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Photopolymerization and photophysical properties of amine linked benzophenone photoinitiator for free radical polymerization

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ABSTRACT

Synthesis of amine linked type II photoinitiator (BPDEA) was achieved in high yields and photopolymerization of mono and multiacrylate monomers was performed with this photoinitiator in the absence of a coinitiator. BPDEA is more effective than benzophenone (BP) with the coinitiator (MDEA) system under inert atmosphere in photoinduced free radical polymerization of acrylates.

1. Introduction

Photoinitiated free radical polymerization has enormous commercial importance and has gained much attention because of extensive commercial applications such as curing of coatings on various materials, adhesives, printing inks, and photoresists, which are based on photoinitiated radical vinyl polymerization [1–3]. Photoinitiated radical polymerization may be initiated by both α-cleavage (type I) and H-abstraction type (type II) initiators.

Because the initiation is based on a bimolecular reaction, type II photoinitiators are generally slower than type I photoinitiators which are based on the unimolecular formation of radicals [1]. Benzophenone (BP) is a well-known type II photoinitiator (PI) for the radiation curing of coatings, printing inks, etc. After triplet state excitation, benzophenone is able to abstract hydrogen from ether, amine, alcohol or thiol functional coinitiators, and so reactive centers can be generated on coinitiator molecules to initiate free radical polymerization. Generally, methyldiethanolamine, triethylamine, or ethyl 4-(dimethylamino) benzoate are used as co-initiators for type II photoinitiators. However, the ketyl radical produced from the carbonyl compound is not able to initiate the polymerization because of sterical hindrance and delocalization of an unpaired electron (Scheme 1) [4].

Amine [5–8], alkyl amino [9,10], acid [11–15] or thiol [16] linked photoinitiators are seen in literature and they may find various applications in the Radiation Curing Industry because of the great advantages of their one-component nature. Due to the one-component structure of the photoinitiator, it can serve as both triplet photosensitizer and as a hydrogen donor during photopolymerization. Thus, these photoinitiators do not require an additional co-initiator.

This paper reports that the diethanolamine linked benzophenone (BPDEA) was synthesized as a new photoinitiator in quantitative yield and its photoinitiation capability was investigated by photopolymerization of monoacrylate (methyl methacrylate) and triacrylate (trimethylolpropane triacrylate) monomers in appropriate concentrations. The chemical structure and photophysical behaviour of BPDEA were determined by elemental analysis, GC–MS, UV, UV-bleaching and phosphorescence measurements.

2. Experimental

2.1. Materials

Benzophenone (BP) was purchased from Aldrich and recrystallized from ethanol. Chloroform (Merck), acryloyl chloride (97%, Aldrich), 2-methyltetrahyrofuran (97%, Aldrich), triethylamine (99%, Merck), 4-hydroxybenzophenone (98%, Aldrich), *N*-methyldiethanolamine (MDEA, 99%, Aldrich), *N*,*N*-diethanolamine (≥98% Aldrich) and ethanol (Merck) were used as received. Methyl methacrylate (MMA) (99%, Aldrich) was washed with 5% aqueous

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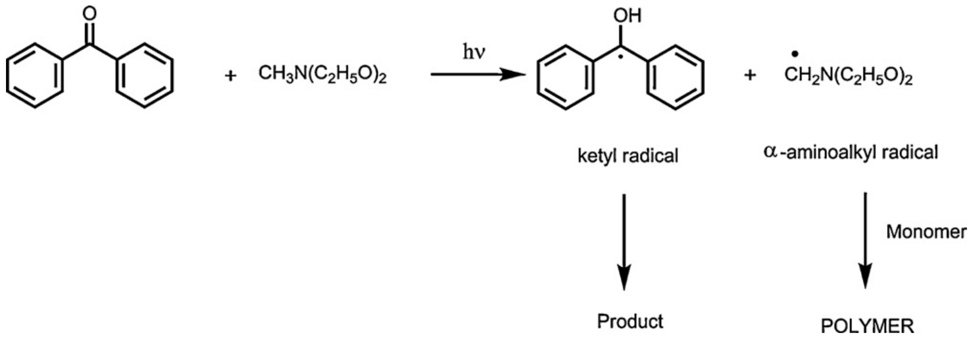


Scheme 1. Photoinitiated free radical polymerization by using aromatic carbonyl compound in the presence of *N*-methyldiethanolamine as a coinitiator.

