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Photochemically masked benzophenone: Photoinitiated free radical polymerization by using benzodioxinone

Mehmet Atilla Tasdelen, Volkan Kumbaraci, Naciye Talinli*, Yusuf Yagci*

Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469, Turkey

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Abstract

A new photoinitiating system for free radical polymerization of methyl methacrylate (MMA) is reported. This system consists of benzodioxinone and hydrogen donors such as triethylamine (TEA), *N*,*N*-dimethyl ethanol amine (DMEA) and tetrahydrofuran (THF). A feasible mechanism involves photoinduced formation of benzophenone from benzodioxinone and subsequent hydrogen abstraction of photoexcited benzophenone from hydrogen donors to yield radicals capable of initiating polymerization of MMA.

Keywords: Photolysis; Polymerization; Benzodioxinone

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1. Introduction

Photoinitiated polymerizations have received considerable attention because of their rapid curing even at ambient temperatures, environmental issues, and low energy consumption. These advantages lead to important industrial advantages including coatings on various materials, adhesives, printing inks and photoresists [1–5]. Among the most studied photoinitiator systems are those in which initiating free radicals are formed by a bimolecular process consisting of a triplet excited state of an aromatic carbonyl compound and a hydrogen donor compound as a co-initiator. The photopolymerization of vinyl monomers is usually initiated by the radicals produced from the hydrogen donor. The ketyl radicals are usually not reactive toward vinyl monomers due to the steric hindrance and the delocalization of unpaired electron. The overall mechanism of the photoinitiation is represented in Scheme 1.

Typical photoinitiators of this type include benzophenone [6–8] and derivatives, thioxanthones [9–11], benzyl [8], and quinones [8] while alcohols, ethers, amines and thiols are used as hydrogen donors. Among these type of photoinitiators, benzophenone is most widely used because of the high quantum efficiency of the hydrogen abstraction particularly with amines. Because the initiation is based on a bimolecular reaction, benzophenones initiate generally slower than cleavage type photoinitiators. These systems are, therefore, more sensitive to the quenching of excited triplet states, which are the reactive precursors of light-induced initiation. Indeed, quenching [12] by monomers with low triplet energy (e.g., styrene and or *N*-vinyl carbazole) or by oxygen or self quenching [13] by ground state benzophenone is often observed and may lead to relatively low curing rates.

$$\mathrm{Ar_2C{=}O} \xrightarrow{h\nu} {}^{3}\left[\mathrm{Ar_2C{=}O}\right]^{*} \tag{1}$$

$${}^{3}\left[\mathrm{Ar_2C{=}O}\right]^{*} + \mathrm{R{-}H} \longrightarrow \mathrm{Ar_2\dot{C}{-}OH} + \mathrm{R}^{\bullet} \tag{2}$$

$$\mathrm{R}^{\bullet} + \text{Monomer} \longrightarrow \text{Polymer} \tag{3}$$

Scheme 1. Photoinitiated free radical polymerization by aromatic carbonyl compounds.

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* Corresponding authors. Tel.: +90 212 285 32 41; fax: +90 212 285 63 86.
E-mail addresses: talinlin@itu.edu.tr (N. Talinli), yusuf@itu.edu.tr (Y. Yagci).

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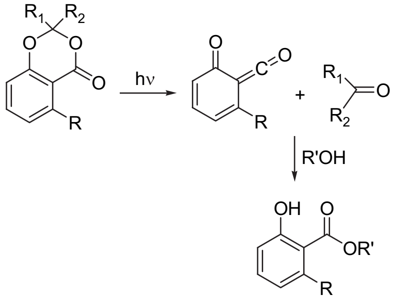


(4)

(5)

Scheme 2. Salicylate esters by photoinduced acylation.

It was recently reported [14] that functionalized salicylate esters can be readily prepared by photochemical acylation process by using benzodioxinones in the presence of alcohols and phenols (Scheme 2). We have recently shown [15] that this process can also be used for the preparation of oligosters when benzodioxinones are equipped with aliphatic hydroxyl groups. Upon irradiation of benzodioxinones, ketene and the corresponding ketone are formed concomitantly. The intermediate ketene readily reacts with the alcohol present in the solution to yield salicylate ester.

In many curing applications of fully formulated mixtures, usually all the initiators are added in the solid form or in a concentrated solution at the beginning of the polymerization and it immediately initiates the polymerization when exposed to the light. This is one of the prerequisite for a rapid curing. However, in turn such formulations may not exhibit a good shelf life due to the initiation on storage. The use of benzodioxinones as photoinitiators may increase shelf life at the expense of initiation ability. In this work, we present that structurally designed benzodioxinones liberate benzophenone only after stimulation by light which can further be excited to initiate free radical polymerization.

