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ORIGINAL PAPER

"Mono" and "bifunctional" aromatic esterificated benzophenone photoinitiators for free radical polymerization

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Abstract Aromatic esterificated benzophenone derivatives, benzoic acid 4-benzoyl-phenyl ester (BPBz) and bis-benzoic acid 4-benzoyl-phenyl ester (BisBPBz) were simply synthesized and characterized. The triplet states of the photoinitiators were determined by laser flash photolysis and phosphorescence spectroscopy. The photodecomposition of the initiators was performed by UV light; the increase in the absorption spectra was attributed to the decreasing number of ester groups which led to an increase in ketone groups according to the Photo-Fries rearrangement of aromatic esters. The photoinitiation capabilities for methyl methacrylate (MMA) polymerizations were investigated under air and nitrogen atmospheres. Ester-functional benzophenone photoinitiators were found to be more effective than benzophenone (BP) in the presence of a co-initiator for photoinduced free radical polymerization of MMA. The kinetics of photopolymerization for different formulations which consist of multifunctional acrylates was also studied using the Real-Time Fourier Transform infrared spectroscopy (RT-FTIR) method. The film properties of these formulations were investigated after curing of films by Mini-UV-Cure equipment.

Keywords Benzophenone · Free radical polymerization · Photo-fries rearrangement · Type II system · UV curing

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Introduction

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

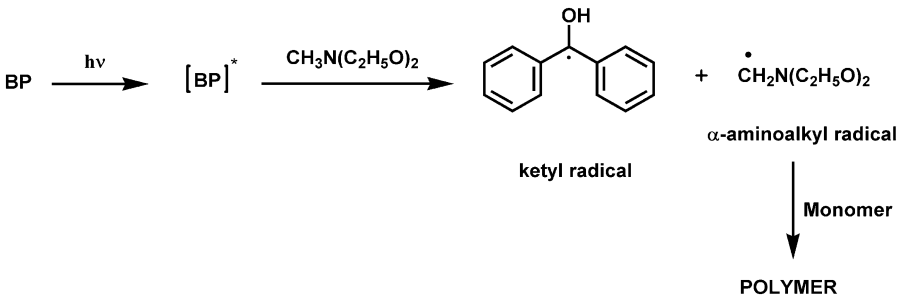
Typical type II photoinitiators include aromatic carbonyls such as benzophenone and derivatives [3–11], thioxanthone [12–15], benzil, quinones, and organic dyes. Benzophenone (BP) is a well-known type II photoinitiator for the radiation curing of coatings, printing inks, etc. After triplet-state excitation, benzophenone is able to abstract hydrogen from ether, amine, alcohol or thiol functional co-initiators and thus reactive centers can be generated on co-initiator molecules to initiate free radical polymerization [4, 6]. The ketyl radical is not able to initiate the polymerization because of sterical hindrance and delocalization of an unpaired electron. Generally, methyldiethanolamine, triethylamine, or ethyl 4-(dimethylamino) benzoate are used as the co-initiators for type II photoinitiators (Scheme 1).

In this study, "mono" and "bifunctional" aromatic esterificated benzophenone photoinitiators (BPBz and BisBPBz) were synthesized [7, 16] and the structures of the photoinitiators were determined by FT-IR, elemental analysis and ^{1}H NMR. The photophysical behavior and initiating mechanism of the initiators were investigated using phosphorescence and laser flash photolysis measurements. Previously, Packowski et al. reported the photophysical properties of BPBz [7]. In this text, a detailed study is presented in terms of the synthesis as well as the photophysical and free radical photopolymerization results of BPBz and BisBPBz.

Experimental

Materials

4-Hydroxybenzophenone (98+ %, Aldrich), 4, 4′-dihydroxybenzophenone (97 %, Aldrich), Benzophenone (99 %, Aldrich), benzoylchloride (98 %, Fluka),



Scheme 1 Type II mechanism of benzophenone photoinitiator in the presence of a co-initiator

triethylamine (99 %, Merck) and dichloromethane (DCM, ≥99.5 %, Merck) were used as received. Methyl methacrylate (MMA, 99+ %, Merck) was washed with 5 % aqueous NaOH solution, dried over $CaCl_2$, and distilled over CaH_2 under vacuum just before use. *N*-methyldiethanolamine (MDEA, 99 %, Aldrich) was used as received. Tripropylene glycol diacrylate (TPGDA), P-3038 (75 % epoxyacrylate oligomer (P-3016) + 25 % TPGDA) and trimethylol propane triacrylate (TMPTA) were obtained from Cognis France.