NaOH solution and dried over Na_2SO_4 just before use. Trimethylolpropane triacrylate (TMPTA) was purchased from Cognis and used as received.

2.2. Instruments

UV–vis spectra were taken on a Varian UV-Visible Carry 50 Spectrophotometer. Phosphorescence spectra were recorded on a Jobin Yvon–Horiba Fluoromax-P in cold finger at 77 K. A Nicolet 6700 FT-IR spectrophotometer was used for recording IR spectra. 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^{-1}. 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^{-1}), and detection was carried out with the aid of a differential refractometer. The number-average molecular weights were determined using polystyrene standards.

2.3. Synthesis of acrylic acid 4-benzoyl-phenyl ester (BPAc)

Acryloyl chloride (0.6 mL, 7.5 mmol) in DCM (3 mL) was added dropwise at 0 °C to a solution of 4-hydroxybenzophenone (0.99 g, 5 mmol) and triethylamine (0.70 mL, 5 mmol) in dichloromethane (DCM) (5 mL), and the resulting mixture was stirred at room temperature overnight. Then the mixture was washed two times with water (100 mL): a saturated aqueous solution of $NaHCO_3$ (200 mL) and a saturated aqueous solution of NaCl (100 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered, and then the solvent was evaporated. The resulting residue was purified by recrystallization from n-hexane. Yield: 80%, mp: 48.5 °C.

^1H NMR (250 MHz, $CDCl_3$), 7.87–6.04 ppm (m, 9H, aromatic), 6.68–6.61 ppm (d, 1H, $CH{=}CH_2$), 6.38–6.34 ppm (m, 2H).

FT-IR (ATR): 3060, 2363, 1730, 1646, 1594 cm^{-1}.

GC–MS (EI, 70 eV); 252 (M^+)

2.4. Synthesis of 3-[bis-(2-hydroxy-ethyl)-amino]-propionic acid 4-benzoyl-phenyl ester (BPDEA)

BPAc (0.5 g, 1.98 mmol) and then diethanolamine (0.2 g, 1.98 mmol) were added to 10 mL of ethanol. The mixture was stirred at room temperature for 30 min. Then the temperature of the solution was raised to 35 °C and kept at that temperature for 4 h. After the TLC control, ethanol was removed under high vacuum at room temperature.

FT-IR (ATR): 3362, 2949, 1731, 1638, 1599 cm^{-1}.

UV ($CHCl_3$): $\lambda_{max}(\varepsilon)$ = 294 nm (10,400 mol^{-1} L cm^{-1}).

GC–MS (EI, 70 eV): 198, 121, 105, 77.

2.5. General photopolymerization procedure of MMA

Appropriate solutions of the MMA, photoinitiators and coinitiator were irradiated in a photoreactor consisting of 12 lamps at $\lambda = 350$ nm for 60 min in either air or N_2 atmosphere. The photoreactor consists of 12 Philips black lights the light intensity was measured as $I_{0(UV\text{-}A)} = 13\ W\,m^{-2}$. Polymers were obtained after precipitation in methanol and drying under vacuum. Conversions were calculated gravimetrically.

