Naphthodioxinone-1,3-benzodioxole as Photochemically Masked One-Component Type II Photoinitiator for Free Radical Polymerization

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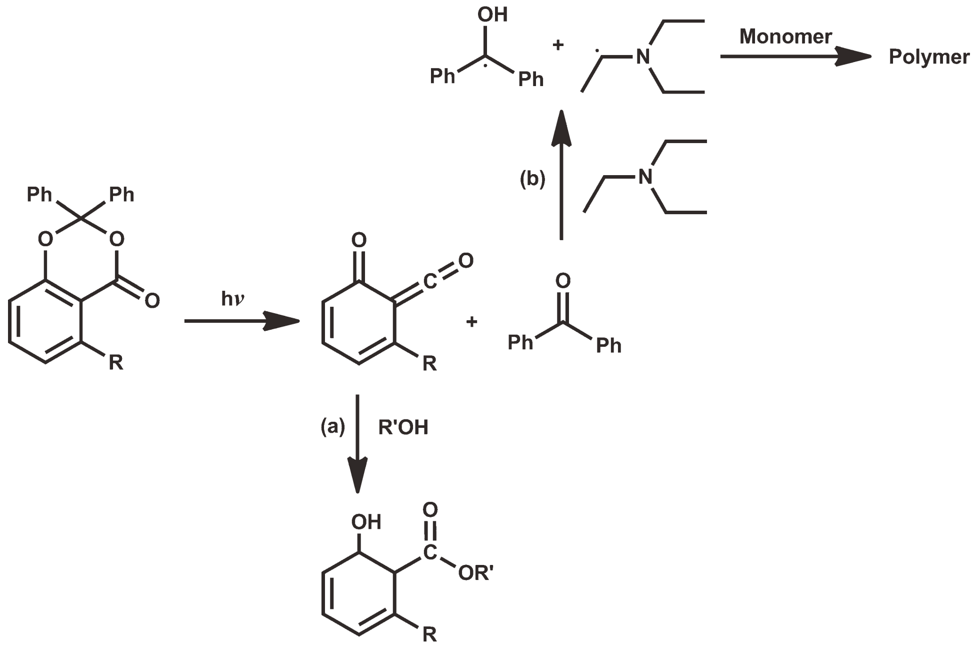
ABSTRACT: A 1,3-benzodioxole derivative of naphthodioxinone, namely 2-(benzo[*d*][1,3]dioxol-5-yl)-9-hydroxy-2-phenyl-4*H*-naphtho[2,3-*d*][1,3]dioxin-4-one was synthesized and characterized. Its capability to act as caged one-component Type II photoinitiator for free radical polymerization was examined. Upon irradiation, this photoinitiator releases 5-benzoyl-1,3-benzodioxole possessing both benzophenone and 1,3-dioxole groups in the structure as light absorbing and hydrogen donating sites, respectively. Subsequent photoexcitation of the benzophenone chromophore followed by hydrogen abstraction generates radicals capable of initiating free radical polymerization of appropriate monomers. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 000: 000–000, 2012

KEYWORDS: irradiation; naphthodioxinone; photopolymerization; radical polymerization; Type II photoinitiator

INTRODUCTION Photoinitiated polymerization is a powerful industrial process widely used in various applications including printing inks, adhesives, surface coating, optical waveguides, microelectronics, and printing plates.[1–4] Photoinitiated polymerizations have gained considerable attention because of their superior advantages such as rapid curing even at ambient temperatures, environmental issues, and low energy consumption.[5] Much effort has been devoted to free radical systems mainly due to the availability of wide range of monomers polymerizable by free radical mechanism and photoinitators having sensitivity in both UV and visible range.[6] 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 effective in initiating free radical polymerization due to the steric hindrance and the delocalization of unpaired electrons. Benzophenone and derivatives,[7–9] thioxanthones,[10–14] benzil,[8] quinones,[8] and organic dyes[15–19] are typical examples of this type of photoinitiators. Based on their hydrogen donating capability, alcohols, amines, ethers, and thiols are used as co-initiators. Benzophenone is one of the most widely used photoinitiator due to its good surface curing and solubility properties together with the high quantum efficiency of the hydrogen abstraction particularly with amines.