Instruments

UV–Vis spectra were taken on a Varian UV–Visible Cary 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. Elemental analysis was performed on a CHNS-932 LECO instrument. Laser flash photolysis experiments employed the pulses from an Applied Photophysics with YAG laser (355 nm, pulse, 5 ns) and a computer-controlled system. Solutions of the benzophenone derivatives were prepared at concentrations such that the absorbance was ~0.3 at the excitation wavelength (355 nm). A Flexicure UV system was employed which consists of a medium-pressure mercury lamp and a light guide. A Primarc Mini-UV-Cure system was employed for curing of formulations on paper.

Synthesis of benzoic acid 4-benzoyl-phenyl ester (BPBz)

To a solution of 4-hydroxybenzophenone (0.99 g, 5 mmol) and triethylamine (0.70 mL, 5 mmol) in dichloromethane (DCM) (15 ml), benzoyl chloride (1.5 mL, 12.5 mmol) in DCM (5 mL) was added dropwise at 0 °C, and the resulting mixture was stirred at room temperature overnight. The mixture was washed two times with water (100 mL), a saturated aqueous solution of $NaHCO_3$ (100 mL × 2), and a saturated aqueous solution of NaCl (100 mL). The organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent evaporated. The resulting residue was purified by recrystallization from ethanol. Mp: 116–118 °C, yield: 75 %.

IR (ATR): ν cm^{-1} 3064 (Ar–H), 1731 (C=O), 1641 (C=O), 1596 (C=C) cm^{-1}.

Elemental analysis $C_{20}H_{14}O_3$: Calc, C: 79.46; H: 4.67. Found, C: 79.36; H: 4.62.

^1H NMR ($CDCl_3$, 500 MHz): $\delta = 7.38$ (d, $J = 6.62$ Hz, 2H), 7.51–7.58 (m, 4H), 7.63 (t, $J = 8.19$ Hz, 1H), 7.69 (t, $J = 8.19$ Hz, 1H),7.85 (d, $J = 7.25$ Hz, 2H), 7.94 (d, $J = 6.62$ Hz, 2H), 8.25 (d, $J = 8.19$ Hz, 2H) ppm.

Synthesis of bis-benzoic acid 4-benzoyl-phenyl ester (BisBPBz)

To a solution of 4, 4′-dihydroxybenzophenone (1.06 g, 5 mmol) and triethylamine (1.4 mL, 10 mmol) in dichloromethane (DCM) (15 mL), benzoyl chloride (2.4 mL, 20 mmol) in DCM (5 mL) was added dropwise at 0 °C, and the resulting mixture was stirred at room temperature overnight. The mixture was washed two times with water (100 mL), a saturated aqueous solution of $NaHCO_3$ (100 mL × 2), and a saturated aqueous solution of NaCl (100 mL). The organic layers were dried over

anhydrous Na_2SO_4, filtered, and the solvent evaporated. The resulting residue was purified by recrystallization from ethanol. Mp: 184–186 °C, yield: 70 %.

IR (ATR): ν cm^{-1} 3054 (Ar–H), 2928 (C–H), 1727 (C=O), 1660 (C=O) 1596 (C=C) cm^{-1}.

Elemental analysis $C_{27}H_{18}O_5$: Calc, C: 76.77; H: 4.29. Found, C: 76.74; H: 4.22.

^1H NMR ($CDCl_3$, 500 MHz): $\delta = 7.27$ (d, $J = 6.62$ Hz, 4H), 7.44 (t, $J = 7.25$ Hz, 4H), 7.57 (t, $J = 8.19$ Hz, 2H), 7.84 (d, $J = 6.62$ Hz, 2H), 7.94 (d, $J = 6.62$ Hz, 4H), 8.13 (d, $J = 7.25$ Hz, 4H) ppm.

Photopolymerization

Appropriate solutions of the MMA and photoinitiators in the presence of the co-initiator (MDEA) were irradiated in a photoreactor equipped with a cooling fan and twelve Philips' lamps emitting nominally at $\lambda = 350$ nm at room temperature for 60 min either in an air or nitrogen atmosphere. Polymers were obtained after precipitation in methanol and dried under vacuum. Conversions were calculated for all samples gravimetrically.

