearance of absorption at 1714 cm^{-1} verified the formation of imide groups (−N−CO−) and ester groups (−O−CO−) in P(MTPBP-*co*-DMAEMA). Therefore, both the photosensitive chromophore and the coinitiator amine were successfully introduced into the macromolecular backbones. Moreover, the expected structure of P(MTPBP-*co*-DMAEMA) was further confirmed by the signals in the 4.4−1.4 ppm region related to methyl and methylene protons given by DMAEMA in ^{1}H NMR spectra as well as the signals in the region 7.77−7.03 ppm given by aromatic protons.

Scheme 1. Synthesis of Poly(*N*,*N*-dimethylaminoethyl methacrylate) P(DMAEMA) and Poly(4-[(4-maleimido)thiophenyl]benzophenone-*co*-*N*,*N*-dimethylaminoethyl Methacrylate) P(MTPBP-*co*-DMAEMA) with 2,2′-Azo-bis-isobutyronitrile (AIBN) as Thermal Initiator

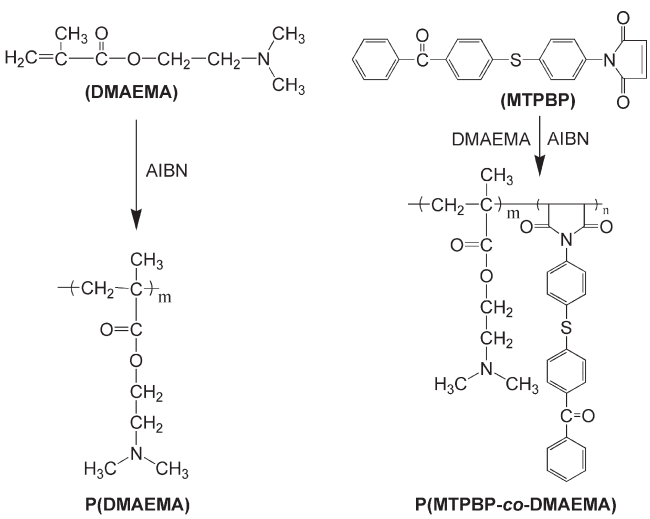


Table 1. Synthesis and Characterization Data for Macroamine P(DMAEMA) and Macrophotoinitiator P(MTPBP-*co*-DMAEMA)

properties	P(DMAEMA)[a]	P(MTPBP-*co*-DMAEMA)[b]
feed molar ratio (initiator/coinitiator)	0:1	1:2
product molar ratio (initiator/coinitiator)[c]	0:1	1:0.44
M_n (g mol^{-1})	295 800	3068
M_w/M_n	1.51	1.30

[a] GPC determined by using THF as the eluent. [b] GPC determined by using DMF as the eluent. [c] Determined by elemental analysis.

The average molecular weight of P(DMAEMA) and P(MTPBP-*co*-DMAEMA) was determined by GPC. From Table 1, the average molecular weight of P(MTPBP-*co*-DMAEMA) is much lower than that of P(DMAEMA), which can be attributed to the following three aspects: First, because of the steric hindrance of the rigid maleimide group, the chain propagation reaction will be limited in the copolymerization, which is confirmed by the results of elemental analysis that the content of DMAEMA moieties in P(MTPBP-*co*-DMAEMA) is lower than that of the primal feed ratio. Second, the imide group may cause a chain transfer reaction in the copolymerization.[36] Finally, the electrophilic group in the para-position of the aromatic N-substituted maleimide will favor the copolymerization.[37] However, the thiophenyl group belongs to the electron-donating group, which will certainly be unfavorable for attaining high-molecular-weight product. As a result, the number-average molecular weight of P(MTPBP-*co*-DMAEMA) is only 3068. This value, as seeing from its appearance, may be very low. However, in fact, it is enough to avoid migration in the postcured materials, and the compatibility between too high-molecular-weight macrophotoinitiator and the photocurable resins is usually unsatisfactory.

