Aminimide Derived from Benzoylformic Acid Ester as Photolatent Base/Radical Initiator

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ABSTRACT: An aminimide possessing a benzoyl substituent, 1,1-dimethyl-1-(2-hydroxypropyl)amine benzoylformimide (BFI), proved to serve as an excellent photobase catalyst. BFI decomposes smoothly by the UV irradiation to give products containing tertiary amines. The effective nature of BFI as a photo/thermal dual-base catalyst was convinced by the thermal and photoinduced polymerization of epoxide/thiol system. Based on the facts that the mixture of BFI and epoxide/thiol exhibit a long pot life in dark and that it undergoes smooth polymerization by UV irradiation and heating, it was supported that BFI serves as an efficient photo/thermal latent dual-base catalysts. It was also found that BFI initiates the free radical polymerization of vinyl monomers such as 2-hydroxylethyl methacrylate (HEMA) under the UV irradiation while the mixture of BFI and HEMA also exhibit a long pot life in dark, indicating the excellent ability of BFI as a photoradical initiator. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1556–1563, 2012

KEYWORDS: anionic polymerization; catalysts; photopolymerization; radical polymerization

INTRODUCTION The photocuring technique is important for many practical applications in the fields of adhesives, sealants, paints, coatings, molding resins, and so on. Especially, photoinitiated radical and cationic curing systems have been studied widely, and they have been utilized in various industrial applications.[1,2] Although these photocuring systems are effective for practical applications, curing does not occur sufficiently if the materials are not transparent enough toward the photoirradiation. To improve this issue, the postpolymerization technique by heat or moisture (so-called "dual-cure") is expected to assist the incomplete photocuring process. In the radical and/or cationic systems, various initiators have been applied to the photo/thermal dual-cure processes.[3] For instance, peroxides, azo compounds, and azo-benzoin initiators have been utilized as photo/thermal dual-radical initiators,[4–7] and some onium salts have been also applied as photo/thermal dual-cationic initiators.[8–12] However, both the radical and the cationic systems have inevasible drawbacks: the radical system is often deactivated by oxygen, and the cationic system is susceptible to weak bases originated from moisture or impurities in monomers and/or prepolymers.

In contrast, the anionic and the base-catalyzed curing system are known to be free from these inhibition processes. Accordingly, polymerization systems catalyzed by base species would be promising methods for industrial applications. A number of photobase catalysts have been evaluated their ability to catalyze polymerizations of epoxide, epoxide/thiol, epoxide/carboxylic acid, alcohol/isocyanate, and cyanoacrylate.[2,13,14] However, few photo/thermal dual-base catalyst has been reported so far.

Aminimides are attractive candidates for photo/thermal dual-base catalysts, because they are reported to undergo the thermal cleavage of the N—N bonds to produce tertiary amines,[15,16] which are applicable as thermal latent base catalysts for epoxides,[17–21] epoxide/acid anhydride system,[17] and epoxide/thiol system,[22,23] and because some of the aminimide derivatives such as benzimides, aminimides possessing Ph—CO—N⁻—N⁺ moieties, undergo photolysis to produce tertiary amines and amides,[22–25] that can be utilized as photobase catalysts for epoxide/thiol system.[22,23] Despite their potential ability of photo/thermal dual-base catalysts, their poor thermal activity (i.e., their relatively high activation temperature) made it difficult to attain practical applications.

Recently, we synthesized a new class of aminimide, 1,1-dimethyl-1-(2-hydroxypropyl)amine benzoylformimide (BFI; Fig. 1), which was found to serve as a thermal latent base catalyst exhibiting high activity at lower temperature. That is, BFI generates benzoyl isocyanate, 1,1-dimethylamino-2-
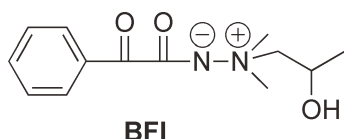
FIGURE 1 Structure of BFI.

propanol (**1**), and their further reaction products by heating above 80 °C via the Curtius-type rearrangement mechanism, and **1** catalyzes the polymerization of epoxide and epoxide/thiol system.[26] Because BFI has phenyl α-diketone moiety, it is also expect that BFI also exhibits photoactivity. Thus, we evaluated the photobase activity of BFI in detail to realize a novel photo/thermal dual-base catalyst. The possibility of BFI as photoradical initiator was also investigated in the photoinitiated polymerization of an acrylate monomer.

