# Synthesis of Main Chain Polymeric Benzophenone Photoinitiator via Thiol-ene Click Chemistry and Its Use in Free Radical Polymerization

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**ABSTRACT:** Main chain polymeric benzophenone photoinitiator (PBP) was synthesized by using "Thiol-ene Click Chemistry" and characterized with <sup>1</sup>H NMR, FTIR, UV, and phosphorescence spectroscopies. PBP as a polymeric photoinitiator presented excellent absorption properties ( $\varepsilon_{294} = 28,300 \text{ mol}^{-1} \text{ L}^{-1} \text{ cm}^{-1}$ ) compared to the molecular initiator BP ( $\varepsilon_{252} = 16,600 \text{ mol}^{-1} \text{ L}^{-1} \text{ cm}^{-1}$ ). The triplet energy of PBP was obtained from the phosphorescence measurement in 2-methyl tetrahydrofurane at 77 K as 298.3 kJ/mol and according to phosphorescence lifetime, the lowest triplet state of PBP has an *n*- $\pi$ \* nature. Triplet–triplet absorption spectrum of PBP at 550 nm following laser excitation (355 nm) were recorded and triplet lifetime of

PBP was found as 250 ns. The photoinitiation efficiency of PBP was determined for the polymerization of Hexanedioldiacrylate (HDDA) with PBP and BP in the presence of a coinitiator namely, *N*-methyldiethanolamine (MDEA) by Photo-DSC. The initiation efficiency of PBP for polymerization of HDDA is much higher than for the formulation consisting of BP. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5306–5312, 2010

**KEYWORDS**: benzophenone; click chemistry; photopolymerization; photochemistry; polymeric photoinitiator; radical polymerization; thiol-ene

**INTRODUCTION** Photopolymerization processes receive continuous interest because of their wide application in UV-curable coatings, printing inks, photoresist, and microelectronics. Free radical photoinitiators can be classed as  $\alpha$ cleavage (Type I) and H-abstraction (Type II) initiators. Free radical generation process is H-abstraction reaction of triplet photoinitiator from hydrogen donors such as amines and alcohols. The radical derived from the donor can initiate the polymerization while ketyl radicals stemming from aromatic carbonyl compound are usually not reactive toward vinyl monomers due to bulkiness and/or the delocalization of the unpaired electrons. The overall process is depicted on the example of benzophenone in Scheme 1.

There have been many new developments in synthesis and photochemical studies of novel polymeric photoinitiators. Polymeric photoinitiators have attracted much attention in recent years for they combine the properties of polymers with those of low molecular weight photoinitiators.<sup>1-11</sup> Solubility and miscibility problems, often observed with coatings containing low molecular weight photoinitiators, do not occur with the polymeric ones since polymers are easily miscible with the resin to be cured as well as with the final cured film. Moreover, odor and toxicity problems do not occur with macrophotoinitiators owing to the low volatility of the large molecules. The low migration tendency of poly-

meric photoinitiators and of photoproducts means that cured coatings are less prone to yellowing.<sup>12,13</sup>

In our previous studies, to overcome some of the problems, we successfully synthesized novel side chain thioxanthone and benzophenone containing polystyrene based polymeric photoinitiators and they were used as polymeric photoinitiators in free radical polymerization.<sup>5,6,10,14-16</sup>

Over the last decade, efficient and versatile cross reactions such as radical coupling reactions,<sup>14,17,18</sup> click chemistry,<sup>5,16,19–32</sup> diels alder reactions,<sup>5,33,34</sup> thio-bromo click reaction,<sup>35–37</sup> etc., have been used to obtain functional polymers in quantitative yield. Cu (I) catalyzed 1,3-Huisgen dipolar cycloaddition is the most widely used reaction to synthesize telechelic poly-mers,<sup>26,27</sup> functional dendrimers,<sup>23,38,39</sup> hyperbranched polymers,<sup>40</sup> biopolymers,<sup>41</sup> polymeric photoinitiators<sup>5,16</sup> and so on. High temperature conditions or the requirement of metal catalysts, which generally need to be removed by various purification methods after the reaction, are the only deterrents of the click method. Recently, thiol-ene chemistry has appeared as a new type of click chemistry method in the absence of a toxic metal catalyst.<sup>20,42</sup> Thiol-ene click chemistry has been successfully employed to synthesize biomaterials,43,44 star polymers,45 crosslinked materials,<sup>42,46,47</sup> and UV-curable coatings.<sup>42,48,49</sup> However, thiol-ene reactions can be initiated photochemically or thermally in the presence of a photo or thermal initiator.<sup>20,42</sup>