Benzodioxinones were recently reported as new photosensitive compounds, which form functionalized salicylate esters upon irradiation in the presence of alcohol and phenols.[20] In our previous studies, we reported several photoinduced reactions of benzodioxinones in polymer synthesis and UV curing applications.[21] Typical examples include oligoester synthesis,[22] initiation of free radical and cationic polymerizations,[23,24] UV curing of monomers or preformed polymers,[25] and graft copolymer synthesis.[26] In these processes, depending on the particular application, two different reactive species are involved. Upon irradiations, benzodioxinone forms benzophenone and ketene. Although benzophenone can participate in radical forming process by a second photon excitation under variety of conditions, the ketene compound readily reacts with nucleophiles such as hydroxyl and amine groups leading to the formation of esters and amides. The overall use of benzodixoxinones in synthetic polymer chemistry and as photoinitiators for free radical polymerization is summarized in Scheme 1. Reportedly, ketene type reactive intermediates can also be produced thermally from dialkyl Meldrum's acid and successfully used for the modification of macromolecular structures and crosslinking of polyolefines.[27,28]

Cyclic acetals were shown to be alternative hydrogen donors for bimolecular photoinitiating systems. Typical example includes a natural component, 1,3-benzodioxole, which replaced conventional hazardous amine co-initiators for dental applications.[29] More recently, it was shown[30] that 6-benzoyl-1,3-benzodioxolane (BBDO) can initiate the polymerization of



SCHEME 1 Photoinduced reactions of benzodioxinone. Ester formation (a) and initiation of free radical polymerization (b).

acrylates and multifunctional monomers without an additional hydrogen donor in the mixture. This benzophenone derivative contains both light absorbing and hydrogen donating sites in the structure.

As part of our continuing interest in design and development of photoinitiating systems, and expand their use in macromolecular syntheses, we report herein the use of naphthodioxinone-1,3-benzodioxole as one-component Type II photoinitiator.

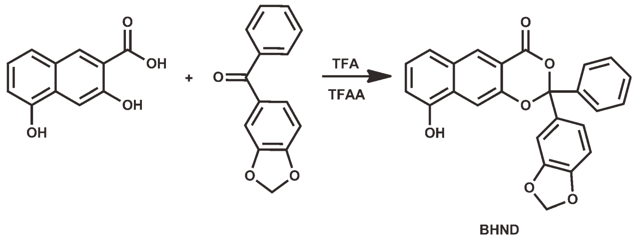
RESULTS AND DISCUSSION

As stated in the "Introduction" section, the aim of this work is to exploit a new masked Type II photoinitiator which does not require additional hydrogen donor. The approach is to use specially designed benzodioxinone containing hydrogen donating sites that upon irradiation with UV light undergoes photodecomposition to release benzophenone for the subsequent photoinitiation process. For this purpose, first, the precursor 5-benzoyl-1,3-benzodioxole (BBDO), known as Type II photoinitiator possessing hydrogen donating groups, was synthesized by a Friedel-Crafts reaction. The ultimate compound, 2-(benzo[*d*][1,3]dioxol-5-yl)-9-hydroxy-2-phenyl-4*H*-naphtho[2,3-*d*][1,3]dioxin-4-one (BHND), was then synthesized by reacting 3,5-dihydroxynaphthoic acid with BBDO according to literature procedures (Scheme 2).[31]

The structures of both BBDO and BHND were confirmed by ^{1}H NMR and UV–vis analysis. Figure 1 shows the ^{1}H NMR spectra of BBDO and the corresponding masked photoinitiator BHND. As can be seen, both compounds exhibit characteristic protons and signals emerging from the dioxolane and aromatic groups. UV–vis spectral analysis also revealed that both compounds exhibit absorption characteristics similar to benzophenone (Fig. 2). Notably, BHND has a spectrum which is typical for napthodioxinone chromophore absorbing strongly in far UV and possessing an absorption maximum of the $\pi \rightarrow \pi^*$ transition of the long conjugated π-ring system around 376 nm typically with high extinction coefficient.[23] On the other hand, BBDO has an additional absorption at 316 nm which belongs to benzodioxole structure.