EXPERIMENTAL

Materials

BFI was synthesized from benzoylformic acid methyl ester, 1,1-dimethylhydrazine, and propylene oxide as described in our previous article.[26] Benzoylformic acid methyl ester, 1,1-dimethylamino-2-propanol (**1**), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), and benzophenone were purchased from Tokyo Kasei Kogyo (Japan). Benzyl alcohol, pentaerythritol tetrakis(3-mercaptopropionate), EXA-850CRP (pure grade bisphenol A diglycidyl ether), and Irgacure 184 (1-hydroxy-cyclohexyl phenyl ketone) were purchased from Wako Pure Chemical Industries (Japan), Aldrich (Milwaukee), DIC (Japan), and BASF (Germany), respectively, and they were used as received. ACRYESTER HO (2-hydroxylethyl methacrylate (HEMA), containing 50 ppm of 4-methoxyphenol as a radical polymerization inhibitor) were purchased from Mitsubishi Rayon (Japan) and used both as received and after purification by distillation under reduced pressure.

Methods

The UV irradiation was performed with a Hamamatsu Photonics LC8/L8251 (200 W mercury-xenon lamp) equipped with a direct beam uniform illumination unit (E10052-01) without UV filter. The light intensity at 365 nm was 20 or 100 mW cm^{-2}. UV–vis spectra were measured by a Shimadzu UV-3100PC spectrometer. The pH values were measured by a Horiba D-54 pH meter. IR spectra were taken on a BIO-RAD FTS-40 FTIR system using a SPECAC MK II heated diamond ATR system. Melting points were measured on a Mettler Toledo FP90/FP82HT thermo system and an Olympus BX50 microscope at a heating rate of 2 °C min^{-1}. Nuclear magnetic resonance (NMR) spectra were recorded with a JEOL ECP300 spectrometer in CDCl$_3$ (300 and 75 MHz for ^{1}H NMR and ^{13}C NMR, respectively). The high-resolution mass spectrometry (HRMS) was performed with a JEOL JMS700 system (ion mode: FAB+, matrix: nitrobenzyl alcohol with NaI). Gas chromatographic–mass spectrometric (GC–MS) analyses were performed on a Thermoquest GCQ GC–MS system equipped with a Frontier Laboratories UA5 (MS/HT)-30M-0.25F GC column and a liquid nitrogen cryo-trap. The samples were heated at 50 °C for 1 min, and the volatile

fractions were directly trapped by liquid nitrogen and were analyzed by GC–MS (conditions: sample temperature: 120 °C; split flow: 40 mL min^{-1} (He gas); split ratio: 1/40; GC heating profiles: 50 °C for 5 min and then heated to 300 °C at a heating rate of 10 °C min^{-1}; ionization voltage: 70 eV). Differential scanning calorimetry analyses (DSC) were performed on a Seiko Instruments DSC 220 under a nitrogen atmosphere.

UV Spectra of BFI before and after UV Irradiation

A sealed crystal UV cell containing a methanol solution of BFI (7.0 × 10^{-5} M) was subjected to the UV irradiation (100 mW cm^{-2}) with stirring. UV–vis spectra were measured after designed periods.

pH Value of BFI Aqueous Solution before and after UV Irradiation

In a sealed glass sample tube equipped with a pH electrode, a water solution of BFI (4.0 × 10^{-3} M) was subjected to the UV irradiation (100 mW cm^{-2}) with stirring, and the pH value was evaluated after designated period.

Identification of Photodegradation Products of BFI

In a sealed quartz glass UV cell, a methanol (2.2 ml) solution of BFI (1.0 g, 4.0 mmol) was irradiated with UV light (100 mW cm^{-2}) at 20–30 °C for 50 min with stirring. During the irradiation, white powder started precipitating out from the solution after about 10 min. The resulting mixture was then completely evaporated to dryness under reduced pressure (30 °C/0.23 mmHg), and the volatile portions were collected by dry ice/acetone trap. The residual paste (0.70 g) containing the white powder was washed twice with methanol to give 2,3-dihydroxy-2,3-diphenyl-succinic acid diamide (**2**) (0.060 g, 0.20 mmol, 10% yield) as white powder in an essentially pure form; mp 186.0–187.0 °C (decomposition). IR (solid, ATR): 3465, 3332, 3255, 3184, 1662 (s, C=O), 1593, 1495, 1426, 1307 cm^{-1}.