2. Experimental

2.1. Materials

Benzophenone (BP, 99%, Acros) was used after being recrystallized from ethanol. Methyl methacrylate (MMA, 99%, Aldrich) was passed through basic alumina column to remove the inhibitor. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone–Na. Dichloromethane (99.8%, Baker) was extracted first with sulfuric acid, then with 5% NaOH solutions. After washing with water, the dichloromethane was dried over anhydrous $CaCl_2$ and CaH_2 and finally distilled with a fractionation column.

2.2. Synthesis of benzodioxinone (5-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one)

The precursor compound was synthesized according to the literature procedure [16]. Thus, to a flask containing 2,6-dihydroxybenzoic acid (5.0 g, 16 mmol) and DMAP (0.192 g, 1.6 mmol), ethylene glycol dimethyl ether (20 mL) and benzophenone (4.37 g, 24 mmol) were added. This solution was cooled to 0 °C under N_2 followed by the dropwise addition of thionyl chloride (1.74 mL, 24 mmol). The reaction was brought to room temperature and stirred for 18 h after which the volatiles were removed via N_2 flushing while under vacuum. When the volume was reduced by approximately 50%, the remaining solution was purified by flash chromatography (5/95, EtOAc/Hex) and afforded 3.6 g (35%).

2.3. Photopolymerization

Monomer (MMA, 9.2 mmol) in CH_2Cl_2 (1 mL) solution, photoinitiator (benzodioxinone or benzophenone (5.0×10^{-3} mmol), and hydrogen donor (15×10^{-3} mmol) were put into a Pyrex tube, degassed with nitrogen and irradiated at room temperature in a photoreactor (Rayonet) equipped with 16 lamps and emitting light nominally at 350 nm. At the end of irradiation, the reaction mixture was precipitated in excess methanol. After being collected by filtration, the polymer was kept in a vacuum oven for drying. Conversions were determined gravimetrically.

2.4. Characterization

^1H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Molecular weights were determined by gel-permeation chromatography (GPC) instrument equipped with Waters Styragel column (HR series 2, 3 and 5E) with THF as the eluent at a flow rate of 0.3 mL/min and a Waters 410 Differential Refractometer detector and using polystyrene standards. GC–MS measurements were performed by using Thermo Finnigan Trace DSQ instrument equipped with Zebron ZB-5MS capillary GC column (5% silarylen, 95% polydimethylsiloxane).

3. Results and discussion

In this report, we wish to present a new photoinitiating system for free radical polymerization by using benzodioxinone as photochemically masked benzophenone. For this purpose, first UV spectral change of benzodioxinone on irradiation was investigated. As shown in Fig. 1, upon irradiation, the absorption at 325 nm which belongs to the benzodioxinone rapidly diminishes while the absorption at about 360 nm corresponding to benzophenone increases.

This was further substantiated by finding that benzophenone is formed during the irradiation of benzodioxinone in CH_2Cl_2. After irradiation the products were analyzed by GC–MS. Fig. 2 shows a plot of the benzodioxinone to benzophenone concentrations versus irradiation time.

The next question concerns whether benzophenone thus formed undergoes reactions on irradiation to generate reactive species and consequently initiates the polymerization. Indeed,

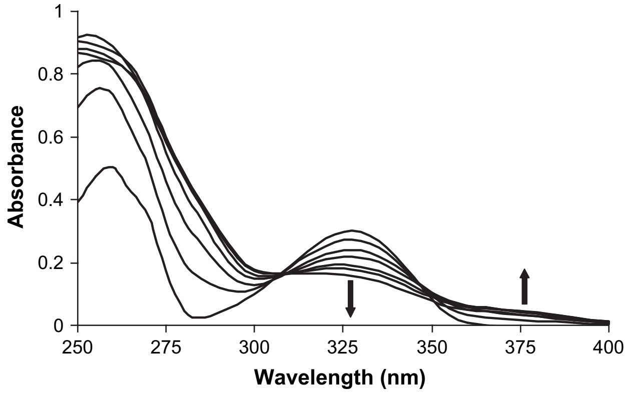


Fig. 1. Typical UV spectral change of benzodioxinone on irradiation at $\lambda = 350$ nm under nitrogen in CH_2Cl_2. UV spectra were taken at every 15 min.