UV spectral change of BHND upon irradiation at $\lambda > 300$ nm was also investigated. As shown in Figure 3(a), upon irradiation, the absorption at 238 nm which belongs to benzophenone diminished and prolonged irradiation resulted in the development of a new absorption band at 315 nm corresponding to the absorption of BBDO. Considering BBDO has both benzophenone and hydrogen donors in the structure, further irradiation induces radical generation. Thus, the absorption of BBDO correspondingly decreases [Fig. 3(b)].

To gain more insight into the reaction mechanism, the formation of descendant product, BBDO during the photolysis of BHND at $\lambda > 300$ nm in the absence of monomer was investigated by GC analysis. It is apparent from Figure 4 that the concentration of BBDO as determined with respect to the



SCHEME 2 Synthesis of 2-(benzo[*d*][1,3]dioxol-5-yl)-9-hydroxy-2-phenyl-4*H*-naphtho[2,3-*d*][1,3]dioxin-4-one (BHND).

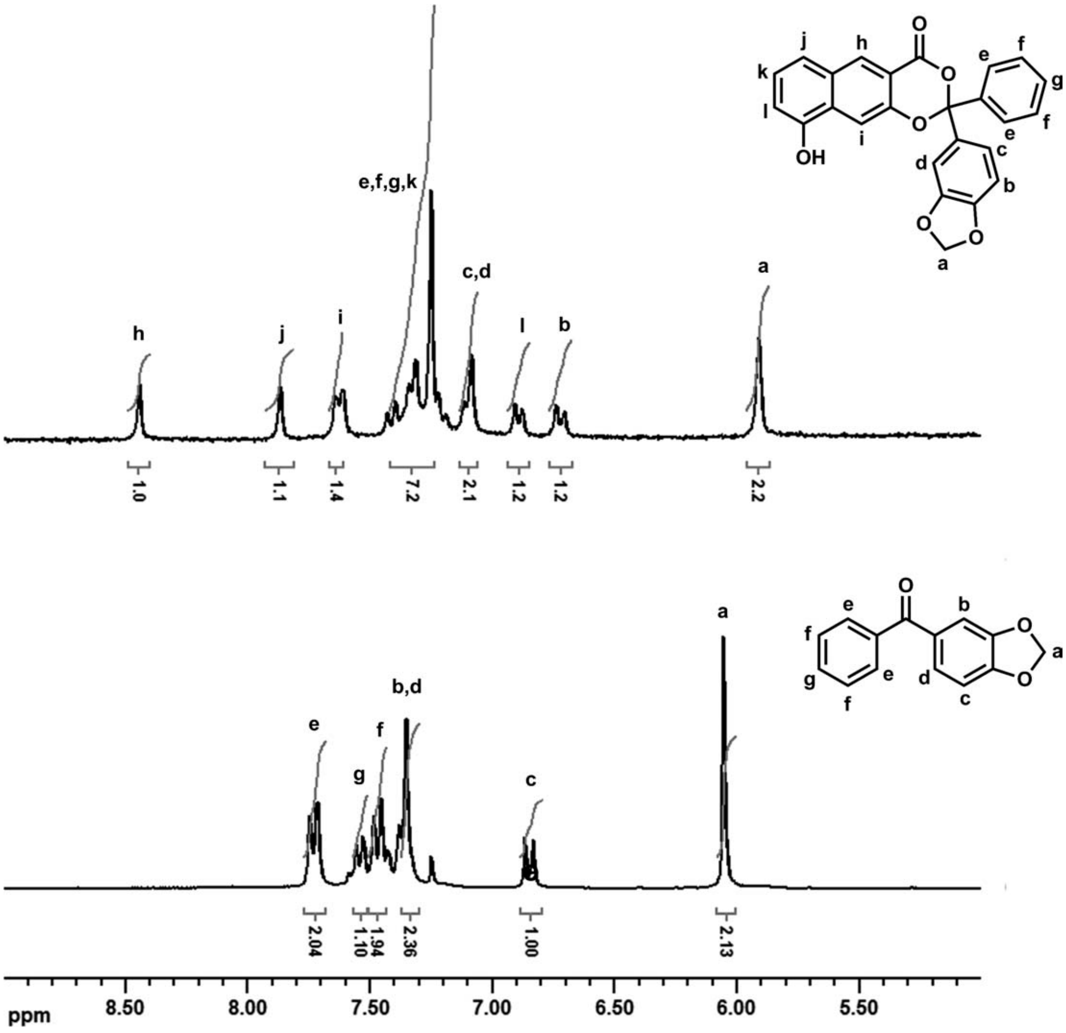


FIGURE 1 ^{1}H NMR spectra of (a) BBDO and (b) BHND in $CDCl_3$.

standard 1,4-dimethoxybenzene increased rapidly up to the certain irradiation time from which point a leveling off is observed. Presumably, at this point, the precursor BHND is completely consumed or the competing absorption