^{1}H NMR (DMSO-d_6): δ 7.25 (s, 2H, OH), 7.28–7.36 (m, 6H, C$_6$H$_5$), 7.56 (s, 2H, NH$_2$), 7.66 (s, 2H, NH$_2$), 7.76–7.79 (m, 4H, C$_6$H$_5$). ^{13}C NMR (DMSO-d_6): δ 78.7, 127.0, 127.4, 127.5, 140.9, 175.7. HRMS (FAB+) [M+H]$^{+}$: Calcd for C$_{16}$H$_{17}$N$_2$O$_4$: m/z 301.1188. Found: m/z 301.1192, [M+Na]$^{+}$: Calcd for C$_{16}$H$_{16}$N$_2$O$_4$Na: m/z 323.1008, Found: m/z 323.1004. TLC analysis of the methanol-soluble part exhibited three spots. However, its purification by column chromatography (silica gel and ethyl acetate/methanol) was unsuccessful, and the unreacted BFI (0.37 g, 37%) was recovered from the mixture. From the cryo-trap GC–MS analysis of the volatile portions, a number of GC peaks were observed. Among them, one GC peak was identified to be **1** from its MS spectrum in comparison with that of the authentic sample. However, the other GC peaks could not be identified by their MS patterns.

IR Spectra of BFI under UV Irradiation

A small portion of a benzyl alcohol solution of BFI (1.0 M) was placed on a FTIR ATR stage (thickness of the sample: 0.004 mm, protected with a cover glass) and its real-time FTIR spectra were measured at 25 °C under the UV irradiation (20 mW cm^{-2}). Conversions of the carbonyl group in

BFI (N$^-$—CO) were estimated from the intensity of the peak at 1594 cm^{-1} with respect to that of the C—O absorption peak in benzyl alcohol at 1014 cm^{-1}. As control experiments, measurements of benzyl alcohol, a 1.0 M solution of **1** in benzyl alcohol, and a 0.5 M solution of **2** in benzyl alcohol were likewise performed.

Photoinduced Polymerization Studies of Epoxide/Thiol System with BFI

To a homogenous mixture of BFI (0.0250 g, 0.100 mmol) and benzyl alcohol (0.108 g, 1.00 mmol), EXA-850CRP (0.688 g, 2.00 mmol) and pentaerythritol tetrakis(3-mercaptopropionate) (0.489 g, 1.00 mmol) were added at room temperature. Small portions of this mixture were subjected to DSC and real-time FTIR analyses as follows.

DSC Measurements

A portion of the mixture (50 mg) was placed in a sealed clear borosilicate glass vial (diameter: 12 mm) and was irradiated with UV light (100 mW cm^{-2}) from the bottom of the vial at 25 °C. After the irradiation for designated period, 5.0 mg of the sample was transferred into an aluminum pan and completely sealed. The polymerization profile was monitored by the DSC, where the temperature of the sample was raised from 20 to 200 °C at a heating rate of 10 °C min^{-1}. Subsequent heating cycles were monitored for determining the glass transition temperature (T_g) from −30 to 100 °C at a heating rate of 10 °C min^{-1}.

Real-Time FTIR Observations

A small aliquot of the mixture was put on a FTIR ATR stage, whose surface was protected with a cover glass to avoid the inhibition by oxygen. The thickness of the sample was 0.004 mm. The measurements were performed at 25 or 85 °C under the UV irradiation of 100 mW cm^{-2} for 30 or 60 s. The conversion was determined from the peak intensities of both the thiol (2568 cm^{-1}) and the epoxide (914 cm^{-1}) with respect to that of the carbonyl absorption for the ester (1736 cm^{-1}) in pentaerythritol tetrakis(3-mercaptopropionate).

Photoinitiated Radical Polymerization of Acrylic Monomer with BFI under UV Irradiation
Bulk Polymerization

A homogeneous mixture of BFI (0.010 g, 0.040 mmol) and HEMA (used both as received and after purification by distillation) (1.3 g, 10 mmol) was placed between two PET films with a thickness of 0.5 mm. The sample was irradiated with UV light (100 mW cm^{-2}) for 50 s (5 J cm^{-2}).