2.6. Real-time infrared spectroscopy photopolymerization studies

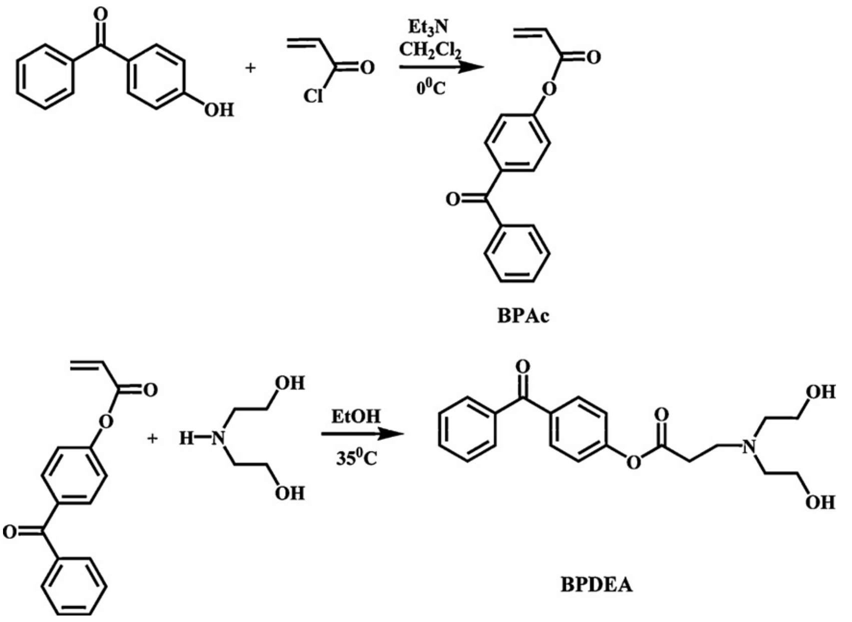
Uniform samples of photocurable formulations consisting of a photoinitiator, co-initiator and multifunctional monomer (TMPTA) were prepared by casting on a KBr pellet. The samples were placed in the compartment of a Fourier transform infrared spectrometer and were simultaneously exposed to a UV photolyzing light and an IR analyzing light beam. The photolyzing light was generated by a medium-pressure mercury lamp (Flexicure UV system) and was directed through a flexible fiber optic to the IR compartment. The spectrometer was operated in the absorbance mode and the detection wavelength was set at 810 cm^{-1} (C═C–H twist) to monitor the disappearance of the double bonds. The degree of conversion, α, can be expressed by the following relation:

$$\alpha = \frac{(A_0 - A_t)}{A_0}$$

where A_0 is the initial absorbance at 810 cm $^{-1}$ and A_t is the absorbance value at irradiation time t.

2.7. Photo differential scanning calorimetri (Photo-DSC)

The photoinitiated polymerization of TMPTA 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 40 mW cm^{-2} as measured by a UV radiometer capable of broad UV range coverage. The mass of the samples was approximately 2 ± 0.1 mg and the measurements were carried out in isothermal mode at room temperature under a nitrogen atmosphere (nitrogen flow: 50 mL min^{-1}). The samples were irradiated for 300 s 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 $\Delta H_p^{theor} = 86$ kJ/mol was used as the theoretical heat evolved for acrylate double bonds [17]. 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 is the molar mass of the monomer, n is the number of double bonds per monomer molecule and m is the mass of monomer in the sample.



Scheme 2. Synthesis of amine linked photoinitiator.

3. Results and discussion

Synthesis of the diethanolamine linked type II photoinitiator (BPDEA) was achieved in two steps: first, acrylation of 4-hydroxybenzophenone with acryloylchloride was performed and second, Michael addition reaction between acrylated benzophenone (BPAc) and *N*,*N*-diethanolamine was carried out (Scheme 2).

The absorption spectra of BPDEA, BP and obtained poly (methylmethacrylate) in $CHCl_3$ are given in Fig. 1. Although BPDEA exhibits a similar absorption spectrum to benzophenone (λ_{max} = 294 nm), 40 nm of the wavelength shifted to the red region of the electromagnetic spectrum and the molar absorbance of BP and BPDEA were 16,600 and 10,400 $mol^{-1}\,L\,cm^{-1}$, respectively.

Photobleaching experiment of BPDEA photoinitiator was performed under air atmosphere in $CHCl_3$. Fig. 2 presents a plot of the UV absorption versus the wavelength and shows the decrease in the absorbance at 294 nm. The decrease in absorbance at 294 nm possibly resulted from the hydrogen abstraction of the benzophenone carbonyl group from the ethanolamine. When irradiation was prolonged to 420 s, a rapid decrease in absorbance at 294 nm was observed and it almost disappeared (Fig. 2).

To obtain more information about the photophysical properties, luminescence experiments were performed. BPDEA fluorescence emission was not observed as usual for most of the BP derivatives. Therefore, phosphorescence measurements were performed in 2-methyl tetrahydrofuran at 77 K. It is very useful to get information about the triplet configuration of the initiator. BPDEA exhibited a phosphorescence emission spectrum similar to its parent compound benzophenone. The (0, 0) emission band occurs at 417 nm, corresponding to approximate triplet energy of ca 286.9 kJ mol^{-1} (see Fig. 3). The phosphorescence lifetime of BPDEA was calculated as 25 ms. Since the phosphorescence lifetime for n–π^* triplets are significantly shorter than π–π^* triplets, we can comment that the lowest triplet state of BPDEA is an n–π^* nature.