of BBDO prevents further decomposition. It should also be pointed out that concomitantly formed naphthalene ketene transient may also absorb light. However, its absorption could not be detected by stationary photolysis as it is short lived and rapidly reacts with the hydroxyl group present in the structure. The absorption of the resulting ester does not interfere with that of BBDO since naphthalene derivatives have absorption below 300 nm.[23]

BHND was used as a photoinitiator for the polymerization of methyl methacrylate (MMA) under nitrogen atmosphere. A comparison of the results obtained with different solvents and initiator concentrations is listed in Table 1. As can be seen, the conversion increased with increasing photoinitiator concentration. Among the several solvents tested, tetrahydrofuran (THF) seemed to be a quite suitable solvent for the polymerization that is known to be a good hydrogen-donating solvent for excited aromatic carbonyl compounds. The lowest conversion was obtained in the case of dimethylformamide as it is known that radical polymerizations are not sensitive to the polarity of the solvent.

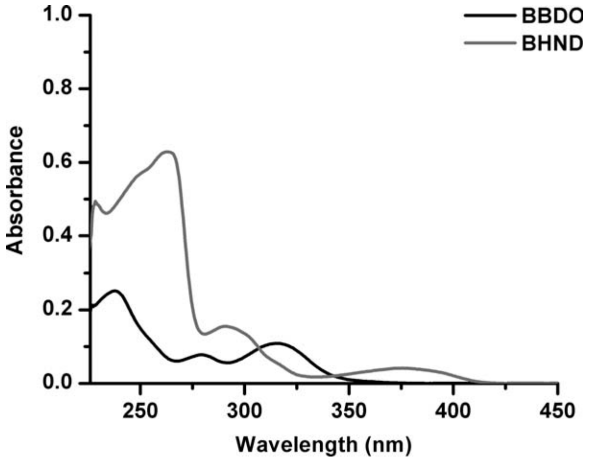


FIGURE 2 UV spectra of BBDO (1.2×10^{-5} mol L^{-1}) and BHND (1.2×10^{-5} mol L^{-1}).