Real-Time FTIR Observations

A clear homogeneous mixture of HEMA (as received, 1.3 g, 10 mmol) and BFI (0.010 g, 0.040 mmol) was put on a FTIR ATR stage, and the surface of the sample was protected with a cover glass to avoid the inhibition by oxygen. The thickness of the sample was 0.004 mm. The real-time FTIR spectra were measured under the UV irradiation of 20 mW cm^{-2}. The conversion was estimated from the peak intensity of the vinyl absorption in HEMA (1635 cm^{-1}) with respect to that of the carbonyl groups (1713 cm^{-1}). The measurements of
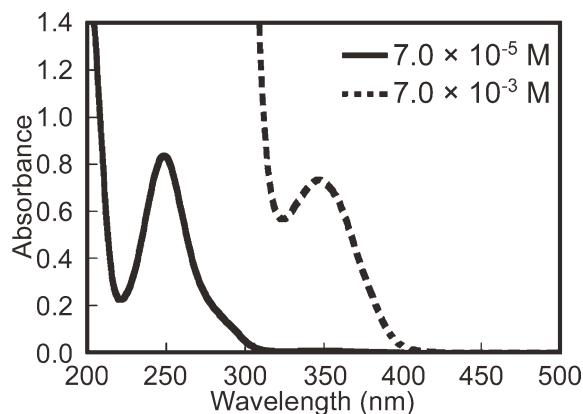

FIGURE 2 UV–vis spectra of methanol solutions of BFI (7.0 × 10^{-5} and 7.0 × 10^{-3} M, cell length: 1.0 cm).

HEMA without the initiator and a mixture consisting of HEMA (10 mmol), BFI (0.040 mmol), and TEMPO (0.020 or 0.040 mmol) were also performed to support the radical mechanism. Mixtures of HEMA (10 mmol) and various additives (0.040 mmol) such as **1**, benzophenone, benzoylformic acid methyl ester, and 1-hydroxycyclohexyl phenyl ketone were also subjected to the same measurements to compare the polymerization behavior. The measurement of a mixture consisting of HEMA (10 mmol), benzoylformic acid methyl ester (0.040 mmol), and **1** (0.040 mmol) was also performed to compare the photoradical activity of BFI and benzoylformic acid methyl ester in the presence of tertiary amine.

RESULTS AND DISCUSSION

UV Absorption Spectra of BFI

As shown in Figure 2, the UV–vis spectra of BFI in methanol exhibited two absorption peaks at 249 and 346 nm whose molar extinction coefficient (ε) were 1.2 × 10^4 L mol^{-1} cm^{-1} and 1.0 × 10^2 L mol^{-1} cm^{-1}, respectively. As expected, BFI was found to exhibit absorptions suitable for emission lines of the high-pressure mercury lamp at 254, 313, and 365 nm (ε = 1.1 × 10^4, 1.3 × 10^2, 7.8 × 10 L mol^{-1} cm^{-1}, respectively).

To evaluate the photoreaction behavior of BFI, the UV–vis spectra of BFI (7.0 × 10^{-5} M in methanol) were measured after the irradiation of the high-pressure mercury lamp (Fig. 3). Consequently, the intensity of the peak at 249 nm decreased and that of a new peak at 229 nm increased until the total exposure of the UV irradiation of 4.0 J cm^{-2}.

Variation of pH Value of Aqueous Solution of BFI by UV Irradiation

The variation of the pH value of an aqueous solution of BFI (4.0 × 10^{-3} M) by the UV irradiation was studied to evaluate the basicity of photoreaction products generated from BFI. Before the UV irradiation, the solution was almost neutral (pH = 6.2), which immediately turned to basic (pH = 9–10) after the photoirradiation (Fig. 4). This result indicates that BFI can generate base by the UV irradiation.
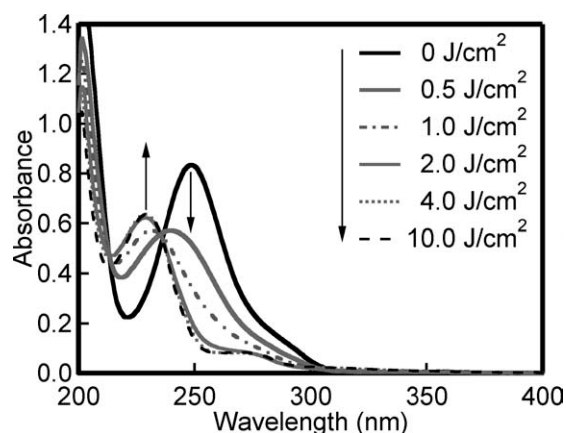
FIGURE 3 Variation of the UV–vis spectra of BFI in methanol ($[BFI]_0 = 7.0 \times 10^{-5}$ M) after the UV irradiation of 0, 0.5, 1.0, 2.0, 4.0, and 10.0 J cm^{-2}.