Polymerization experiments for MMA were performed with BPDEA in air atmosphere. The obtained results were compared with BP in the presence of MDEA. The results are tabulated in Table 1.

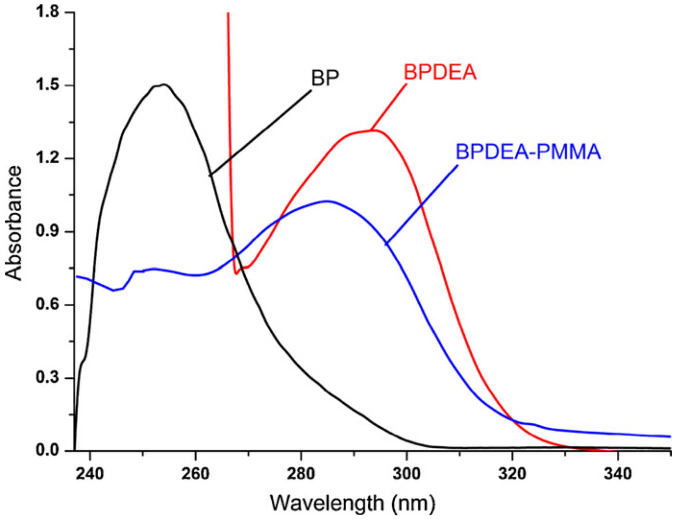


Fig. 1. Absorption spectra of BP [9×10^{-5}], BPDEA [1.25×10^{-4} M] and PMMA obtained by photoinitiated free radical polymerization by using BPDEA as a photoinitiator in $CHCl_3$.

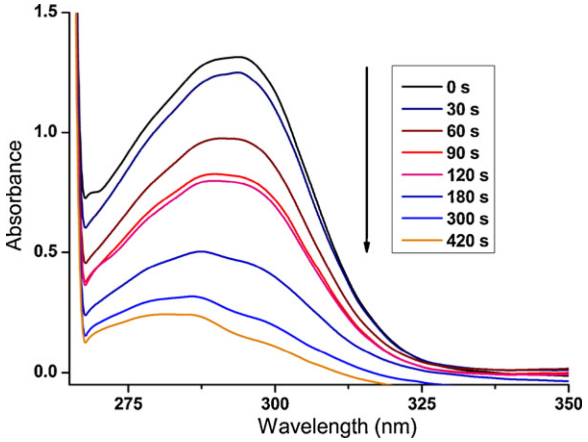


Fig. 2. Photobleaching experiment of BPDEA photoinitiator under air atmosphere in $CHCl_3$.

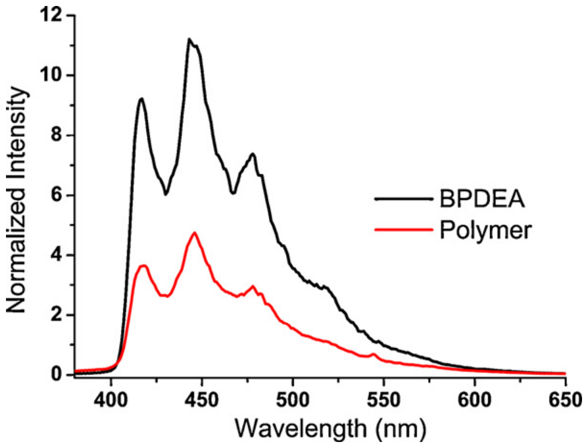


Fig. 3. Phosphorescence spectra of BPDEA in ethanol at 77 K (λ_{exc} = 290 nm) (delay time: 10 ms).