UV curing

Some curing experiments were performed on a bench-type UV line (Primarc-Minicure-80 W cm^{-1}) operated at a belt speed of 5 m min^{-1}. Formulations were coated onto transparent tracing paper by means of a calibrated wire-wound applicator. The thickness of the UV-curable film was set at 12 μm. The coated papers were passed under a lamp at a known belt speed. The degree of cure was measured by using a hard rubber bulb. When no visible deformation of the surface occurred the film was considered cured. This test was repeated on a minimum of three samples.

Real-time infrared spectroscopy photopolymerization studies (RT-FTIR)

Real-time infrared spectroscopy, with millisecond time resolution, is more useful in determining photopolymerization kinetics. In real-time spectra, reactions are followed by monitoring the disappearances of a reactive bond [17, 18]. The relationship between monomer structure and reactivity was investigated extensively by Decker [19].

Uniform samples of photocurable formulations consisting of a photoinitiator and multifunctional monomers in the presence of MDEA were prepared by casting on a KBr pellet. The samples were placed in the compartment of a Fourier transform infrared spectrometer (Nicolet 6700 FT-IR) 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:

$$\alpha = \frac{A_0 - A_t}{A_0} \quad (1)$$

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

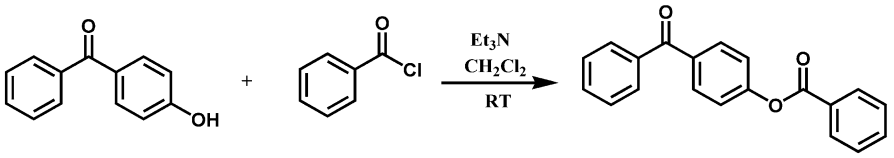
Results and discussion

"Mono" and "bifunctional" aromatic esterificated benzophenone photoinitiators (BPBz and BisBPBz) were obtained by simple esterification of hydroxyl benzophenones with excess amount of benzoyl chloride in DCM (Schemes 2, 3).

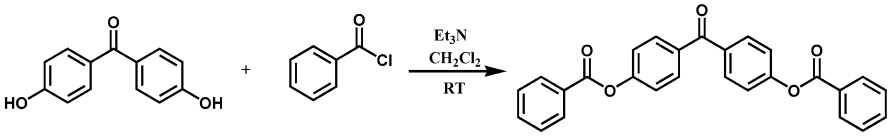
The structures of the photoinitiators were confirmed by spectroscopic and elemental analysis (see "Experimental"). The absorption properties of benzophenone and two different substituted benzophenone derivatives (BPBz and BisBPBz) in DCM are shown in Fig. 1. As can be seen from Fig. 1, BPBz and BisBPBz possess similar absorption characteristics to BP itself with maximums at 337 and 334 nm, respectively.

The photodecomposition of BPBz and BisBPBz was followed by detecting UV spectral changes upon photolysis. The UV spectra of BPBz and BisBPBz (1×10^{-3} M) in DCM were recorded after the solution had been exposed to the light of a UV lamp (see Fig. 2). As the photolysis proceeded, the absorption spectra of both initiators increased and this effect might be attributed to the Photo-Fries rearrangement of aryl esters to hydroxy ketones as first observed by Anderson and Reese in 1960 [20–23]. This photoreaction mainly yields a mixture of ortho- and para-hydroxy ketones (see Scheme 4).

Another useful method to follow the decrease of the ester group band and increase of the ketone peak is by FT-IR spectroscopy. The analysis was made from the FT-IR spectra of the initiator containing solutions, both before and after irradiation. The depletion of the ester group band at 1731 cm^{-1} is accompanied by an increase at 1641 cm^{-1}.