FIGURE 5 GC profile of volatile fractions obtained by the photoreaction of BFI in methanol.

Photoreaction Mechanism of BFI

To identify the photoreaction products, we carried out the GC–MS measurement of the volatile fractions obtained by the photoirradiation of BFI in methanol. That is, after the UV irradiation of a methanol solution of BFI, volatile fractions in the resulting mixture were collected by the trap-to-trap distillation at 30 °C/0.23 mmHg. In the GC analysis (Fig. 5), a number of peaks appeared, among which a peak at 2.81 min could be identified as **1** from its MS spectrum in comparison with that of the authentic sample (Supporting Information Fig. 1).

From the nonvolatile residue remained in the trap-to-trap distillation in 70 wt %, 2,3-dihydroxy-2,3-diphenyl-succinic acid diamide (**2**) was isolated in 10% yield as white solid (Scheme 1). Besides, the unreacted BFI was recovered in 37%. These results indicate that the photolysis takes place at least partly via the cleavage of the N—N bond in BFI.

The photolysis of BFI was studied in detail by the FTIR measurements. Among the good solvents for BFI such as water, alcohols, and other polar media, benzyl alcohol was chosen as a solvent because of its high boiling point. From
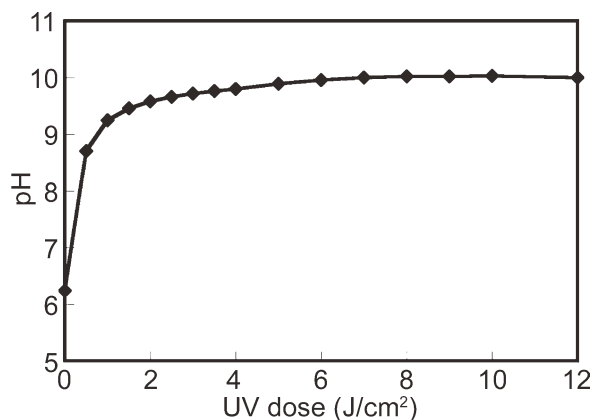
the real-time FTIR measurements of a benzyl alcohol solution of BFI after the UV irradiation, a peak at 1594 cm^{-1} attributable to the carbonyl group in the aminimide (N$^-$—CO) gradually decreased [Fig. 6(a–d)]. Based on the variation of this peak intensity, the conversion of BFI was estimated which indicates the smooth progress of photoinduced reactions (Fig. 7). After the photolysis reaction, a peak at 1679 cm^{-1} for the benzoyl group (Ph-CO) in BFI shifted to 1666 cm^{-1} which is attributable to the amide carbonyl group in **2**. In our recent report,[26] we described that the thermal reaction of BFI accompanies the formation of urethane derivatives on the basis of the similar FTIR observation, in which a peak of aminimide decreased and a new sharp peak of the carbonyl group in the urethane at 1771 cm^{-1} could be observed by the thermal treatment. As the urethane is most probably produced by the reaction of benzoyl isocyanate and 1,1-dimethylamino-2-propanol (**1**), it was supported that the thermal reaction proceeds through the Curtius-type rearrangement. In contrast, no sharp peak attributable to the isocyanate at 2224 cm^{-1} or to the carbonyl group in the urethane at 1771 cm^{-1} was observed in the present photolysis

FIGURE 4 Variation of the pH value of an aqueous solution of BFI by the UV irradiation ($[BFI]_0 = 4.0 \times 10^{-3}$ M).
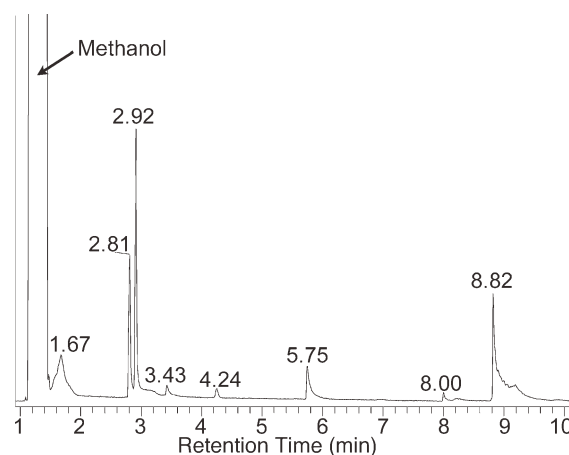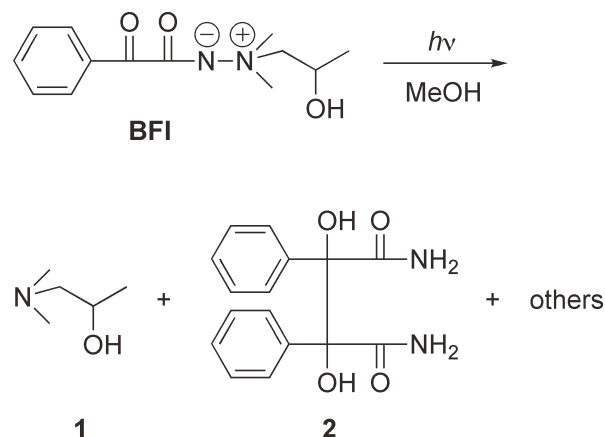