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**SCHEME 1** Photoinduced radical polymerization mechanism of benzophenone in the presence of a coinitiator.

In this study, we used the thiol-ene click chemistry method to synthesize benzophenone based macromolecular photoinitiator and it was used in photoinduced free radical polymerization as the photoinitiator in the presence of a coinitiator namely *N*-methyldiethanolamine. The main chain polymeric photoinitiator was characterized by GPC, <sup>1</sup>H NMR, UV, and phosphorescence spectroscopy and the monomer conversions and rate of polymerization of diacrylate monomer were also determined by Photo-DSC experiments in air and nitrogen atmospheres.

#### **EXPERIMENTAL**

### Materials

2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) and Benzophenone (99%, Aldrich) were recrystallized from ethanol. 4,4'-Dihydroxybenzophenone (97%, Aldrich), allyl bromide (97%, Aldrich), 1, 2-ethanedithiol (>90%, Aldrich), and *N*-methyldiethanolamine (MDEA, 99%, Aldrich) were used as received. Hexandioldiacrylate (HDDA, 93%, ABCR) was passed through the basic alumina just before use. All other reagents were purchased from Aldrich and Merck and used as received.

## Synthesis of Diallyl Benzophenone (BP-Al)

A solution of 4,4'-dihydroxybenzophenone (1 g, 4.67 mmol) and anhydrous potassium carbonate (1.6 g, 12 mmol) in 30 mL of acetone was stirred for 6 h. After that, allyl bromide (1.32 g, 11 mmol) was added and the mixture was refluxed for 24 h. Acetone was removed on the rotary evaporator, and the residue was diluted with dichloromethane and washed with water. Then, it was dried over  $Na_2SO_4$ . The crude product was recrystallized from ethanol (yield 75%).

GC-MS (70 eV) m/e: 294 (M<sup>+</sup>). ELEM. ANAL. for  $C_{19}H_{18}O_3$  (294.13 g mol<sup>-1</sup>): Calc., C, 77.53%; H, 6.16%; Found, C, 77.49%; H, 6.09%. IR (ATR):  $\nu$  (cm<sup>-1</sup>) 3069 (C—H, aromatic), 2930 (C—H, aliphatic), 1636 (C=O, ketone), 1599 (C=C, aromatic) cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub> 250 MHz):  $\delta$  = 7.78-7.75 (d, 4H, aromatic), 7.24-6.97 (d, 4H, aromatic), 6.13-5.98 (m, 2H, CH), 5.46-5.29 (m, 4H, CH<sub>2</sub>), 4.61-4.59 (d, 4H, CH<sub>2</sub>).

## Synthesis of Polymeric Photoinitiator with Thiol-ene Click Chemistry (PBP)

BP-Al (0.5 g, 1.7 mmol) and a catalytic amount of AIBN (1–2% w/w) were dissolved in 3 mL of DMF in a Schlenk tube and the solution was bubbled with argon for 15 min. 1, 2-ethanedithiol (1.7 mmol, 143  $\mu$ L) was added to this solution and the solution was bubbled for another 5 min with argon. After that tube was kept under argon and stirred at 85 °C for 24 h. At the end of the period, polymeric photoinitiator was isolated by two times of precipitation in excess methanol. The white product was filtered and dried *in vacuo* at room temperature. (Yield: 60%,  $M_{n,GPC} = 2300$  g mol<sup>-1</sup>,  $M_w/M_n = 1.28$ ).

IR (ATR): v (cm<sup>-1</sup>) 3068 (C=C, aromatic), 2926 (C-H, aliphatic), 1637 (C=O ketone), 1599 (C=C, aromatic) cm<sup>-1</sup>.

