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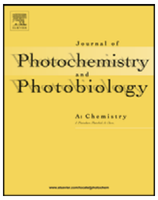

6-Benzoyl-1,3-benzodioxolane as a photoinitiator for free radical polymerization

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ABSTRACT

6-Benzoyl-1,3-benzodioxolane (BBDO), a hydrogen abstraction type photoinitiator for free radical polymerization, was synthesized and characterized. Its capability to act as an initiator for the polymerization of methyl methacrylate (MMA), styrene (St) and multifunctional monomers in the presence of air was examined. Relative photopolymerization efficiencies of BBDO, benzophenone (BP), and their combination with an amine synergist such as ethyl-4-dimethylaminobenzoate (EDAB) are compared. UV–vis, FT-IR, ^{13}C NMR and polymerization studies revealed that the postulated mechanism is based on the intermolecular reaction. In contrast to BP-based photoinitiators, BBDO does not require an additional hydrogen donor for initiation.

1. Introduction

Photoinitiated free radical polymerization is a technologically important process owing to extensive applications in the curing of coatings on various materials, adhesives, printing inks, and photoresists [1–3]. In these systems, a key to control the photopolymerization process is photoinitiator, which absorbs light and generates active radicals to initiate the polymerization [4]. Photoinitiated free radical polymerization may be initiated by both cleavage (type I) and H-abstraction type (type II) initiators [5]. The type I photoinitiators which undergo a direct photo fragmentation process (α- or less common β-cleavage) upon absorption of light and formation of initiating radicals capable of inducing polymerization. The type II photoinitiators are a second class of photoinitiators based on compounds whose triplet excited states readily react with hydrogen donors, thereby producing an initiating radical [6–8].

Although the rate of the type II photoinitiators are slower than the type I photoinitiators due to a bimolecular initiation reaction, so for efficient polymerization, the bimolecular H-abstraction reaction must compete with other side reactions, such as the quenching of excited triplet state by oxygen or self quenching or by monomers with low triplet energy [9,10]. Therefore, these systems are more sensitive to oxygen, and polymerization in air may lead to relatively low curing rates. So the selection of a co-initiator (H-donor) is undoubtedly of great significance [2]. Tertiary amines are more reactive co-initiators than alcohols or ethers [11].

Since the active hydrogen between two alcohoxy groups in the cyclic acetals is abstractable and could form a radical [12], Elad and Youssefyeh proposed the photochemical rearrangement mechanism of 1,3-dioxolane (DO) compounds to give esters is shown in Scheme 1 [13]. It has ever been reported that the monoester radical generated by the photoirradiation onto cyclic acetal compounds could initiate the polymerization of vinyl compounds and methyl methacrylate [14–19]. Recently, photosensitized hydrogen abstraction from 2-alkyl-1,3-dioxolanes by triplet benzophenone gives the corresponding 1,3-dioxolan-2-yl radicals and these are trapped by α,β-unsatured ketones yielding monoprotected 1,4-ditetones [20]. More recently, Shi reported that cyclic acetals were used as hydrogen donors for bimolecular photoinitiating systems [21] and a natural component, 1,3-benzodioxole (BDO), was used as co-initiator for replacing the conventional amine for dental composite [22].

Benzophenone is by far one of the most widely used conventional photoinitiators.

The photoreduction of triplet-state benzophenone by tertiary amines has been extensively investigated [23–25].

In this context, taking into account that there might be a significant interaction between benzophenone and cyclic acetals, 6-benzoyl-1,3-benzodioxolane (BBDO) comprising cyclic acetals and benzophenone has been synthesized and the photochemical behaviors has been investigated. As it will be shown below, a great advantage is that this photoinitiator does not require an additional co-initiator.

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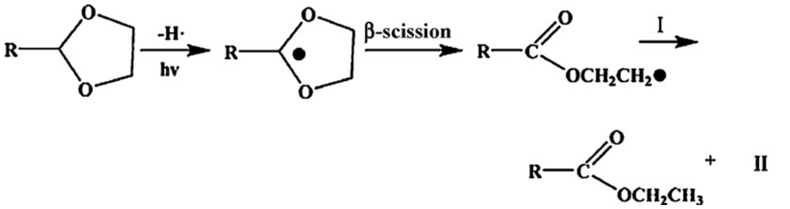


(1)

Scheme 1. The photochemical rearrangement mechanism of 1,3-dioxolane (DO).