UV−vis Spectra. UV absorption spectra of P(MTPBP-*co*-DMAEMA) were measured in chloroform with benzophenone and MTPBP as the references, as shown in Figure 1. The maximum of absorption ($\lambda_{\max}$) and the logarithmic values of molar extinction coefficient at $\lambda_{\max}$ (log ε) are summarized in Table 2. From Figure 1 and Table 2, the maximum of absorption of benzophenone is 254 nm, which can be ascribed to the main benzenoid $\pi-\pi^*$-type transitions[38] because the n−π^*-type transitions are usually found between 300 and 350 nm.[39] Compared with benzophenone, both MTPBP and P(MTPBP-*co*-DMAEMA) exhibit significantly red-shifted $\pi-\pi^*$ absorption, and their maxima are 316 and 317 nm, respectively. This result can be addressed to the strong electron-donating ability of the thiophenyl group that is directly linked to benzophenone moieties in MTPBP and P(MTPBP-*co*-DMAEMA).[21,31] Moreover, there were only slight differences in the maximum of absorption and the molar extinction coefficient of MTPBP and P(MTPBP-*co*-DMAEMA), which indicates that the macromolecular structure has no obvious influence on the UV−vis absorption of benzophenone moieties in the macrophotoinitiator. It is noted that the maximum of absorption and the molar extinction coefficient are important to the photoefficiency of photoinitiators. Therefore, similar to the polymerizable photoinitiator MTPBP, the copolymer P(MTPBP-*co*-DMAEMA) is also attractive as a photoinitiator.

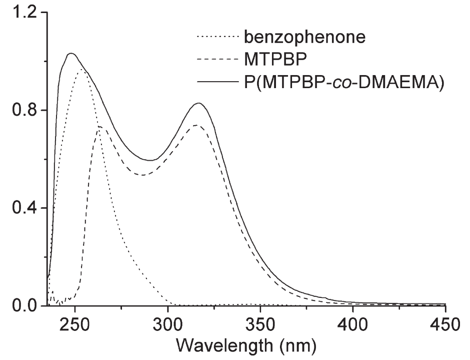


Figure 1. UV−vis absorption spectra of benzophenone, 4-[(4-maleimido)thiophenyl]benzophenone (MTPBP) and poly(MTPBP-*co*-*N*,*N*-dimethylaminoethyl methacrylate) P(MTPBP-*co*-DMAEMA) in chloroform solution (the concentration is 5×10^{-5} M in terms of benzophenone moieties).

Table 2. Absorption Properties of Benzophenone, MTPBP, and P(MTPBP-*co*-DMAEMA) in Chloroform Solution with the Concentration of 5×10^{-5} M

photoinitiator	$\lambda_{\max}$ (nm)	log ε (mol^{-1} cm^{-1} L)
benzophenone	254	4.29
MTPBP	316	4.17
P(MTPBP-*co*-DMAEMA)	317	4.22

Photopolymerization of HDDA. Figure 2 exhibits the photo-DSC profiles of HDDA initiated by benzophenone/DMAEMA, MTPBP/DMAEMA, MTPBP/P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems. Their polymerization behaviors appear to be similar to those of other multifunctional monomers.[40−43] Figure 3a shows that the conversion corresponding to the maximum rate of polymerization ($R_{p,\max}$) is dependent on the photoinitiator. The data for $R_{p,\max}$ and the final conversion of HDDA are summarized in Table 3. According to Figures 2 and 3 and Table 3, P(MTPBP-*co*-DMAEMA) is the most efficient photoinitiator for the photopolymerization of HDDA. This result may be ascribed to the effect of the following two opposite factors. On one hand, with copolymerization of MTPBP and DMAEMA, the C=C double bond of MTPBP will be converted into a single bond. Therefore, the chemically bonded effect between *N*-phenylmaleimide and benzophenone, which has been verified to be favorable for the promotion of the photoefficiency of photoinitiator,[32] will certainly disappear. On the other hand, to attain efficient electron/proton transfer, both of the benzophenone moieties

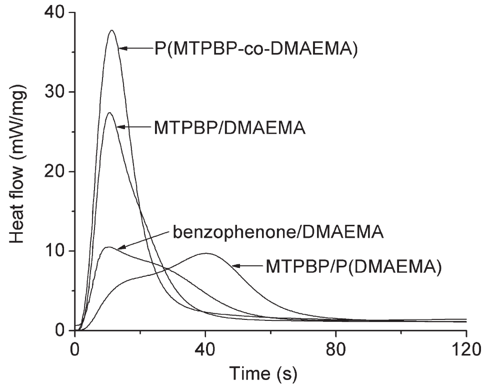


Figure 2. Photo-DSC profiles for the polymerization of 1,6-hexanediol diacrylate (HDDA) initiated by benzophenone/*N*,*N*-dimethylaminoethyl methacrylate (DMAEMA), 4-[(4-maleimido)thiophenyl]-benzophenone (MTPBP)/DMAEMA, MTPBP/poly(*N*,*N*-dimethylaminoethyl methacrylate) P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems cured at 25 °C under a nitrogen atmosphere by UV light with an intensity of 55 mW/cm^2. (The photoinitiator concentration is 0.04 M in terms of benzophenone moieties with the same concentration of DMAEMA moieties.)