<sup>1</sup>H NMR (CDCl<sub>3</sub> 250 MHz):  $\delta$  = 7.76-6.91 (m, 8H, aromatic), 6.10-6.00 (m, 2H, CH), 5.46-5.29 (m, 4H, CH<sub>2</sub>), 4.61-4.59



**SCHEME 2** Synthesis of bisallylbenzophenone (BP-AI) and polymeric photoinitiator (PBP) via Thiol-ene click polymerization.



FIGURE 1 <sup>1</sup>H NMR spectra of BP-AI and PBP in CDCI<sub>3</sub>.

(d, 4H, CH<sub>2</sub>), 4.12 (t, 4H, CH<sub>2</sub>), 2.86-2.75 (m, 8H), 2.1-2.0 (m, 4H).

#### Instrumentation

<sup>1</sup>H NMR measurements were recorded in  $CDCl_3$  with Si  $(CH_3)_4$  as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FTIR spectra were recorded on a Perkin–Elmer FTIR Spectrum One-B spectrometer. UV-Vis spectra

were taken on a Varian UV-Visible Carry 50 Spectrophotometer. Gel permeation chromatography (GPC) analyses of the polymers were performed with a set-up consisting of a pump (Waters) and four ultrastyragel columns of different porosities. Tetrahydrofuran (THF) was used as the eluent (flow rate 0.3 mL min<sup>-1</sup>), and detection was carried out with the aid of a differential refractometer. The number-average molecular weights were determined using polystyrene





FIGURE 2 UV absorption spectra of BP  $[9\times10^{-5}]$  M and PBP  $[6\times10^{-5}]$  in CHCl3.

standards. Gas chromatography-mass spectroscopy (GC-MS) was performed using an Agilent 6890/ 5973 inert gas chromatograph/mass selective detector system in electrospray ionization mode (70 eV), through an HP-5MS capillary column using helium as the carrier gas at a flow rate of 1.6 mL/min. Laser flash photolysis experiments employed the pulses from an Applied Photophysics with YAG laser (355 nm, pulse, 5 ns) and a computer controlled system. A chloroform solution of polymeric benzophenone photoinitiator (PBP) was prepared with a concentration of BP such that the absorbance was 0.5 at the excitation wavelength (355 nm).

#### Photo Differential Scanning Calorimetry (Photo-DSC)

The photoinitiated polymerization of HDDA was carried out by TA-DSCQ100 equipped with a medium pressure mercury arc lamp. This unit emits radiation predominantly in the 220–400 nm range, and provides light intensity of 50 mW cm<sup>-2</sup> as measured by a UV radiometer capable of broad UV range coverage. The mass of the samples was  $\sim 2 \pm 0.1$  mg



FIGURE 3 Phosphorescence spectra of PBP in 2-methyl tetrahydrofurane at 77 K ( $\lambda_{exc} = 300$  nm).



FIGURE 4 Transient optical absorption spectrum recorded at 280 and 480 ns following laser excitation (355 nm, 5 ns) in argon saturated chloroform solution of PBP. Inset: Triplet decay at 550 nm.

and the measurements were carried out in isothermal mode at room temperature under a nitrogen atmosphere (nitrogen or air flow: 50 mL min<sup>-1</sup>). The samples were irradiated for 4 min. at room temperature. The heat flow as a function of reaction time was monitored using Photo-DSC under isothermal conditions, and both the rate of polymerization and conversion were then calculated as a function of time. The heat of reaction value  $\Delta H_p^{\text{theor}} = 86 \text{ kJ/mol}$  was used as the theoretical heat evolved for acrylate double bonds.<sup>50</sup> Rates of polymerization were calculated according to the following equation; Rp = (Q/s)M/n  $\Delta H_p$ m where Q/s is heat flow per second, M the molar mass of the monomer, n the number of double bonds per monomer molecule and m the mass of monomer in the sample.