2. Experimental

2.1. Materials

1,3-Benzodioxolane (98%, Aldrich), benzoyl chloride (98+%, Across), ethyl-4-dimethylaminobenzoate (EDAB, 99%, Aldrich) were used as received. Styrene (St, 99%, Aldrich) and methyl methacrylate (MMA, 99%, Aldrich) were washed by 5% aqueous NaOH solution, dried overnight by $CaCl_2$, and distilled over CaH_2 under vacuum just before use. Tetrahydrofuran and dichloromethane (99.9%, HPLC grade, Aldrich) were distilled over CaH_2. Dimethylformamide (DMF, 99%, Aldrich) was distilled over CaH_2 under reduced pressure. 2,2-Bis[4-(2-hydroxy-3-methacryloxy propoxy)phenyl]propane (Bis-GMA) and 2-hydroxyethyl methacrylate (HEMA) were used as received.

2.2. Synthesis of 6-benzoyl-1,3-benzodioxolane

14.6 g (56 mmol) of anhydrous $SnCl_4$ was added at 0–5 °C to a mixture of 50 mL of anhydrous CH_2Cl_2, 6.1 g (50 mmol) of 1,3-benzodioxolane and 7.7 g (55 mmol) of benzoyl chloride. The mixture was stirred for 2 h at room temperature. The mixture was poured into ice, acidified with HCl, and extracted with CH_2Cl_2. The extract was washed with water, dried and concentrated to obtain a brown oil that solidified on standing. Yields: 68%. ^{1}H NMR (250 MHz) in $CDCl_3$: δ7.74–6.85 ppm (8H, aromatic), 6.06 ppm (2H, CH_2). ^{13}C NMR (62.86 MHz) in $CDCl_3$: δ195.12 ppm (C=O), 151.52–107.67 ppm (aromatic), 101.88 (OCH_2O).

2.3. Photopolymerization

Typical procedure: appropriate solutions of MMA and BBDO in DMF were irradiated in a photoreactor consisting of a 400 W medium pressure mercury lamp and a water cooling system in air. Poly(methyl methacrylate) formed at the end of irradiation was precipitated in 10-fold excess methanol and dried in vacuum oven. All the other polymerizations using different solvents and concentrations and additives were performed under identical experimental conditions unless otherwise stated. Conversions were calculated for all samples gravimetrically.

2.4. Real-time infrared spectroscopy

Uniform samples of photocurable formulations consisiting of a photoinitiator 6-benzoyl-1,3-benzodioxolane, 2,2-bis [4-(2-hydroxy-3-methacryloxy propoxy) phenyl]propane (Bis-GMA) (60 wt%) and 2-hydroxyethyl methacrylate (HEMA) (40 wt%) in the presence and absence of EDAB were placed in a mold made from glass slide and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness. A mixture of Bis-GMA (60 wt%) and HEMA (40 wt%) was employed as the photopolymerizable resin. The samples were placed in the compartment of a Fourier transform infrared spectrometer (Nicolet 5700 FT-IR) and were simultaneously exposed to a UV-light source (Rolence-100 UV) and an IR analyzing light beam. The light intensity on the sample was 30 mW/cm^2 (Hole UV meter, Germany). The spectrometer was operated in the absorbance mode and the absorbance change of =C–H peak area from 6101 to 6219 cm^{-1} in the near IR range was correlated to the extent of polymerization. The degree of conversion, DC, can be expressed by the following relation:

$$\mathrm{DC\%} = \frac{(A_0 - A_t) \times 100}{A_0}$$

where A_0 is the initial peak area before irradiation, and A_t is the peak area of the double bonds at t time.

2.5. Analysis

GPC analyses of the polymers were performed at room temperature with a setup consisting of a pump (Waters 600E) and four Waters ultrastryra gel columns: HR5E (2000–4 × 10^6 g/mol), HR4 (5000–60,0000 g/mol), HR3 (500–30,000 g/mol), and HR2 (500–20,000 g/mol). THF was used as the eluent (flow rate 1 mL min^{-1}), and the detection was carried out with the aid of a Waters 410 differential refractometer. The number-average molecular weights were determined by using Polymer Laboratories polystyrene standards.