Scheme 2 Synthesis of BPBz as a Type II photoinitiator



Scheme 3 Synthesis of BisBPBz as a Type II photoinitiator

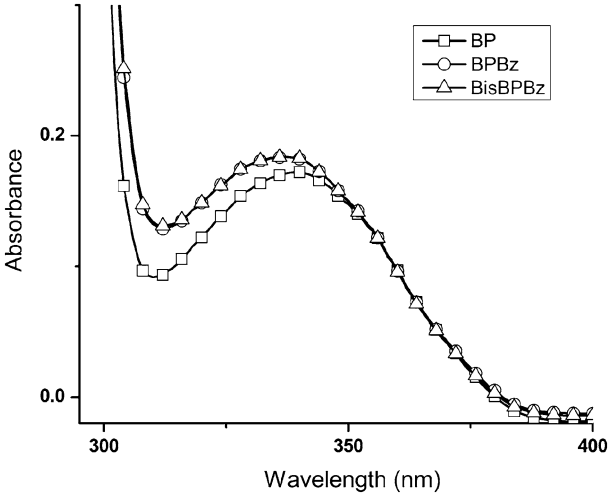


Fig. 1 Absorption spectra of benzophenone (BP), benzoic acid 4-benzoyl-phenyl ester (BPBz) and bis-benzoic acid 4-benzoyl-phenyl ester (BisBPBz) [1×10^{-3} M] in DCM

Some photophysical properties of BPBz have already been reported by other research groups [7]. The results obtained showed some differences, possibly as a result of irradiation sources. The triplet states of both BPBz and BisBPBz in a degassed solution of acetonitrile were investigated by laser flash photolysis. After irradiation with laser pulses (355 nm) the spectra of BPBz and BisBPBz showed peaks at 530 and 540 nm (Figs. 3, 4), respectively.

These transients decay kinetics with a first-order contribution and show lifetimes of 1.2 and 1.1 μs, respectively. Benzophenone triplets and benzophenone ketyl radicals are known to have some absorption between 300 and 400 nm. The transient absorption at 320 and 330 nm decayed in the order of 1.3 and 1.45 μs for BPBz and BisBPBz, respectively. To confirm the triplet nature of the transients, oxygen-quenching experiments were performed and it was observed that both transients were quenched by oxygen.

Additionally, phosphorescence measurements are useful to gain information on the nature of the triplet states of photoinitiators. The phosphorescence spectra of both photoinitiators in ethanol displayed almost the same features at 77 K and the phosphorescence emission spectra of BPBz and BisBPBz were similar to the parent benzophenone (BP) compound. BPBz and BisBPBz possessed emission bands at maximum 440 and 439 nm, respectively (see Fig. 5). The (0, 0) emission bands for BPBz and BisBPBz occurred at 412 and 410 nm, corresponding to approximate triplet energies of ca 290 and ca 291 kJ/mol, respectively. The triplet energy for the benzophenone parent compound is given as 285.5 kJ/mol in the literature [7].

The phosphorescence lifetimes were found to be 13 and 10 ms for BPBz and BisBPBz, respectively. The phosphorescence emission spectrum of BPBz and BisBPBz (Figs. 3, 4) with short phosphorescence lifetime, 13 and 10 ms, respectively, in a matrix at 77 K indicates a $n-\pi^*$ nature of the lowest triplet state.