#### **RESULTS AND DISCUSSION**

Etherification reaction of the allyl bromide with 4,4'-dihydroxybenzophenone photoinitiator was preferred because it has a reactive click component, and it can be easily obtained in high yield. In addition, allyl ethers are more reactive than styrenes, acrylates, and methacrylates in thiol-ene reactions.<sup>42</sup> Therefore, the main chain PBP was synthesized with "Thiol-ene Click Polymerization" method with diallyl benzophenone (BP-Al) and 1,2-ethanedithiol in the presence of catalytic amounts of AIBN via thermal initiation (Scheme 2). The resulting polymer was precipitated two times in methanol to obtain a pure polymeric photoinitiator. According to <sup>1</sup>H NMR and FTIR studies, the desired polymeric structure was entirely characterized. Allylic methine proton in 5.97-6.13 and allylic methylene protons in 5.46-5.29 ppm showed that a diallyl-end functional polymer was formed. Furthermore, a thiol signal could not be observed in either <sup>1</sup>H NMR or FTIR spectroscopic analyses (Fig. 1). According to <sup>1</sup>H NMR spectrum, allylic protons at the end of the polymer and aromatic protons of the benzophenone in the main chain

were used to determine the molecular composition of the polymeric photoinitiator. PBP has five repeating units and possesses diallyl end groups according to calculations from <sup>1</sup>H NMR spectrum and these results were in strong agreement with GPC results ( $M_n = 2300 \text{ g mol}^{-1}$ ).

The absorption behavior of the polymeric photoinitiator, PBP, was compared with the low molecular weight analogue (BP) which is used as a photoinitiator for many UV curing and photopolymerization applications. As can be seen in Figure 2, the absorption of PBP shifted to the red region wavelength ( $\lambda_{max} = 294$  nm,  $\varepsilon = 28,300$  mol L<sup>-1</sup> cm<sup>-1</sup>) compared to the low molecular weight analogue ( $\lambda_{max} = 252$  nm,  $\varepsilon = 16,600$  mol L<sup>-1</sup> cm<sup>-1</sup>).

To gain more insight into the photophysical properties, PBP fluorescence emission could not be observed as usual for most of the BP derivatives. Therefore, phosphorescence measurements were performed at 77 K in 2-methyl tetrahydrofurane to get information about the triplet configuration of the photo-initiator. PBP exhibited a phosphorescence emission spectrum similar to the parent benzophenone. The (0, 0) emission band occurred at 401 nm, corresponding to approximate triplet energy of ca 298.3 kJ/mol (see Fig. 3). The phosphorescence lifetime of PBP was calculated as 6.5 ms. Since the phosphorescence lifetime for  $n-\pi^*$  triplets are significantly shorter (in the order of several milliseconds) than  $\pi-\pi^*$  triplets, we can comment that the lowest triplet state of PBP has an  $n-\pi^*$  nature.

Laser flash photolysis studies were performed to investigate the triplet state behavior of the PBP. Figure 4 exhibits the transient absorption spectra of degassed CHCl<sub>3</sub> solution containing polymeric photoinitiator after irradiation with laser pulses of 355 nm. The maximum absorption is at 550 nm, which is similar to the triplet-triplet absorption of parent BP.<sup>51,52</sup> The transient was recorded at 250 ns, after the pulse for PBP. However, a short triplet lifetime ( $\tau = 250$  ns at 550



**FIGURE 5** Rate of polymerization versus time for the polymerization of HDDA initiated by PBP/MDEA (0.1/1.0 w/w) and BP/MDEA (0.1/1.0 w/w) systems cured at 30 °C by UV light with an intensity of 50 mW cm<sup>-2</sup> in the presence and absence of an air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 6** Conversion versus time for the polymerization of HDDA initiated by PBP/MDEA (0.1/1.0 w/w) and BP/MDEA (0.1/ 1.0 w/w) systems cured at 30 °C by UV light with an intensity of 50 mW cm<sup>-2</sup> in the presence and absence of an air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nm) observed in the case PBP indicates a fast quenching process due to the polymeric effect of the photoinitiator.