The ^{1}H NMR spectra were recorded on a BrukerAV600 unity spectrometer operated at 600 MHz, with $CDCl_3$ as solvent and tertamethysilane (TMS) as the internal standard.

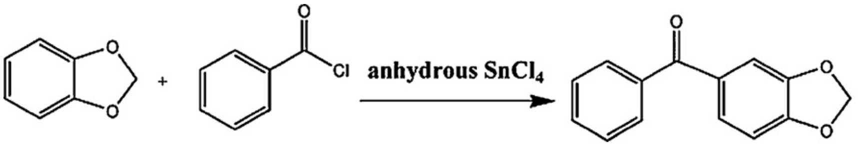
FT-IR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA, USA).

UV–vis absorption spectra were recorded in DMF solution on a Hitachi U-3010 UV–vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan). A cell path length of 1 cm was employed.

3. Results and discussion

6-Benzoyl-1,3-benzodioxolane was synthesized by the method described in the literature according to Scheme 2 [26].

Structure of the photoinitiator was confirmed by spectra analysis (see Section 2). The UV spectra of 6-benzoyl-1,3-benzodioxolane in DMF shows an absorption characteristic similar to the par-



(2)

Scheme 2. Synthesis of 6-benzoyl-1,3-benzodioxolane.

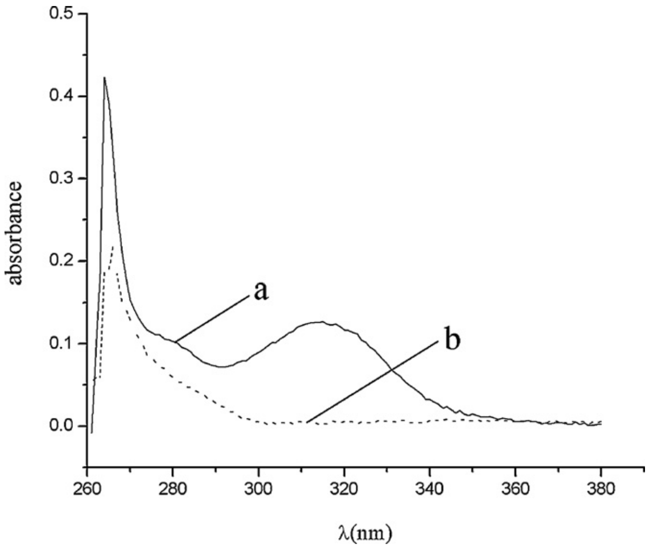


Fig. 1. Absorption spectra of BBDO (a) and BP (b) 1×10^{-5} M in DFM in the presence of air.