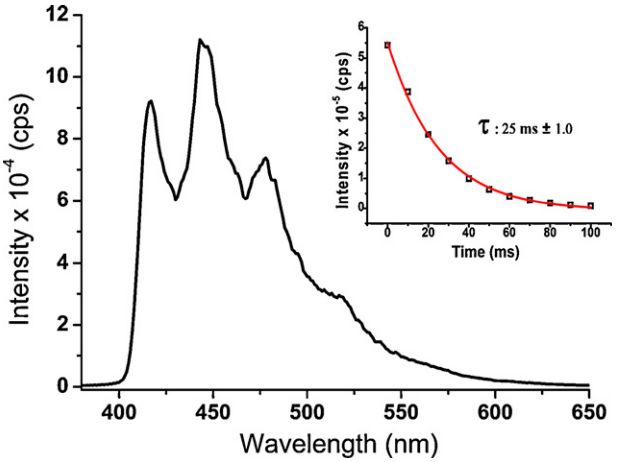


Fig. 4. Phosphorescence spectra of BPDEA and PMMA obtained by photoinitiated free radical polymerization by using BPDEA as a photoinitiator in 2-methyltetrahydrofuran at 77 K (λ_{exc} = 290 nm) (delay time: 10 ms).

To exclude the inhibition effect of air, some experiments were carried out in nitrogen atmosphere and this helped to distinguish the reactivity of initiating radicals which are α-amino alkyl radicals in both cases. Polymerization of MMA with BPDEA (1×10^{-2} M) under nitrogen atmosphere gave the highest conversion percentage value. Decreasing the photoinitiator concentration led to a decrease in the conversion of monomer to polymer. When polymerization experiments were performed in air atmosphere with BPDEA (1×10^{-2} M) without any co-initiator, the conversion percentage value was 5.9. The diethanolamine group on the benzophenone helped the initiator to work even in air atmosphere against the benzophenone. Possibly, the carbonyl group of benzophenone abstracted a hydrogen atom from diethanolamine and the resulting aminoalkyl group initiated the polymerization of MMA. Indeed, these results were confirmed by the absorption spectrum of the initiator attached BP. The phosphorescence lifetime of PMMA was calculated as 13 ms. The absorption and phosphorescence emission spectra of the resulting PMMA show that BP moiety was successfully incorporated into the PMMA structure (see Figs. 1 and 4).

Conversion percentage values and the molecular weights of PMMA also helped to understand the effect of α-aminoalkyl as an initiating radical. Run 1 in Table 1: α-aminoalkyl radicals had two roles for the photoinitiated polymerization of MMA in air atmosphere; scavenging of oxygen and initiating of polymerization. Therefore, conversion values were nearly half that of the experiments carried out in nitrogen atmosphere. Run 2 in Table 1, since experiment was performed under nitrogen atmosphere, produced α-aminoalkyl radicals just initiated the polymerization of acrylates. The chain transfer agent effect of amines was more distinct for the experiments carried out in air atmosphere. When polymerization experiments were performed with BP/MDEA, conversion of monomer to polymer was lower than BPDEA initiator.

RT-FTIR and Photo-DSC methods were employed to study the initiating effect of photoinitiators for multifunctional acrylate (TMPTA). According to RT-FTIR studies, as can be seen from the inset of Fig. 5, during the first 5 s of irradiation time, the formulation consisting of BPDEA (0.1%) lead to little higher conversion percentage values than BP/MDEA (0.1%/1.0%, w/w). The BPDEA initiator competes slightly better to inhibit the effect of oxygen than the BP/MDEA system at early irradiation time. Eventually, nearly similar conversion percentage values were obtained for prolonged irradiation times (t_{irr} = 300 s) for both formulations (Fig. 5).

To follow the photopolymerization kinetics of various formulations, Photo-DSC was employed. Heat flow and conversion % values are given in Figs. 6 and 7 (experiments were performed in air free atmosphere). α-Aminoalkyl radical produced from *N*-methyldiethanolamine was more efficient at the beginning of the irradiation time than the α-aminoalkyl radical produced from our initiator. But BPDEA (1.0%) achieved almost the same conversion percentage values obtained for both formulations BP/MDEA (1.0%/10.0%, w/w) and BP (1%) for prolonged irradiation time. The initiation effect of the photoinitiators was more clearly seen when photoinitiator concentration was reduced to 0.1% for both BP and BPDEA initiators. The amine linked type II initiator BPDEA worked much better at the low initiator concentration levels than the BP (0.1%) formulation. The rate of producing the initiating radicals was

Table 1
Photoinitiated free radical polymerization of MMA[a] in $CHCl_3$ for 60 min with λ_{max} = 350 nm photoreactor in air.