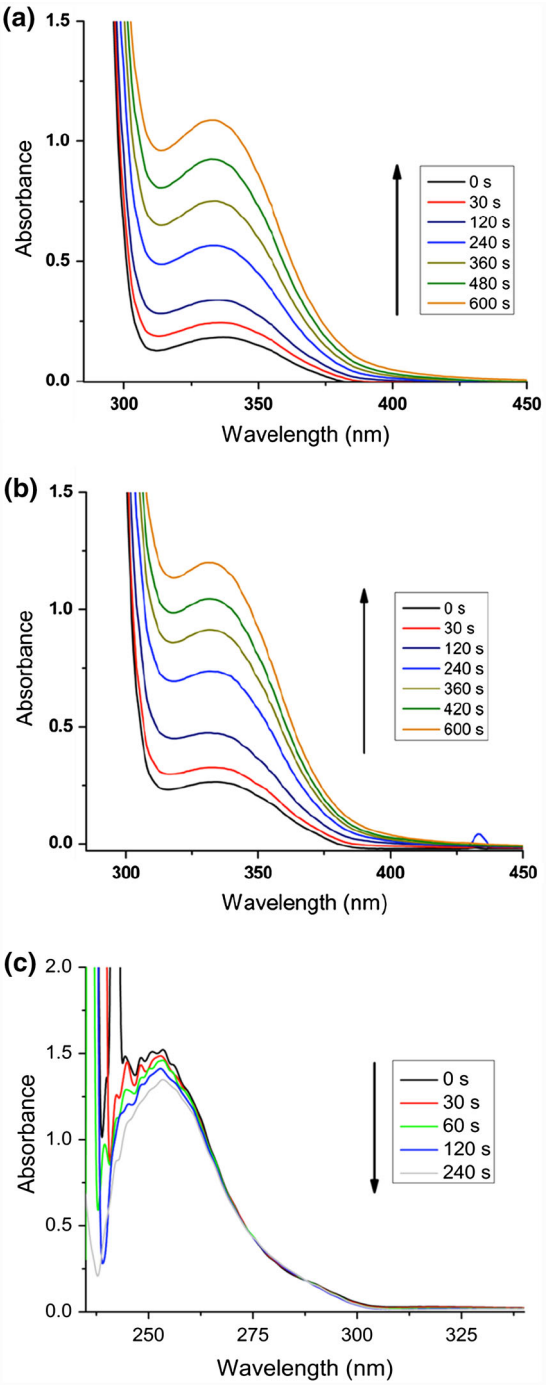
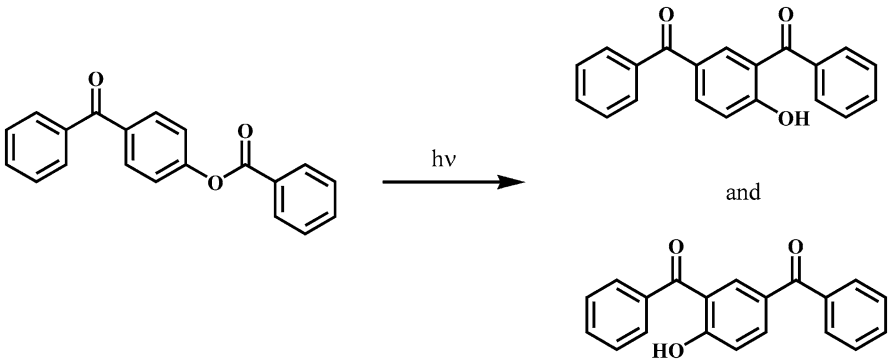


Fig. 2 Absorption spectra of **a** BPBz [1 × 10^{-3} M], **b** BisBPBz [1 × 10^{-3} M] in DCM and **c** BP [2.5 × 10^{-5}] in $CHCl_3$ solution in air atmosphere after irradiation



Scheme 4 Possible mechanism of Photo-Fries rearrangement of BPBz

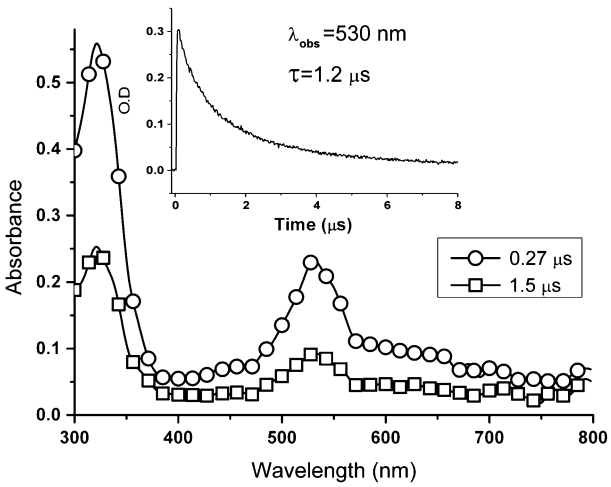


Fig. 3 Transient optical absorption spectrum recorded 0.27 and 1.5 μs following laser excitation (355 nm, 5 ns) of BPBz in argon-saturated acetonitrile solution. *Inset* triplet decay at 530 nm

Photopolymerization experiments of MMA in air and nitrogen-saturated DCM solutions were performed using BPBz and BisBPBz as the initiators in the presence of MDEA. The gravimetrically determined conversions of monomer (MMA) to polymer depending on the concentration of the initiator are shown in Tables 1 and 2. The results obtained using BPBz and BisBPBz were compared with BP itself (see Tables 1, 2).