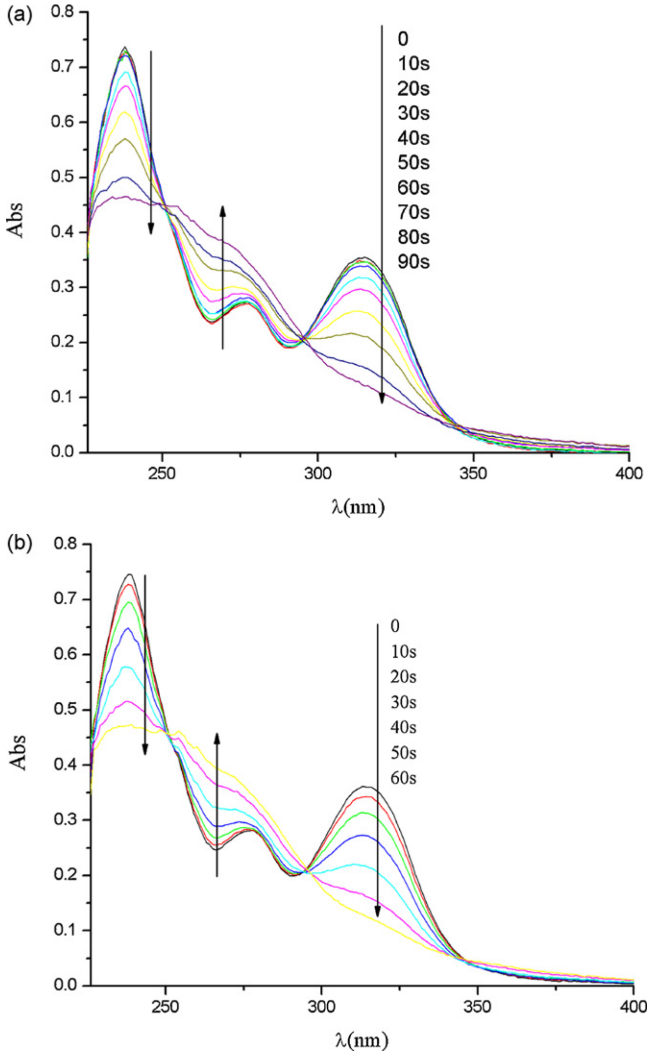


Fig. 2. Typical UV spectra change of BBDO on irradiation in CH_2Cl_2 in air (a) and nitrogen (b).

ent benzophenone with a maximum absorption peak at 265 nm and benzodioxolane with a maximum absorption peak at 315 nm (Fig. 1). The high molar absorptivity makes BBDO an attractive photoinitiator because of its efficient light absorption.

The photodecomposition of BBDO was monitored by detecting UV spectra change upon photolysis. The UV spectra of BBDO in CH_2Cl_2 were recorded after the solution had been exposed to the light of a UV lamp at the intervals of 10 s (Fig. 2). During photolysis proceeded, the photoinitiator was consumed and the absorption spectra changed. The absorption at 315 nm which belongs to the benzodioxolane and at 238 nm which belongs to the benzophenone were diminished while the absorption at about 266 nm was increased, these accorded with UV spectral change of benzodioxinone [27]. The purge of nitrogen caused rapid decrease of BBDO absorption peak indicated that the oxygen inhibited the photochemical reaction of BBDO.

BBDO was used as a photoinitiator in the free radical polymerization of MMA in the presence and absence of air. The results were compiled in Table 1. For comparison, photopolymerization by using either BP itself or BP–EDAB combination were also included.

BP is a low efficient photoinitiator in the absence of a co-initiator. The presence of an amine such as ethyl-4-dimethylaminobenzoate is important for effective photoreduction and photopolymerization. EDAB plays a dual action in the polymerization. Besides hydrogen donation, EDAB can react with oxygen, thereby reducing the retarding effect of oxygen on the polymerization [28]. In order to determine the concentration of initiator required to optimize the rate of polymerization, different concentrations of initiator were performed. The degree of conversion of formulation increased with increase of photoinitiator concentration. Further increase in the BBDO (1×10^{-2} M) concentration resulted in a decrease in the rate of polymerization. Among the several solvents tested in our experiments, dimethylformamide seemed to be the most suitable solvent for the photopolymerization initiated by BBDO (see Table 1). Although radical polymerizations were not sensitive to the polarity of the solvent [29], triplet-state lifetime of photoinitiators involving electron transfer might depend on polarity effects [30].

Since the BP–EDAB system was still the most efficient photoinitiator, it was clear that BBDO photoinitiator avoided the use of large

Table 1
Photoinitiated polymerization*a* of methyl methacrylate in various solvents in air.

Photoinitiator	[PI] (mol/L)	Solvent	EDAB (mol/L)	Conversion (%)	Mn[a] ($\times 10^{-4}$ g/mol)	Mw/Mn
BBDO	3×10^{-3}	DMF		47.2	1.57	2.33
BBDO	5×10^{-3}	DMF		49	1.52	2.27
BBDO	8×10^{-3}	DMF		49.3	1.60	2.32
BBDO	1×10^{-2}	DMF		47	1.77	2.15
BBDO	8×10^{-3}	CH_2Cl_2		21.6	2.78	2.30
BBDO	8×10^{-3}	THF		31.6	1.21	2.48
BBDO	8×10^{-3}	DMF	8×10^{-3}	52.6	1.42	2.21
BP	8×10^{-3}	DMF	8×10^{-3}	36.3	0.87	2.72
BP	8×10^{-3}	DMF		29.4	1.13	2.0

Irradiation time = 60 min, [MMA] = 4.68 mol/L.

[a] Determined by GPC.