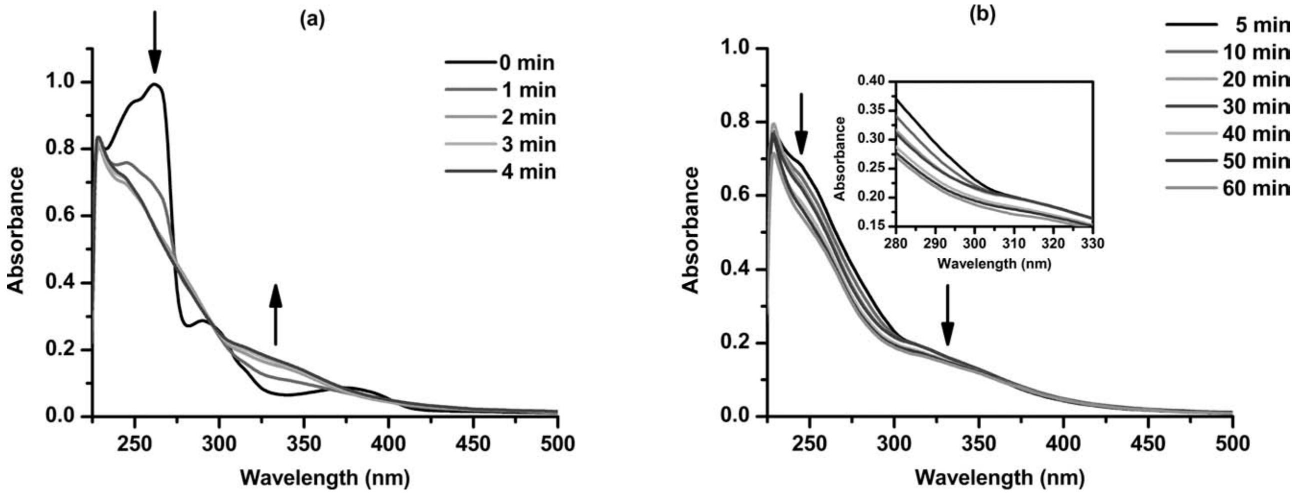


FIGURE 3 Typical UV spectral change of BHND (a) at first 4 min and (b) after 4 min on irradiation at $\lambda > 300$ nm under nitrogen in CH_2Cl_2.

The overall polymerization process can be represented by Scheme 3. The excited triplet of BBDO, which is populated by the successive absorption of the ground state BBDO released by the photolysis of BHND, abstracts hydrogen from another ground state BBDO to generate the initiating radicals. The ketene intermediate also formed (see Scheme 3) in the first stage rapidly reacts with hydroxyl groups to form an ester.

The results of the polymerization allow no definitive conclusion whether or not the hydrogen abstraction occurs from the BHND under these conditions as well. UV–vis absorption spectrum of poly(methyl methacrylate) obtained by the described photoinitiating system (Table 1, Run 1) exhibits a weak absorption band at longer wavelengths indicating incorporation of BHND units into polymer chain (Fig. 5). The observed behavior gives strong hint that the precursor BHND also takes part in the hydrogen abstraction process to generate initiating radicals.

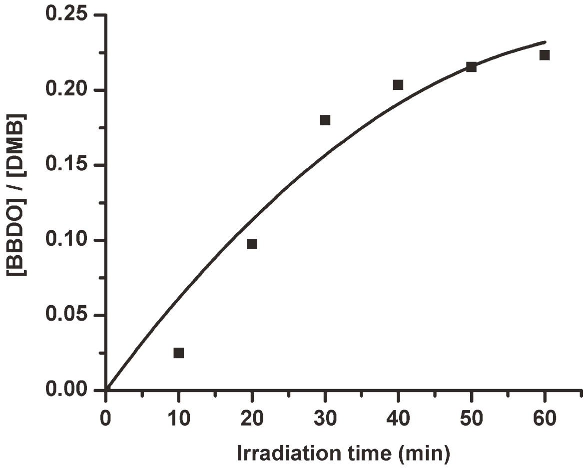


FIGURE 4 Plot of the released BBDO concentration during the photolysis of BHND versus irradiation time in CH_2Cl_2.

The efficiency of BHND in photocuring of formulations containing multifunctional monomer was also studied. The heat released during the photocuring of the formulations containing BHND, BBDO, and BP/TEA was followed by photo-DSC. Kinetic profiles referring to the polymerization of trimethylolpropane triacrylate (TMPTA) under polychromatic light emitting at $\lambda = 315$–450 nm are shown in Figure 6. Although the photoinitiation occurred only after a sufficient amount of BBDO is released by the photolysis of BHND, the final conversion was nearly the same with bare BBDO used formulation. Apparently, BHND can initiate the photopolymerization of TMPTA more efficiently than BP/TEA. The system has the advantage of overcoming the presence of migratables in a coating due to the incorporation of both initiating and hydrogen donating sites in the same structure. This is particularly important for curing applications because formulations containing amine at high concentrations cause a decrease in the pendulum hardness of the cured films as a result of the plasticizing effect of amines.[32] For comparison, BHND containing formulation was also cured in air and a relatively long induction period was observed which can be attributed to the quenching of the excited precursor