According to the polymerization results, both BPBz and BisBPBz photoinitiators with MDEA resulted in higher monomer conversion than BP/MDEA either in an air or nitrogen atmosphere. The most effective initiator concentration for the polymerization of MMA was found to be 5×10^{-3} M for both initiators either in an air or nitrogen atmosphere but generally all photoinitiators showed better initiation efficiency under a nitrogen atmosphere, possibly due to the inhibiting

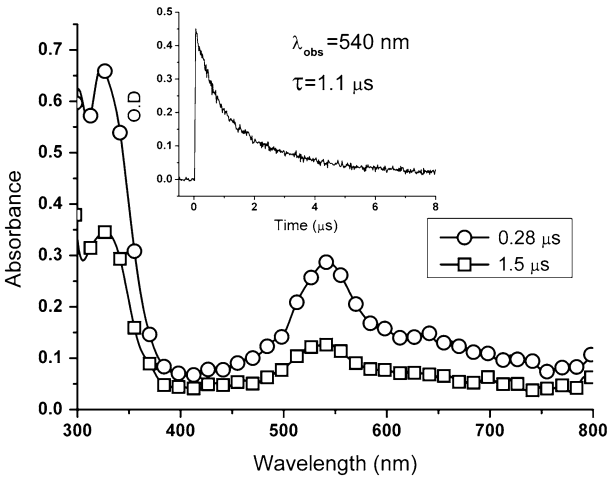


Fig. 4 Transient optical absorption spectrum recorded 0.28 and 1.5 μs following laser excitation (355 nm, 5 ns) of BisBPBz in argon-saturated acetonitrile solution. *Inset* triplet decay at 540 nm

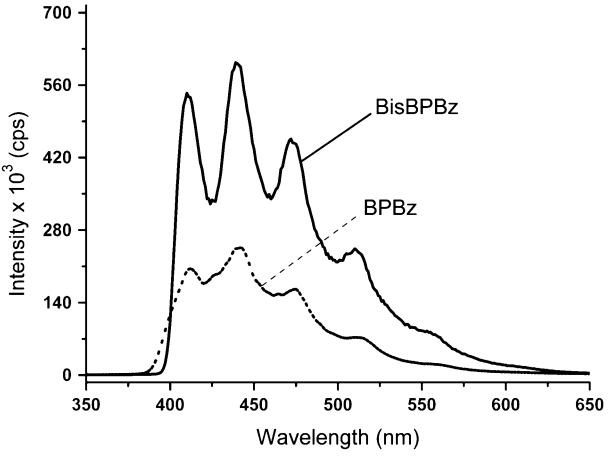


Fig. 5 Phosphorescence emission spectra of *BPBz* and *BisBPBz* in ethanol at 77 K (λ_{ex} = 330 nm)

effect of oxygen on the polymerization, even in the presence of MDEA. Since MDEA is required for both BPBz and BisBPBz to act as the initiator for methacrylate polymerization, it is suggested that both initiators react with MDEA to give α-aminoalkyl radicals that initiate polymerization.

The photopolymerization kinetics was also investigated by Real-Time Fourier Transform Infrared Spectroscopy (RT-FTIR). Several formulations (see Table 3) were prepared and comprised a mixture of monomers in the presence of initiators and MDEA as co-initiator, which were coated onto a KBr tablet. The sample was placed in the compartment of a FT-IR spectrophotometer where it was exposed for a

Table 1 Photoinitiated polymerization of MMA with BP and BPBz in the presence of MDEA in DCM under air and nitrogen atmospheres

[MMA] = 4.68 mol L^{-1}, [MDEA] = 5×10^{-2} mol L^{-1}, irradiation time = 60 min

BP Benzophenone, *BPBz* benzoic acid 4-benzoyl-phenyl ester, *MDEA N*-methyldiethanolamine

Photoinitiator (PI)	[PI] (mol L^{-1})	N_2	Conversion (%)
BPBz	1×10^{-4}	−	2.00
BPBz	1×10^{-4}	+	4.60
BP	1×10^{-4}	+	2.35
BPBz	5×10^{-4}	−	2.85
BPBz	5×10^{-4}	+	6.00
BPBz	3×10^{-3}	−	5.20
BPBz	3×10^{-3}	+	7.15
BPBz	5×10^{-3}	−	6.25
BPBz	5×10^{-3}	+	8.60
BP	5×10^{-3}	+	5.50

Table 2 Photoinitiated polymerization of MMA with BP and BisBPBz in the presence of MDEA in DCM under air and nitrogen atmospheres