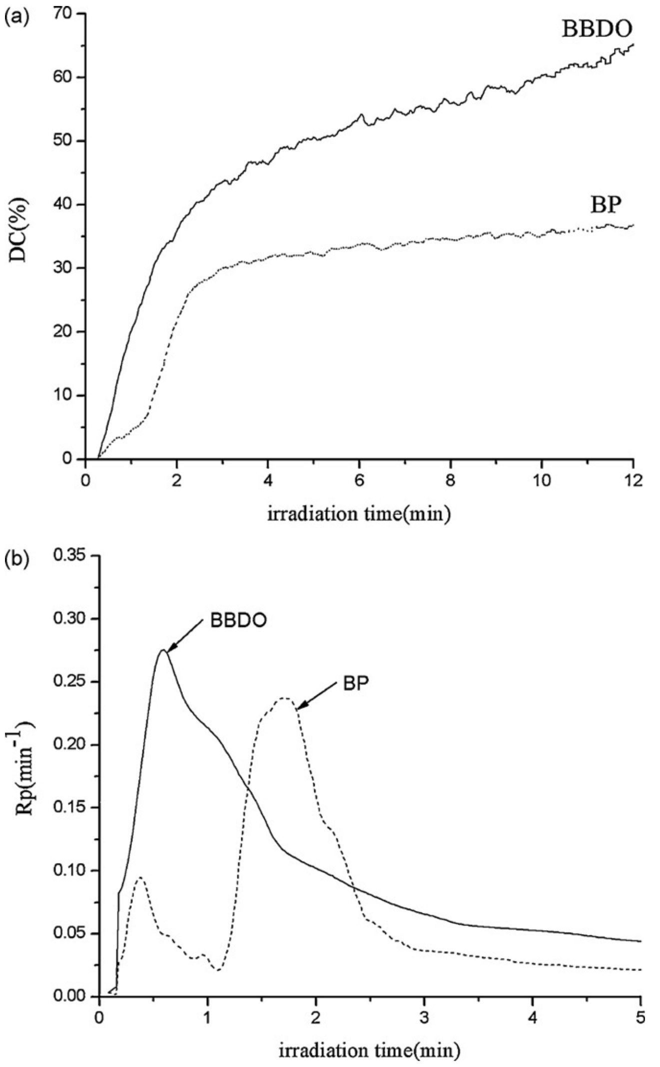


Fig. 3. The polymerization kinetic of Bis-GMA/HEMA mixture (3/2, w/w) initiated by different photoinitiator. (a) Double-bond conversion as a function of irradiation time, (b) polymerization rate as a function of irradiation time. [BBDO] = [BP] = 1 wt%, light intensity I_0 = 30 mW cm^{-2}.

numbers of amines in the system. This is very important for UV curing application, since formulations containing amine at high concentrations caused a decrease in the pendulum hardness of the cured films due to the plasticizing effect of amines [31,32], and amine is also toxic material.

The efficiency of the BBDO in the photocuring of formulations containing multifunctional monomers was also studied. Real-time near FT-IR technique is a convenient method to monitor the extent of polymerization for thick (1 mm) photocured samples [33,34]. Upon irradiation, the extent of polymerization as a function of time was accurately reflected by measuring the decrease of the =C–H absorbance peak area. The rate of polymerization (R_p) could be calculated by the time derivative of the DC curve [35].

In Fig. 3, kinetic profiles referring to the polymerization of the mixture of 2,2-bis[4-(2-hydroxy-3-methacryloxy propoxy) phenyl]propane (60 wt%)/2-hydroxyethyl methacrylate (40 wt%) under polychromatic light were displayed, BBDO and BP served as photoinitiators. The curves were obtained by monitoring the decrease in the =C–H absorption peak area from 6101 to 6219 cm^{-1}. The shape of the curves indicated the same moiety molar concentration, the polymerization rate and final conversion of BBDO was remarkably higher than that of BP (Fig. 3). The photopolymer kinetic study was carried out in air. It was attributed to the quenching of the radicals by atmospheric oxygen. Oxygen diffusion through the thin monomer layer is fast enough to replace the oxygen consumed in the peroxidation process. The effect of oxygen diffusion in thicker layers is more limited so that the core of the sample can be considered as an oxygen-free medium [36,37]. In the system of BP–EDAB and BBDO–EDAB (Fig. 4), it could be seen that polymerization took place more rapidly with BBDO/EDAB than that of the corresponding one with BP/EDAB. The curve for the polymerization with the BBDO/EDAB system indicated high conversion percentage values.