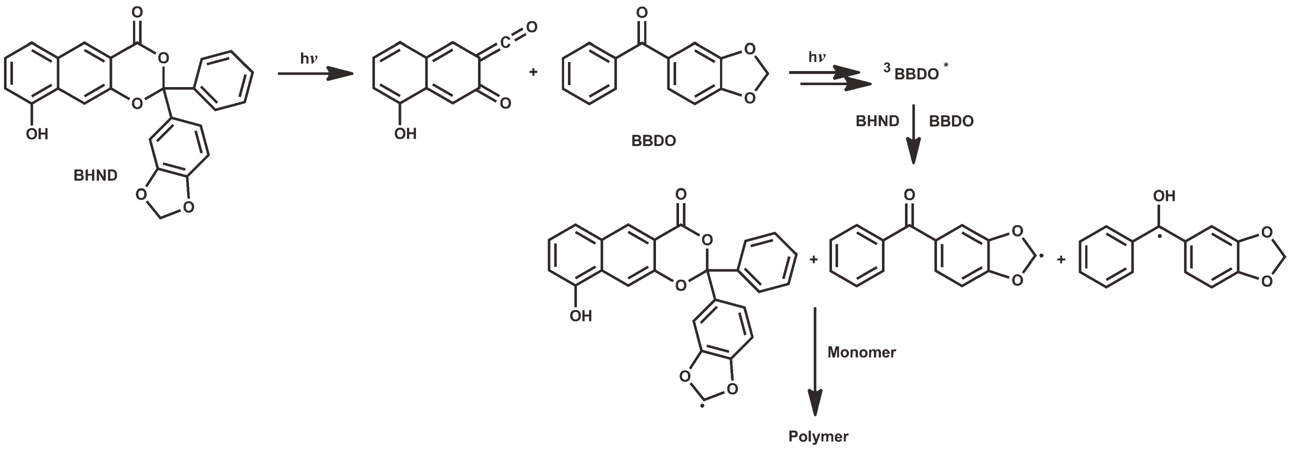
TABLE 1 Photoinitiated Free Radical Polymerization of Methyl Methacrylate at Room Temperature in CH_2Cl_2 for 4 h at $\lambda > 300$ nm

Run	[BHND] × 10^{-3} (mol L^{-1})	Solvent	Conversion[a] (%)	M_n[b] (g mol^{-1})	M_w/M_n[b]
1	4.85	CH_2Cl_2	10	72,000	2.9
2	9.70	CH_2Cl_2	16	60,000	2.3
3	4.85	DMF	8	54,000	2.0
4	4.85	THF	12	45,000	1.9

CH_2Cl_2, dichloromethane; DMF, dimethylformamide; THF, tetrahydrofuran.

[a] Calculated conversion in weight.

[b] Determined by GPC according to polystyrene standards.



SCHEME 3 Photoinitiated free radical polymerization by using 2-(benzo[*d*][1,3]dioxol-5-yl)-9-hydroxy-2-phenyl-4*H*-naphtho[2,3-*d*][1,3]dioxin-4-one (BHND).

compound, BHND. The later stage of the polymerization is expected to involve similar mechanism that is described for BBDO.[30]

EXPERIMENTAL

Materials

Unless otherwise noted, commercially available materials were used without further purification. Thus, 1,3-benzodioxole (Acros, %97), benzoyl chloride (Acorss, %99), benzophenone (≥99%, Aldrich), 3,5-dihydroxy-2-naphthoic acid (≥95.0%, Fluka), trifluoroacetic anhydride (99+%, Acros), trifluoroacetic acid (99.5%, Acros), sodium sulfate anhydrous (≥99.0%, Aldrich), and silicagel 60 (Merck, 0.040–0.063 mm) were used as received. MMA (99%, Acros) and TMPTA (techn., Aldrich) were passed through a column of basic alumina before use. All solvents were of HPLC or ACS grade. Solvents used for moisture sensitive operations were distilled from drying reagents under a nitrogen atmosphere: Et_2O and THF from sodium benzophenone ketyl; toluene from sodium; CH_2Cl_2 from CaH_2 and acetone over 4 Å molecular sieves.