[MMA] = 4.68 mol L^{-1}, [MDEA] = 5×10^{-2} mol L^{-1}, irradiation time = 60 min

BP Benzophenone, *BisBPBz* bis-benzoic acid 4-benzoyl-phenyl ester, *MDEA N*-methyldiethanolamine

Photoinitiator (PI)	[PI] (mol L^{-1})	N_2	Conversion (%)
BisBPBz	1×10^{-4}	−	2.20
BisBPBz	1×10^{-4}	+	3.65
BP	1×10^{-4}	+	2.35
BisBPBz	5×10^{-4}	−	3.00
BisBPBz	5×10^{-4}	+	4.70
BisBPBz	3×10^{-3}	−	6.20
BisBPBz	3×10^{-3}	+	6.70
BisBPBz	5×10^{-3}	−	7.00
BisBPBz	5×10^{-3}	+	7.40
BP	5×10^{-3}	+	5.50

few seconds to the UV radiation of a medium-pressure mercury lamp via a fiber optic light pipe. The progress of polymerization was monitored continuously by following the decrease in intensity of the vibrational band at 810 cm^{-1} for the acrylate alongside the irradiation time. Conversion percentages of polymerization were determined according to Eq. (1) and the results obtained from RT-FTIR are shown in Figs. 6 and 7.

It is known that the rate of polymerization also depends on the reactivity of the functional group and its concentration and the viscosity of the resin. The chemical structure and functionality of both monomer and oligomer are also important, for they will determine the final degree of polymerization, as well as the physical and chemical characteristics of the UV-cured polymer [18]. The influence of the resin constituents on the kinetic parameters can be readily evaluated by RTIR spectroscopy that seems to be an ideal tool for assessing the new initiators. Therefore, several types of monomers were employed and their stoichiometries were changed as well.

Two different photoinitiator concentrations (w/w) were used in the formulations. As indicated in Fig. 6, when the photoinitiator concentration was chosen as 0.5 %,

Table 3 Prepared formulations for RT-FTIR studies

Formulations	BPBz (w/w, %)	BisBPBz (w/w, %)	BP (w/w, %)	MDEA (w/w, %)	TMPTA (w/w, %)	TPGDA (w/w, %)	P-3038 (w/w, %)
1	0.5	–	–	10	89.5	–	–
2	0.5	–	–	10	–	22	67.5
3	1.0	–	–	10	89.0	–	–
4	1.0	–	–	10	–	22	67.0
5	–	0.5	–	10	89.5	–	–
6	–	0.5	–	10	–	22	67.5
7	–	1.0	–	10	89.0	–	–
8	–	1.0	–	10	–	22	67.0
9	–	–	1.0	10	89.0	–	–

the conversion percentage of formulation 1 reached 49 % for the first 1 s of irradiation time for BPBz and 35 % conversion was obtained when the photoinitiator was changed to BisBPBz (formulation 5). When the irradiation was prolonged to 300 s, 69 and 66 % conversions were achieved for the (1) and (5) formulations, respectively. But as indicated in Fig. 6, when the photoinitiator concentration was chosen as 1.0 %, the conversion percentage of formulation 3 reached 62 % for the first 1 s of irradiation time for BPBz and 28 % conversion was obtained when the photoinitiator was changed to BisBPBz (formulation 7). During 300 s of irradiation time, 78 and 50 % conversions were achieved for the (3) and (7) formulations, respectively. Formulation 9 contains BP and NMDEA, was used for polymerization of TMPTA to compare the initiation efficiencies of both photoinitiators namely BisBPBz and BPBz. As can be clearly seen from Fig. 6, the initiating efficiency of BPBz is more efficient than BP itself. At the low concentration of BisBPBz (0.5 %) leads high conversion of monomer to polymer (66 %) compared to BP (1.0 %) in prolonged irradiation time (300 s).

To see the effect of the type of monomer, we also used another formulation which consisted of TPGDA and Epoxydiacrylate (P-3038) mixture. In this case, as indicated in Fig. 7, when the photoinitiator concentration was chosen as 0.5 %, the conversion percentage of formulation 2, reached 39 % for the first 1 s of irradiation time for BPBz and 31 % conversion was obtained when the photoinitiator was changed to BisBPBz (formulation 6). 63 and 62 % conversions were obtained for the (2) and (6) formulations for 300 s of irradiation time, respectively. But as indicated in Fig. 7, when the photoinitiator concentration was chosen as 1.0 %, the conversion percentage of formulation 4, reached 50 % for the first 1 s of irradiation time for BPBz and 35 % conversion was obtained when the photoinitiator was changed to BisBPBz (formulation 8). Conversion values were found as 69 and 61 % during 300 s of irradiation time for the formulations (4) and (8), respectively.