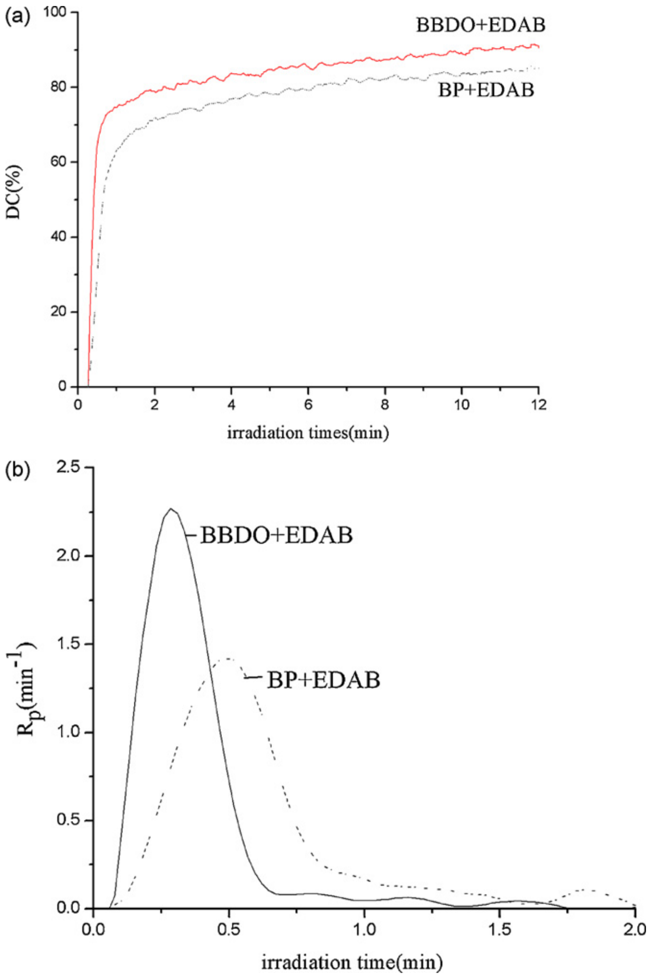
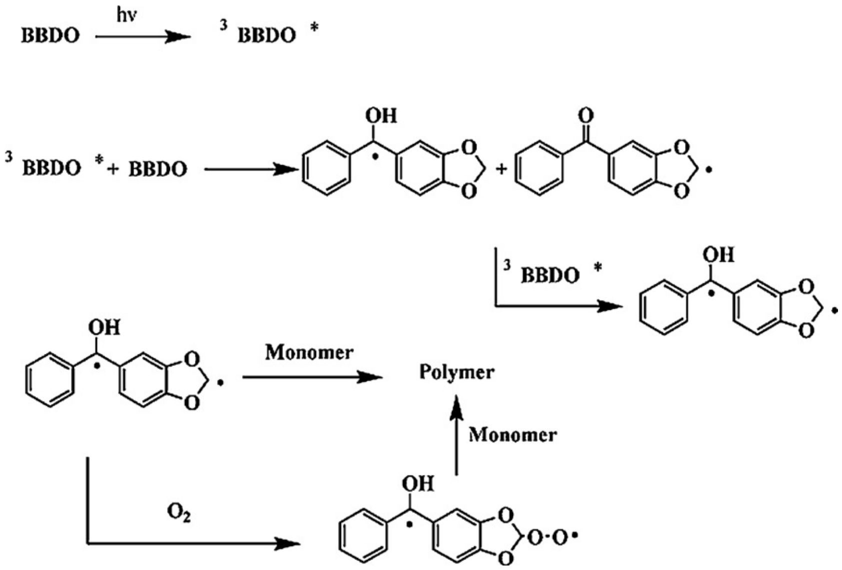


Fig. 4. The kinetic of Bis-GMA/HEMA mixture (3/2, w/w) polymerization initiated by different photoinitiator system. (a) Double-bond conversion as a function of irradiation time, (b) polymerization rate as a function of irradiation time. [BBDO] = [BP] = [EDAB] = 1 wt%, light intensity I_0 = 30 mW cm^{-2}.