Photo-DSC is a unique method to obtain a fast and accurate indication of the photoinitiator's performance. It has been well established that Photo-DSC experiments are capable of providing kinetics data in which the measured heat flow can be converted directly to the ultimate percentage conversion and polymerization rate for a given amount of formulation. Photopolymerization of HDDA formulations containing photoinitiators (BP and PBP) with amine (MDEA) either in air or nitrogen atmosphere was followed by Photo-DSC. To



**FIGURE 7** Rate of polymerization versus time for the polymerization of HDDA initiated by PBP/MDEA (1.0/10.0 w/w) and BP/ MDEA (1.0/10.0 w/w) systems cured at 30 °C by UV light with an intensity of 50 mW cm<sup>-2</sup> in the presence and absence of an air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 8** Conversion versus time for the polymerization of HDDA initiated by PBP/MDEA (1.0/10.0 w/w) and BP/MDEA (1.0/ 10.0 w/w) systems cured at 30 °C by UV light with an intensity of 50 mW cm<sup>-2</sup> in the presence and absence of an air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

evaluate the initiation efficiency of photoinitiator PBP, two different concentrations of initiator were used and the polymerization profiles obtained for the formulations cured in air or nitrogen atmospheres are shown in Figures 5–9 and in Table 1.

Under air, for both of the initiators even with MDEA, the rate of polymerization is very low and the final conversion reaches 12%. When air is omitted, under nitrogen atmosphere the polymerization rate is increased, especially for initiator PBP/MDEA by a factor of 4. However, the formulations consisting of BP/



FIGURE 9 Conversion versus time for the polymerization of HDDA initiated by PBP/MDEA systems in different concentrations cured at 30 °C by UV light with an intensity of 50 mW  $cm^{-2}$  in the presence of a nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**TABLE 1** Photo-DSC Results of BP and PBP in the Absence and Presence of Air (Light Intensity = 50 mW  $cm^{-2}$ )

Photoinitiator (wt %)	$N_2$	t <sub>max</sub> (s)	Rp <sub>max</sub> (s <sup>-1</sup> )	Final Conv. (%)
BP (0.1)	-	4.05	0.006	12
BP (0.1)	+	3.05	0.013	38
BP (1.0)	_	4.90	0.020	35
BP (1.0)	+	1.25	0.052	59
PBP (0.1)	_	10.55	0.010	12
PBP (0.1)	+	7.85	0.045	52
PBP (1.0)	_	2.45	0.050	27
PBP (1.0)	+	2.25	0.153	65

MDEA reached 38% conversion in nitrogen atmosphere. The effect of oxygen inhibition on the photopolymerization reaction is dependent on various parameters, one of which is the type of initiator which was employed in the formulations. In our case the molecular initiator BP and polymeric initiator PBP belong to the type II class and as clearly seen from Figures 5 and 6; the inhibition effect of oxygen is extremely detrimental.

The influence of initiator concentration on the rate of polymerization was also determined and the results are given in Figures 5 and 7. When the initiator concentration was increased from 0.1 to 1.0 wt % (under nitrogen) the rate of polymerization jumped from 0.045 to 0.153 s<sup>-1</sup> for PBP. Even in air atmosphere, the value of the rate of polymerization of formulations consisting of PBP (1.0 wt %) (0.050 s<sup>-1</sup>) was much higher than the formulation containing PBP (0.1 wt %) (0.010 s<sup>-1</sup>). However, the effect of increasing the photoinitiator concentration for BP was not as effective as PBP (Fig. 9). As stated above, the inhibition effect of oxygen is suppressed by increasing the initiator concentration from 0.1 to 1.0% for PBP. The highest polymerization rate was also obtained at high initiator concentrations for both initiators and for both conditions (air and nitrogen).

#### CONCLUSIONS

The synthesis of PBP using thiol-ene click polymerization was successfully achieved. Since PBP contains BP chromophore groups, the initiation efficiency of PBP was compared to low molecular weight analogue. Since the new polymeric initiator PBP presents type II initiator characteristics (see Scheme 3), it showed very good performance with *N*-methyl-diethanolamine for the polymerization of HDDA possibly due to the high molar absorptivity of PBP when compared to the low molecular weight analogue BP.

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