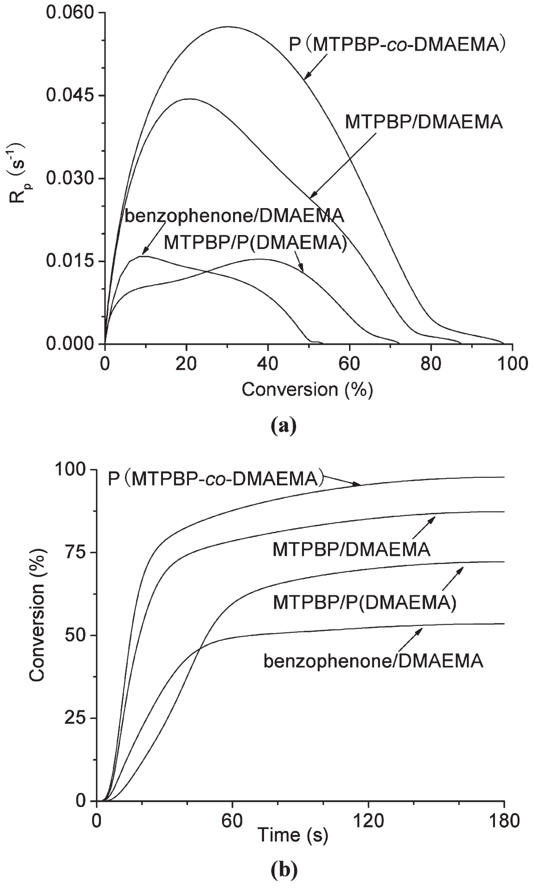


Figure 3. (a) Rate versus conversion. (b) Conversion versus time for the polymerization of 1,6-hexanediol diacrylate (HDDA) initiated by benzophenone/*N*,*N*-dimethylaminoethyl methacrylate (DMAEMA), 4-[(4-maleimido)thiophenyl]benzophenone (MTPBP)/DMAEMA, MTPBP/poly(*N*,*N*-dimethylaminoethyl methacrylate) P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems cured at 25 °C under a nitrogen atmosphere by UV light with an intensity of 55 mW/cm^2. (The photoinitiator concentration is 0.04 M in terms of benzophenone moieties with the same concentration of DMAEMA moieties.)

Table 3. Photopolymerization of HDDA Initiated by Benzophenone/DMAEMA, MTPBP/DMAEMA, MTPBP/P(DMAEMA), and P-(MTPBP-*co*-DMAEMA) Cured at 25 °C under a Nitrogen Atmosphere by UV Light with an Intensity of 55 mW/cm^2[a,b]

photoinitiator	$R_{p,max} \times 10^2$	final conversion	H_{max}	T_{max}
	s^{-1}	%	mW/mg	s
benzophenone/DMAEMA	1.59	54	10.5	10.4
MTPBP/DMAEMA	4.44	87	27.4	10.6
MTPBP/P(DMAEMA)	1.54	72	9.7	40.2
P(MTPBP-*co*-DMAEMA)	5.75	98	37.8	11.2

[a] Photoinitiator concentration is 0.04 M in terms of benzophenone moieties. [b] $R_{p,max}$: maximal polymerization rate; H_{max}: maximal heat flow; T_{max}: time to reach maximal heat flow.

and the coinitiator amine must get as close as possible. The intramolecular electron and proton transfer between the excited state of benzophenone moieties and DMAEMA moieties in P(MTPBP-*co*-DMAEMA) is more efficient than the intermolecular reaction in MTPBP/DMAEMA and MTPBP/P(DMAEMA) systems, which will be favorable to the bimolecular hydrogen abstraction reaction and generate a high concentration of free radicals. Moreover, the steric hindrance of the macromolecular coil could disfavor the coupling termination between the propagating radicals and the macroradicals, thus strongly limiting the extent of termination and preventing a reduction in the concentration of active species. In the above-mentioned two opposite effects on the photoefficiency, the efficient energy transfer may be a more important factor for the photopolymerization. As a result, P(MTPBP-*co*-DMAEMA) is most efficient for the polymerization of HDDA among the four photoinitiating systems, and the final conversion of HDDA runs up to 98%, which indicates that this macrophotoinitiator may possess greatly applied potential in UV-curable systems.