IR and ^{13}C NMR spectra of polystyrene initiated by using BBDO as initiator were shown in Fig. 5. The IR absorption of –OH at 3440 cm^{-1} in polymer was not recognized in monomer and BBDO, in addition, the absorption of C=O at 1739 cm^{-1} in polymer was very small. In the ^{13}C NMR spectrum of polymer, the peaks at 195.12 ppm of BBDO disappeared, and the peaks at about 158 ppm of ester did not appear. These indicated that the functional group of C=O in BBDO had been changed into –C–OH, and cyclic acetals in BBDO did not generate monoester radical. In the photopolymerization process of polystyrene initiated by BBDO, in addition to chain initiation, there are chain propagation, chain transfer, re-initiation, chain termination [38]. So it is difficult to indentify the each small peak of initiator and polymer in IR and ^{13}C NMR spectra.

Based on the above results, the following observations can be made: (i) BBDO shows an absorption characteristics similar to the parent BP and benzodioxolane. (ii) Photoinitiation by BBDO does not need a hydrogen donor in the system and presumed via a type



Scheme 3. Possible photoreaction mechanism of 6-benzoyl-1,3-benzodioxolane.

II hydrogen abstraction mechanism between two BBDO molecules. (iii) Polymerization occurs in the presence of air. (iv) BBDO is a more efficient photoinitiator than BP even if BP is conjunction with a hydrogen donor EDAB.

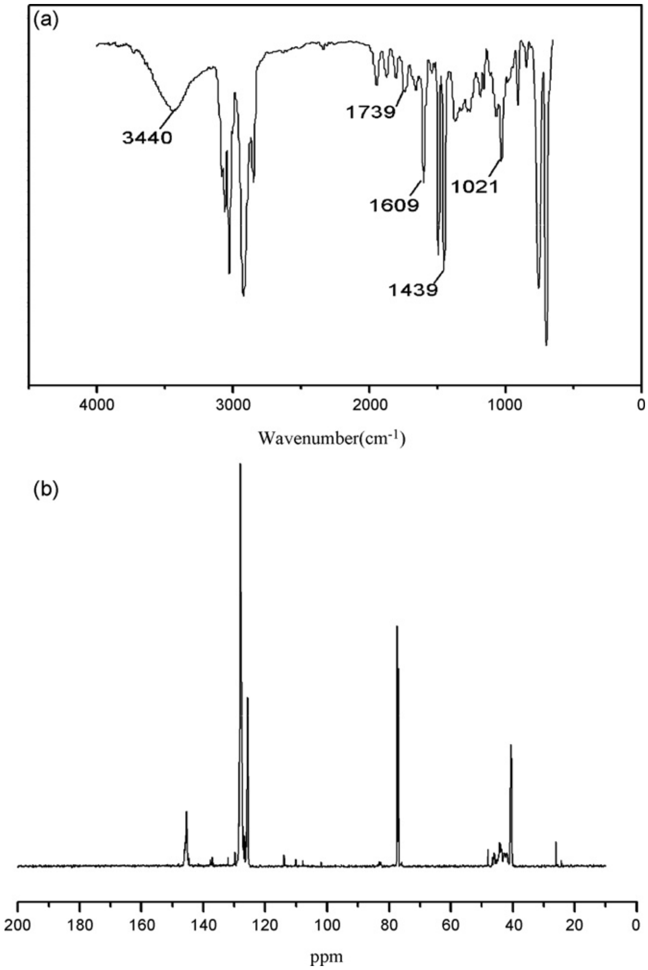


Fig. 5. BBDO photoinitiated polymerization*a* of styrene in bulk, the concentration of BBDO is 10 wt%, the polymer obtained as the precipitate was filtered off, washed with methanol, and dried in vacuum. (a) IR spectra of polystyrene, (b) ^{13}C NMR spectra of polystyrene, reference: TMS; solvent: $CDCl_3$.

Considering the above observations, a nontraditional initiation mechanism is proposed. Because the presence of oxygen is essential for the polymerization to proceed, peroxides are probably involved. The overall polymerization process can be represented by Scheme 3.

4. Conclusion

It is clear that BBDO is an efficient photoinitiator for free radical polymerization. This photoiniator is very attractive, since it does not require an additional hydrogen donor and initiates the polymerization of both acrylate and multifunctional monomers in the presence of air. These properties suggest that BBDO may find use in a variety of practical UV curing applications.

Acknowledgments

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