Synthesis of 5-Benzoyl-1,3-benzodioxole

Anhydrous $FeCl_3$ (9 g, 55 mmol) was added at 0–5 °C to a mixture of 50 mL of anhydrous CH_2Cl_2 (6 g, 49 mmol) of 1,3-benzodioxole and benzoyl chloride (7.5 g, 53 mmol). 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 until to become neutral, dried with Na_2SO_4. Crude product was obtained as brown oil after the evaporation of CH_2Cl_2 with rotary evaporator. It was purified by column chromatography (over silicagel 10% EtOAc-Hexane).

Yield: 4.0 g (36%); ^{1}H NMR ($CDCl_3$): δ = 7.74–7.71 (d, J = 7.5, 2H), 7.55 (t, J = 7.5, 1H), 7.52–7.42 (m, 2H), 7.37–7.35 (m, 2H), 6.85 (d, J = 7.5, 1H), 6.05 (s, CH_2, 2H); FTIR (cm^{-1}): 3065, 3025, 2903, 1746, 1651, 1601, 1578, 1503, 1485, 1445, 1352; UV (CH_2Cl_2): λ_{max}., nm (ε, L mol^{-1} cm^{-1}); 316 (9050), 279 (6492), 238 (20941).

Synthesis of 2-(Benzo[d][1,3]dioxol-5-yl)-9-hydroxy-2-phenyl-4H-naphtho[2,3-d][1,3]dioxin-4-one

BHND was prepared according to the modified literature procedure.[31] Thus, 3,5-dihydroxy-2-naphthoic acid (1.5 g, 7.4 mmol) and above prepared BBDO (2.5 g, 11 mmol) were put into the flask under nitrogen atmosphere and a mixture of trifluoroacetic acid (10 mL) and trifluoroacetic anhydride (11 mL) were added at 0 °C. Then, the solution was stirred for 24 h at room temperature. The crude product was dissolved in ethylacetate and washed with $NaHCO_3$ solution three times. Organic phase was dried over $MgSO_4$ and solvent was evaporated. The obtained product was purified with column chromatograpy using ethylacetate/hexane 10/90 mixture as eluent.

Yield: 0.16 g, (%5), mp 245–247 °C; ^{1}H NMR ($CDCl_3$): δ = 8.44 (s, 1H), 7.86 (s, 1H), 7.62 (d, J = 6.5, 1H), 7.42–7.18 (m, 6H), 7.08 (m, 2H), 6.89 (d, J = 7.5, 1H), 6.71 (d, J = 7.5, 1H),

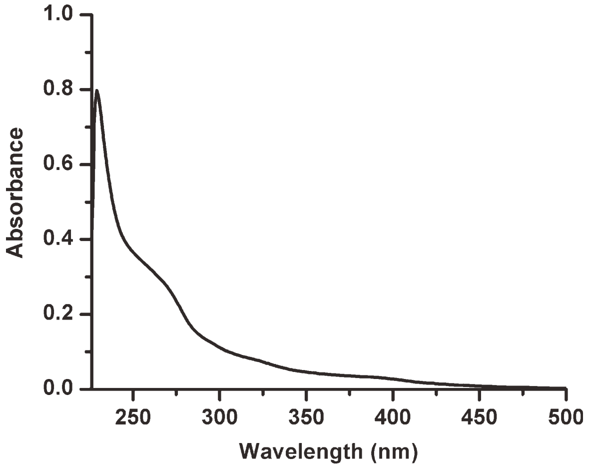


FIGURE 5 UV spectrum of PMMA (8.1 × 10^{-6} mol L^{-1}) initiated by BHND.