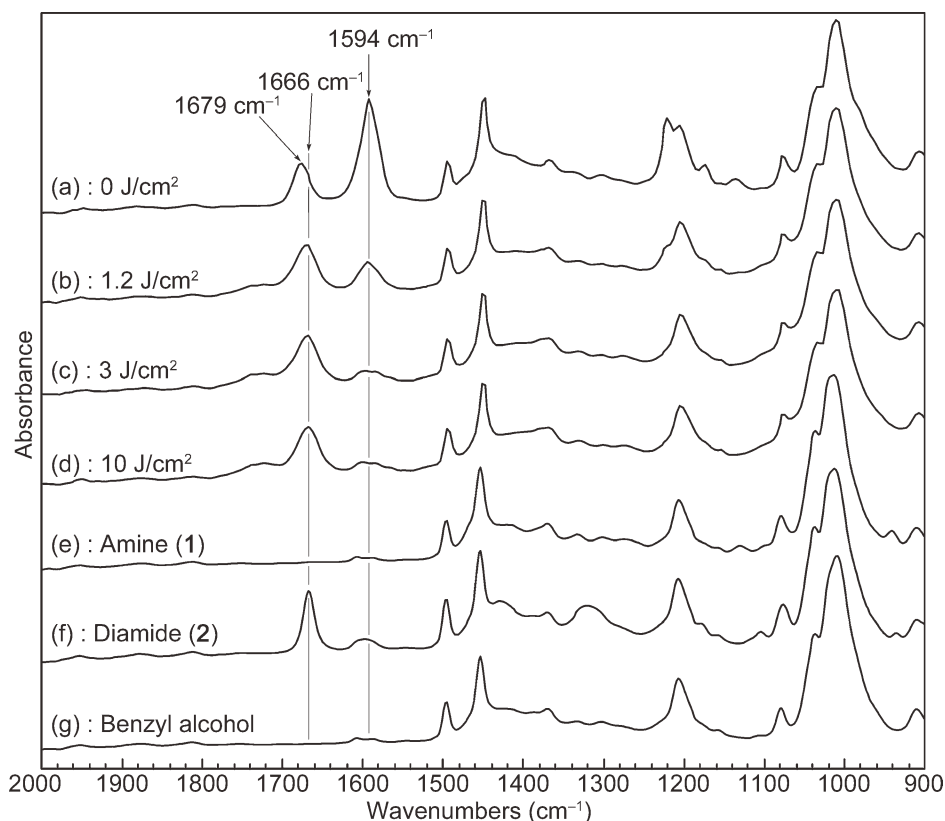**SCHEME 1** Products identified in photoreaction of BFI in methanol.

FIGURE 6 FTIR spectra of a 1.0 M solution of BFI in benzyl alcohol after UV irradiation of 0, 1.2, 3.0, and 10 J cm^{-2} (a–d), 1.0 M solution of **1** in benzyl alcohol (e), 0.5 M solution of **2** in benzyl alcohol (f), and benzyl alcohol alone (g).

process. This result indicates that BFI does not generate isocyanates under the photolysis conditions.

It has been reported that aminimides having R—CO—N$^-$—N$^+$ moieties undergo the photocleavage at the N$^-$—N$^+$ bonds to produce the corresponding tertiary amines and amides. The generation mechanism of the amides may include the hydrogen abstraction by the intermediate triplet nitrenes.[22–25] In the case of benzoylformic acid esters, which have analogous structure to benzoylformic acid amide (**3**), it has been reported that a dimerized products were obtained by the photoirradiation via the ketyl radical intermediate.[27–32] Although further works including the structural elucidation of the major photolysis products from BFI should be performed so as to support the proposed mechanism, we assume that the photoreaction of BFI proceeds at least partly by the cleavage of the N—N bonds to produce **1** and **3**, and the resulting **3** dimerizes to give **2** via the ketyl radical intermediate (Scheme 2).