Run	Photoinitiator (PI)	[PI] (mol L^{-1})	[MDEA] (mol L^{-1})	Conversion (%)	*Mn*[c] (g mol^{-1})	*Mw*/*Mn*[c]
1	BPDEA	1×10^{-2}	–	5.9	33.195	1.84
2	BPDEA	1×10^{-2}	–	13.5[b]	39.045	1.83
3	BPDEA	5×10^{-3}	–	12.4[b]	35.140	1.95
4	BPDEA	1×10^{-3}	–	8.3[b]	62.715	1.67
5	BPDEA	5×10^{-4}	–	7.0[b]	83.800	1.52
6	BP	1×10^{-2}	1×10^{-2}	8.3	25.880	1.40
7	BP	1×10^{-2}	5×10^{-2}	8.1	13.050	1.40
8	BP	1×10^{-2}	1×10^{-2}	4.2[b]	26.240	1.47
9	BP	1×10^{-3}	5×10^{-3}	5.3	27.050	1.63
10	BP	1×10^{-3}	5×10^{-3}	<1[b]	–	–

[a] [MMA] = 4.68 mol L^{-1}, irradiation time = 60 min; BP = benzophenone; BPDEA = [bis-(2 hydroxy-ethyl)-amino]-propionic acid 4-benzoyl-phenyl ester; MDEA = *N*-methyldiethanolamine.

[b] Carried out under nitrogen atmosphere.

[c] Determined by GPC according to linear polystyrene standards.

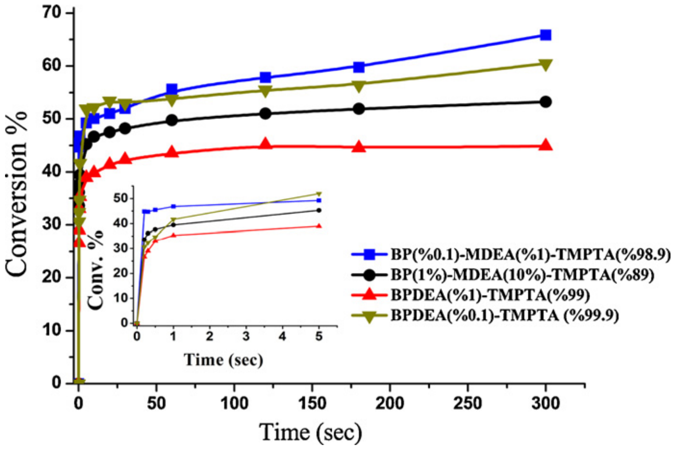


Fig. 5. RT-FTIR kinetic results time versus % conversion of TPMTA monomer in the presence of BPDEA and BP/MDEA in different (w/w) concentrations with polychromatic light source.

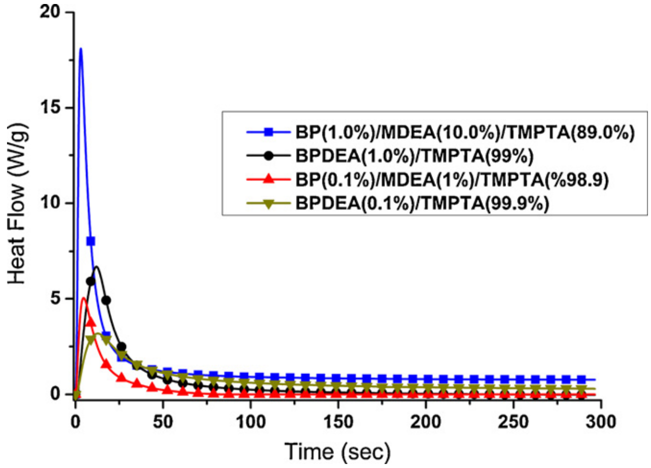


Fig. 6. Heat flow versus time for the polymerization of TMPTA initiated by BPDEA and BP/MDEA systems cured at 30 °C by UV light with an intensity of 40 mW cm^{-2}.