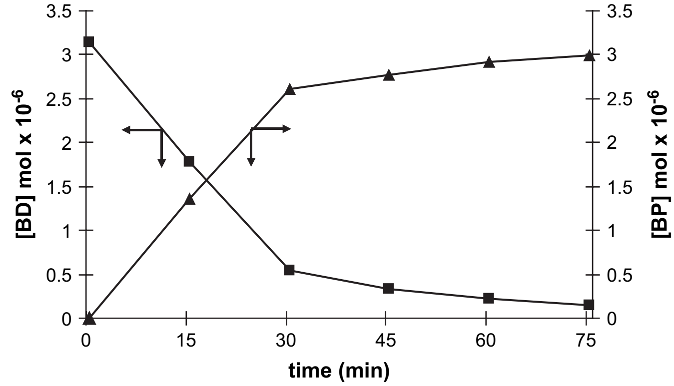
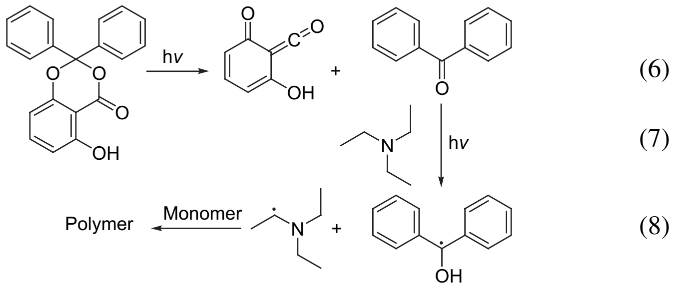


Fig. 2. Plot of concentration of benzodioxinone (■) and benzophenone (▲) versus irradiation time in CH_2Cl_2.

methyl methacrylate (MMA) containing benzodioxinone and one of the following compounds: triethylamine (TEA), *N*,*N*-dimethyl ethanol amine (DMEA), and tetrahydrofuran (THF) are converted into poly(methyl methacrylate) (PMMA) upon irradiation with UV light at $\lambda_{\text{inc.}} = 350$ nm. The excited triplet of benzophenone, which is populated by the successive absorption of the ground state benzophenone formed in the first stage, abstracts hydrogen from the hydrogen donor, i.e., TEA. The carbon-centered radicals stemming from the amine are able to initiate free radical polymerization of MMA (Scheme 3). α-Amino radicals are especially suitable for the polymerization of acrylates and methacrylates [17].



Scheme 3. Photoinitiated free radical polymerization by using benzodioxinones.

Table 1
Photoinitiated free radical polymerization of methyl methacrylate at room temperature in CH_2Cl_2 for 120 min at $\lambda = 350$ nm

Run	Photosensitizer (mol L^{-1})	H-donor (mol L^{-1})	Conversion (%)	M_n[a]	M_w/M_n[a]
1	BD (2.5×10^{-3})	TEA (7.5×10^{-3})	18	16,500	1.34
2	BD (2.5×10^{-3})	–	–	–	–
3	BD (2.5×10^{-3})	DMEA (7.5×10^{-3})	13	19,800	1.43
4	BD (2.5×10^{-3})	THF[b] (6.16)	7	33,000	1.77
5	BD (2.5×10^{-3})	EA (7.5×10^{-3})	1	55,700	2.36
6	BP (2.5×10^{-3})	TEA (7.5×10^{-3})	7	14,900	1.48
7	BP (2.5×10^{-3})	EA (7.5×10^{-3})	10	15,500	1.25

BD, benzodioxinone; BP, benzophenone; TEA, triethylamine; DMEA, *N*,*N*-dimethyl ethanol amine; EA, ethanol amine; THF, tetrahydrofuran.

[a] Determined by GPC according to polystyrene standards.

[b] Polymerization was performed in neat THF.

Table 1 lists the polymerization results of MMA by using benzodioxinone in conjunction with different hydrogen donors. The results indicate the crucial effect of the hydrogen donors. In the absence of hydrogen donor, polymerization was not initiated. It is known [5] that excited carbonyl triplet states are usually by two or three orders of magnitude more reactive toward tertiary amines than toward alcohols and ethers. Thus, TEA and DMEA were found to be very efficient in the generation of the initiating radicals. Notably, another hydrogen donor ethanol amine (EA) is not efficient in the process. This behavior may be explained by less favored hydrogen abstraction from primary amines and the participation of EA in the simultaneous salicylate ester formation. The hydroxyl group of EA reacts with ketene according to reaction (5) and possible hydrogen abstraction from the alcoholic site is precluded. These reasons may also account for the observed relatively high molecular weight and polydispersity. For comparison, photopolymerizations by using directly added benzophenone in combination with respective hydrogen donors are also included. As can be seen, in the case of TEA, benzophenone system is less efficient while EA readily initiates the polymerization.

In conclusion, we report a new photoinitiating system for free radical polymerization based on two-step photolysis of benzodioxinone. In this initiating system, benzophenone, actual photoinitiator, is formed only after photodecomposition of benzodioxinone. The subsequent step is the usual radical formation by the hydrogen abstraction of photoexcited benzophenone from a hydrogen donor. Thus, the time between adding the initiator and the actual initiation can be chosen. This circumstance enables such initiators to be applied for curing formulations, where the curing (polymerization or crosslinking) of a coating may be initiated at exactly the time desired and with the curing rate intended. Further studies in this line are now in progress together with the efforts to synthesize other photochemically masked initiators possessing absorption characteristics at different wavelengths.

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