Photoinduced Polymerization of Epoxide/Thiol System by BFI

As described above, the base-generation from BFI by photoirradiation was confirmed from both pH measurements and GC–MS studies, although the major photoproducts from BFI have not been clarified yet. Therefore, the photoinduced polymerization of epoxide/thiol system was carried out with BFI to demonstrate its activity as a photobase catalyst.

A homogeneous mixture of bisphenol A diglycidyl ether (2.00 mmol), pentaerythritol tetrakis(3-mercaptopropionate) (1.00 mmol), BFI (0.100 mmol), and benzyl alcohol (1.00 mmol) was irradiated with a UV lamp for designated periods, and the resulting samples were then subjected to the DSC measurements in the range of 20–200 °C at a heating rate of 10 °C min^{-1} (Fig. 8 and Table 1). Without the UV irradiation, BFI serves as a highly active thermal latent base catalyst. Thus, the polymerization of the epoxide/thiol takes place
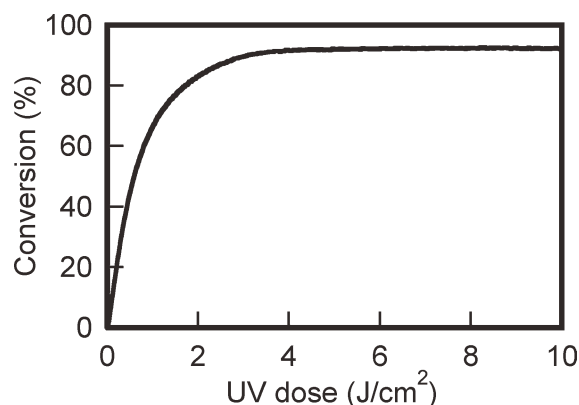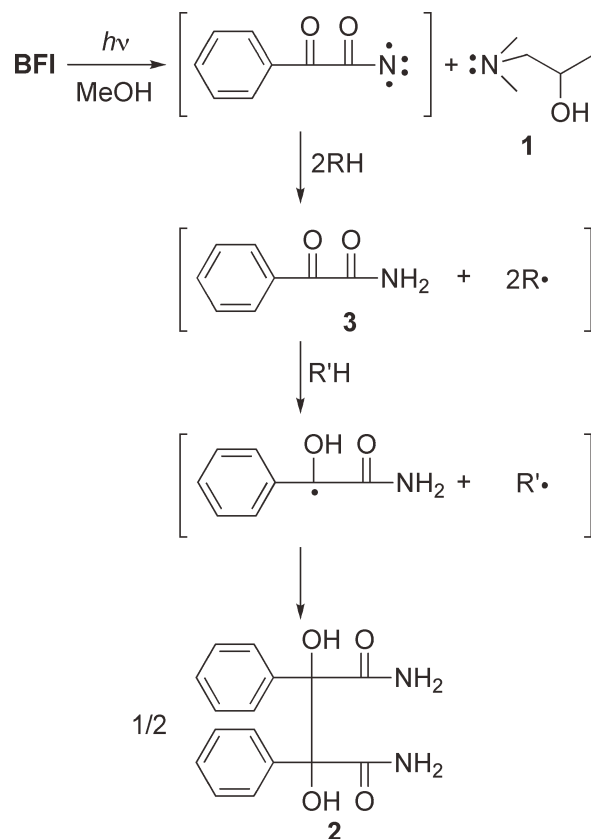

FIGURE 7 Conversion of BFI estimated from the peak intensity of the carbonyl group (N$^-$—CO) at 1594 cm^{-1} by UV irradiation in a benzyl alcohol solution (1.0 M).

SCHEME 2 One plausible photoreaction mechanism of BFI in methanol.

TABLE 1 DSC Onset Temperature, Heat Evolved (ΔH), and T_g of the Products Obtained after DSC for the Mixture of BFI and Epoxide/Thiol System after the UV Irradiation

UV Dose (J cm^{-2})	DSC Onset Temperature (°C)[a]	ΔH (J g^{-1})[a]	T_g (°C)[b]
0	121.1	401	11.8
1	99.3	400	11.1
3	82.7	392	11.1
6	73.2	392	11.3
9	67.9	393	11.0
20	54.8	362	11.8

[a] Measured by DSC (20–200 °C, at a heating rate of 10 °C min^{-1}).
[b] Measured by DSC (–30 to 100 °C, at a heating rate of 10 °C min^{-1}).

the thiol proceeds by base catalysts, the acceleration by the prolonged photoirradiation is most probably due to the increased amount of the photogenerated base.