Compared with P(MTPBP-*co*-DMAEMA) and MTPBP/DMAEMA systems, the MTPBP/P(DMAEMA) system has much lower photoefficiency for the photopolymerization of HDDA. This result may be ascribed to the relatively low mobility of macroamine P(DMAEMA), the intermolecular hydrogen abstraction reaction between benzophenone moieties of MTPBP and DMAEMA moieties of P(DMAEMA) is relatively difficult to take place, resulting in an obviously longer time to reach the $R_{p,max}$ and a much lower final conversion of HDDA. Therefore, the macroamine may avoid the migration of low molecules in the postcured materials; its polymerization rate is unsatisfactory, which is also consistent with our previous research on macroamines.[21,22] As compared with the benzophenone/DMAEMA system, although MTPBP/P(DMAEMA) possesses a relatively lower polymerization rate, its final conversion of HDDA is obviously higher. This result can be attributed to the photolysis reaction of the C−S bond to afford additional active species for photopolymerization.[44−46]

The photoefficiency difference of benzophenone/DMAEMA and MTPBP/DMAEMA systems can be ascribed to the effect of the chemical-bonded maleimides, the cleavage of the C−S bond, and the different maximal UV absorptions, which was discussed in detail in our previous work.[30−32]

Photopolymerization of TMPTA. The polymerization behavior of TMPTA, initiated by benzophenone/DMAEMA, MTPBP/DMAEMA, MTPBP/P(DMAEMA), and P-(MTPBP-*co*-DMAEMA) systems appears to be similar to that of HDDA, as shown in Figures 4 and 5. The data for $R_{p,max}$ and the final conversion of TMPTA are summarized in Table 4. According to Tables 3 and 4, it can be easily found that the time to reach $R_{p,max}$ (T_{max}) in TMPTA is obviously lower than that in HDDA. This result can be ascribed to the high viscosity and double-bond content of TMPTA. It is well accepted that the bimolecular hydrogen abstraction reaction is chemically controlled in the early stage of

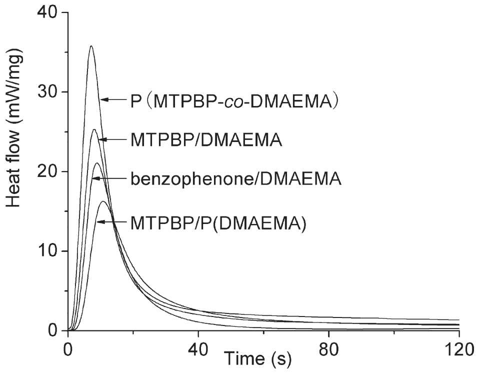
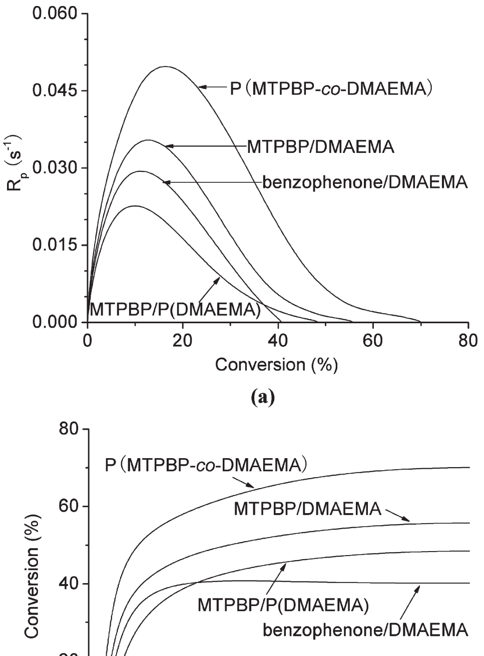


Figure 4. Photo-DSC profiles for the polymerization of trimethylolpropane triacrylate (TMPTA) initiated by benzophenone/*N*,*N*-dimethylaminoethyl methacrylate (DMAEMA), 4-[(4-maleimido)-thiophenyl]benzophenone (MTPBP)/DMAEMA, MTPBP/poly(*N*,*N*-dimethylaminoethyl methacrylate) P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems cured at 25 °C under a nitrogen atmosphere by UV light with an intensity of 55 mW/cm^2. (The photoinitiator concentration is 0.04 M in terms of benzophenone moieties with the same concentration of DMAEMA moieties.)



(a)

(b)

Figure 5. (a) Rate versus conversion. (b) Conversion versus time for the polymerization of trimethylolpropane triacrylate (TMPTA) initiated by benzophenone/*N*,*N*-dimethylaminoethyl methacrylate (DMAEMA), 4-[(4-maleimido)thiophenyl]benzophenone (MTPBP)/DMAEMA, MTPBP/poly(*N*,*N*-dimethylaminoethyl methacrylate) P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems cured at 25 °C under a nitrogen atmosphere by UV light with an intensity of 55 mW/cm^2. (The photoinitiator concentration is 0.04 M in terms of benzophenone moieties with the same concentration of DMAEMA moieties.)