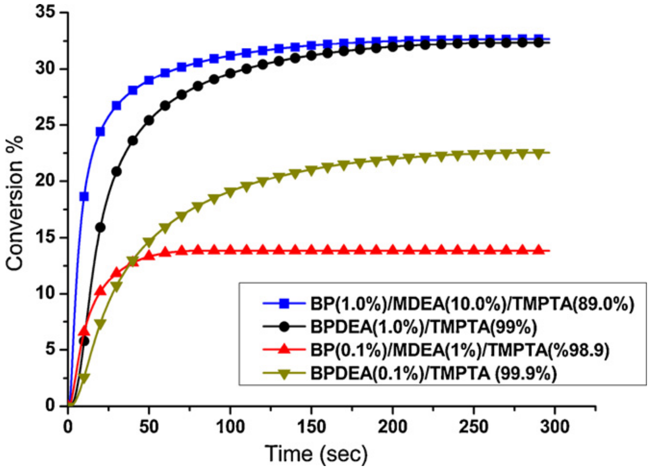
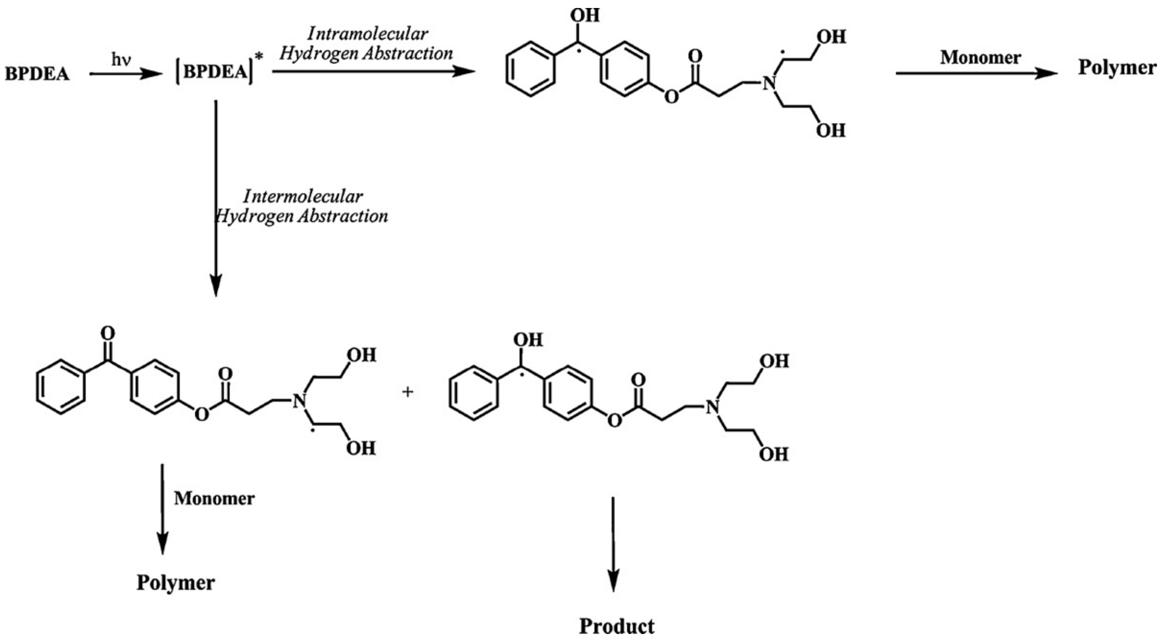


Fig. 7. Conversion versus time for the polymerization of TMPTA initiated by BPDEA and BP/MDEA systems cured at 30 °C by UV light with an intensity of 40 mW cm^{-2}.

faster for BPDEA than for BP/MDEA at low initiator concentrations (0.1%) (Fig. 7).

4. Conclusion

Diethanolamine based type II photoinitiator (BPDEA) readily synthesized in high yields. The photoinitiator was fully characterized and its photophysical properties determined successfully. This photoinitiator was used in photoinduced free radical polymerization of MMA and TMPTA in the absence of an additional co-initiator (MDEA). BPDEA is quite effective in free radical photopolymerization and it also initiates photopolymerization successfully without a hydrogen donor; possibly, the intermolecular hydrogen abstraction process is a more dominant path to produce initiating radicals (Scheme 3).



Scheme 3. Photoinitiated free radical polymerization mechanism of BPDEA.

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