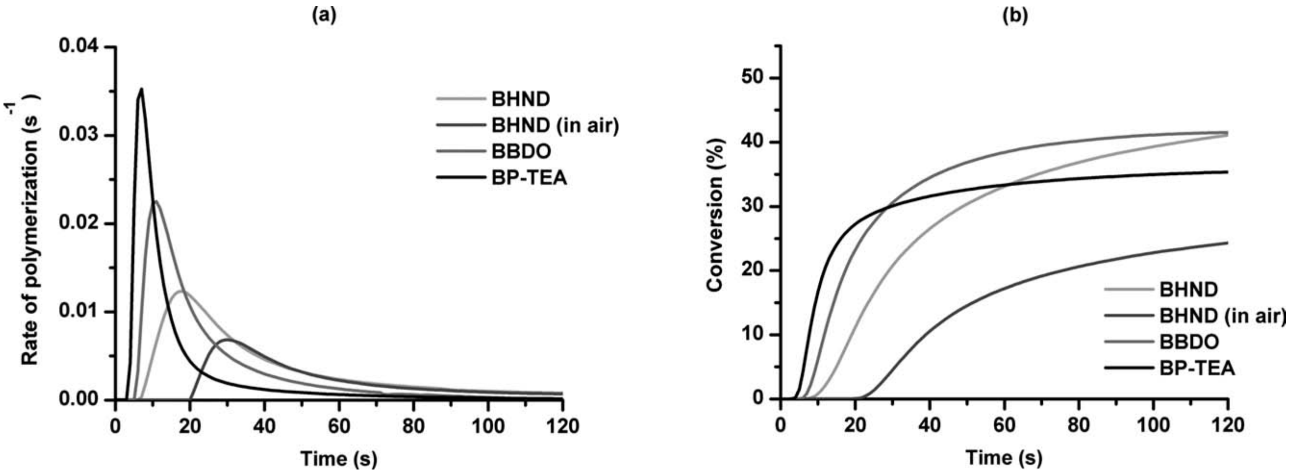


FIGURE 6 Rate of photopolymerization (a) and conversion-time plot (b) for the photoinitiated free radical polymerization of TMPTA at 30 °C. ([BHND] = [BBDO] = [BP] = 0.1 mol %, [TEA] = 1 mol %, light intensity = 76 mW × cm^{-2}).

5.91 (s, CH_2, 2H); FTIR (cm^{-1}): 3447, 3359, 1702, 1628, 1579, 1504, 1484, 1282, 1240, 1103, 1070, 1036, 830; UV (CH_2Cl_2): λ_{max}, nm (ε, L mol^{-1} cm^{-1}); 376 (3458), 291 (12933), 263 (52391).

Photopolymerization

Monomer MMA (1.0 mL, 14 mmol) in CH_2Cl_2 (1.5 mL) solution, BHND (5 mg, 0.01 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 $\lambda > 300$ 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.

Photocalorimetry (Photo-DSC)

The photo-differential scanning calorimetry (Photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high pressure mercury arc lamp. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 76 mW cm^{-2} by a UV radiometer covering broad UV range. The mass of the samples was 3 mg and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate double bonds reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate or methacrylate groups (C) or the extent of the reaction was determined according to eq 1:

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \tag{1}$$

where ΔH_t is the reaction heat evolved at time t and $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion. $\Delta H_0^{\text{theory}} = 86$ kJ mol^{-1} for an acrylic double bond.[33] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by eq 2:

$$R_p = dC/dt = (dH/dt)/\Delta H_0^{\text{theory}} \tag{2}$$

CONCLUSIONS

In conclusion, a naphthodioxinone derivative was synthesized and used as a new one-component Type II photoinitiator. The actual photoinitiator, BBDO, is formed after photodecomposition of naphthodioxinone. The subsequent step includes the radical formation by hydrogen abstraction of photoexcited BBDO from a ground state BBDO and/or BHND. This is an attractive photoinitiator because it does not require an additional hydrogen donor and initiates polymerization of acrylates in the presence and absence of air. The other obvious advantage of the photoinitiating system is related to the different absorption characteristics of the precursor and the successor compounds, that is, λ_{max} (BHND) = 376 nm; λ_{max} (BBDO) = 316 nm. This behavior make the photoinitiating system important alternative for two-photon induced polymerizations[34,35] acting at two different wavelengths for applications involving three-dimensional (3D) microfabrication, optical data storage, imaging, and the controlled release of biological systems. Further studies in this line together with its use in free radical promoted cationic polymerization are now in progress.

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