Table 4. Photopolymerization of TMPTA Initiated by Benzophenone/DMAEMA, MTPBP/DMAEMA, MTPBP/P(DMAEMA), and P(MTPBP-*co*-DMAEMA) Cured at 25 °C under Nitrogen Atmosphere by UV Light with an Intensity of 55 mW/cm^{2a,b}

photoinitiator	$R_{p,max} \times 10^2$	final conversion	H_{max}	T_{max}
	s^{-1}	%	mW/mg	s
benzophenone/DMAEMA	2.94	40	21.1	8.8
MTPBP/DMAEMA	3.54	56	25.3	8.0
MTPBP/P(DMAEMA)	2.27	48	16.3	10.8
P(MTPBP-*co*-DMAEMA)	4.97	70	35.8	7.2

[a] Photoinitiator concentration is 0.04 M in terms of benzophenone moieties. [b] $R_{p,max}$: maximal polymerization rate; H_{max}: maximal heat flow; T_{max}: time to reach maximal heat flow.

photopolymerization. Compared with difunctional monomer HDDA, the viscosity and the double-bond content of trifunctional monomer TMPTA are much higher. Therefore, gelation will occur in an even earlier stage of the reaction in TMPTA than that in HDDA, resulting in relatively shorter time to reach the $R_{p,max}$ in TMPTA. From Tables 3 and 4, we can also find that the final conversion of TMPTA is relatively lower than that of HDDA. This result may be addressed to the fact that the reaction in the later stage mainly depends on the diffusion control. As the reaction goes on, the increased cross-linking level would eventually limit the mobility of active species, and then the propagation reaction may become diffusion controlled along with radical termination.[15] As a result, the final conversion of TMPTA is obviously lower than that of HDDA.

From the photopolymerization of HDDA and TMPTA discussed above, we can conclude that the macrophotoinitiator P(MTPBP-*co*-DMAEMA), formed by the introduction of photoredox pairs MTPBP/DMAEMA into the polymer chain, is more efficient for the polymerization of vinyl monomers than the original photoredox pairs. Therefore, compared with the polymerizable photoinitiating system MTPBP/DMAEMA, P(MTPBP-*co*-DMAEMA) is more attractive for photopolymerization. In a word, this thio-containing macrophotoinitiator bearing side-chain benzophenone and coinitiator amine has great potential application in UV-curing systems.

As described in the Introduction, many kinds of macrophotoinitiators have been recently developed. Because of the differences in chromophore, monomer, photopolymerization condition, and macromolecular structure, it is really difficult to determine which is more appropriate for photopolymerization. However, hardly any literature has reported that the conversion of HDDA can be higher than 90% in the fast curing process (lower than 3 min, as in this article) as well as TMPTA for 70%. Moreover, in this work, because both the photosensitive chromophore and hydrogen donor were introduced into the polymer chain, the macrophotoinitiator can avoid the inherent disadvantages of the low-molecular-weight photoinitiators and the small molecule coinitiators. Therefore, this research may be a beneficial enlightenment for the design and application of photoinitiators.

Conclusions

In this article, through free radical copolymerization of MTPBP and DMAEMA, we obtained a novel macrophotoinitiator P(MTPBP-*co*-DMAEMA) containing side-chain benzophenone, thio group, and coinitiator amine. A macroamine P(DMAEMA) was also synthesized in comparison with the polymerizable coinitiator amine DMAEMA. UV−vis spectra showed that the macromolecular structure has no obvious effect on the absorption of P(MTPBP-*co*-DMAEMA) compared with the parent MTPBP. Photopolymerization of HDDA and TMPTA, initiated by benzophenone/DMAEMA, MTPBP/DMAEMA, MTPBP/P(DMAEMA), and P(MTPBP-*co*-DMAEMA) systems, was studied by photo-DSC. The results indicate that P(MTPBP-*co*-DMAEMA) is more efficient for the polymerization of both HDDA and TMPTA than its polymerizable counterpart MTPBP/DMAEMA. As for the photopolymerization of HDDA initiated by P(MTPBP-*co*-DMAEMA), the final conversion reaches a very high value of 98%. However, the photoinitiating system, with macroamine P(DMAEMA) as coinitiator, has poor photoefficiency for both HDDA and TMPTA. In conclusion, the macrophotoinitiator P(MTPBP-*co*-DMAEMA) might possess enormous potential for application in UV-curable systems.

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Supporting Information Available: FT-IR spectra of MTPBP, P(DMAEMA), and P(MTPBP-*co*-DMAEMA). Samples were prepared as KBr disks. This material is available free of charge via the Internet at http://pubs.acs.org.

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