UV-curing experiments were also performed. All formulations were applied to a transparent tracing paper by means of a calibrated wire-wound applicator (12 μm). Formulations (see Table 3) containing BPBz, BisBPBz and BP as initiators coated onto paper and were passed under the lamp at 5 m min^{-1} belt speed. The degree of

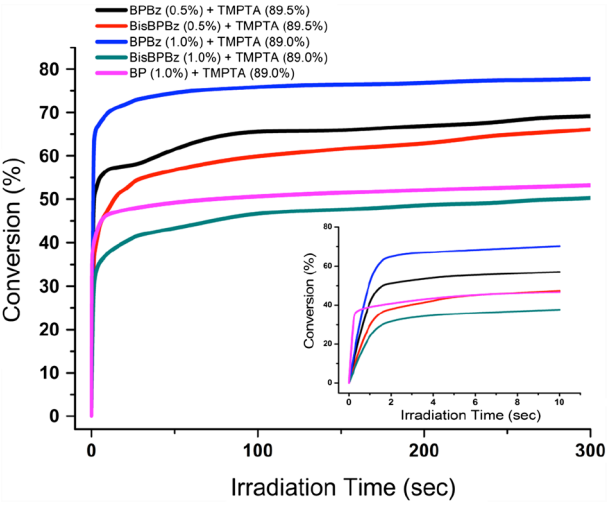


Fig. 6 Kinetic profiles demonstrating the photopolymerization of the TMPTA + MDEA mixture (w/w) containing BPBz, BisBPBz and BP with polychromatic lights in an air atmosphere (for 300 and 10 s of irradiation). Formulations: PI + TMPTA + (10 %) MDEA. The *inset* shows the polymerization kinetics in the initial phase

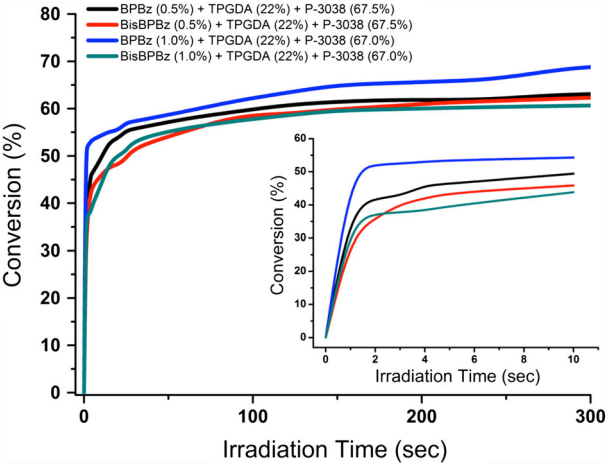


Fig. 7 Kinetic profiles demonstrating the photopolymerization of the TPGDA + P-3038 + MDEA mixture (w/w) containing BPBz and BisBPBz with polychromatic lights in an air atmosphere (for 300 and 10 s of irradiation). Formulations: PI + TPGDA + P-3038 + (10 %) MDEA. The *inset* shows the polymerization kinetics in the initial phase

cure was assessed using of rubber bulb until no visible deformation of the surface occurred. All films were cured with only one pass underneath of UV-cure unit which is sign of efficiency of sensitized initiators compared to well-known commercial initiator BP.

Conclusion

Two different hydroxyl functional benzophenone photoinitiators were successfully converted to ester-functional benzophenone photoinitiators (BPBz and BisBPBz). BPBz and BisBPBz initiate the polymerization of MMA with MDEA, which is similar to benzophenone. However, it was found from polymerization studies that these photoinitiators are more efficient than benzophenone itself. BPBz and BisBPBz were also used as photoinitiators for the polymerization of multifunctional acrylates in the presence of MDEA. Polymerizations were recorded by RT-FTIR spectroscopy. BPBz was found to be much more efficient than BisBPBz as an initiator for polymerization of acrylates and methacrylates.

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