Once the base was generated by the UV irradiation at the initial stage, the present reaction was found to proceed also under dark conditions (Fig. 9). That is, the mixture of the epoxide/thiol system and BFI was irradiated by the UV lamp at 25 °C for 1.0 min (UV dose: 6 J cm^{-2}), and the time–conversion curves of both the thiol and the epoxide groups in the resulting mixture were followed in dark at that temperature using the real-time FTIR measurements. In this case, the polymerization proceeded smoothly and was complete within 100 min (Table 2, run 1). When the similar experiment was carried out at 85 °C (i.e., the UV irradiation at 85 °C for 1 min, run 2), the polymerization took place rapidly, resulting in the complete conversion during the UV irradiation (6 J cm^{-2}). At 85 °C, the polymerization occurred smoothly enough, even after much shorter UV irradiation treatment (i.e., 0.5 min, run 3). Compared to the preceding

above 121.1 °C, while the mixture exhibits long pot life (e.g., more than 2 weeks at room temperature), as described in our preceding article.[26] After the UV irradiation, the DSC onset temperature decreased by increasing the total light irradiated (i.e., UV dose). However, both the heat evolved (ΔH) and T_g of the products obtained after the DSC analyses were almost constant, indicating that the conversions of the epoxide and the thiol, and the crosslink density of the resulting polymers were almost constant irrespective of the irradiation conditions. As the polymerization of the epoxide and
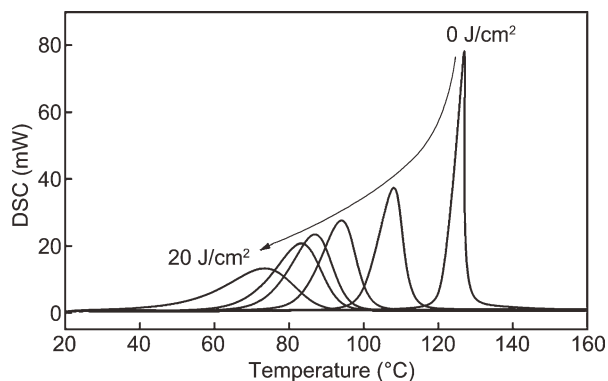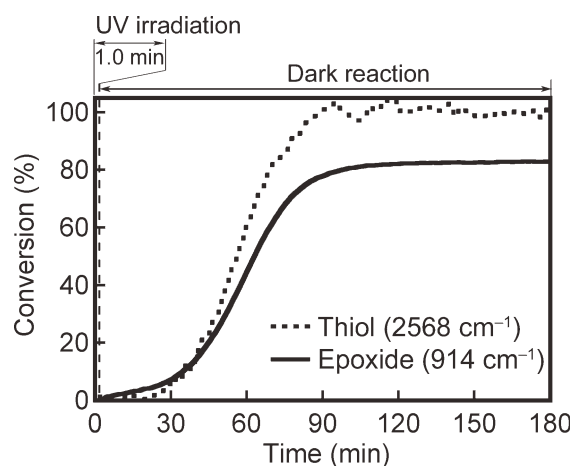

FIGURE 8 DSC profiles of the epoxide/thiol system in the presence of BFI after the UV irradiation of 0, 1, 3, 6, 9, and 20 J cm^{-2}.

FIGURE 9 Time–conversion curves of the thiol and the epoxide functional groups monitored by intensities of the peaks at 2568 and 914 cm^{-1}, respectively, in the IR spectra of a mixture of epoxide/thiol and BFI at 25 °C after the UV irradiation at the initial stage for 1.0 min (UV dose: 6 J cm^{-2}).

TABLE 2 Time Required for the Complete Polymerization of the Epoxide/Thiol System after UV Irradiation at the Initial Stage

Run	Polymerization Conditions			
	Temperature (°C)[a]	UV Irradiation Time (min)	UV Dose (J cm^{-2})	Polymerization Period (min)[b]
1	25	1.0	6	100
2	85	1.0	6	1.0
3	85	0.50	3	1.5

[a] Temperature for both UV irradiation and postpolymerization in dark.
[b] Total time (i.e., UV irradiation and postpolymerization time) required for complete conversion of thiol and epoxide, determined by the peak intensities at 2568 and 914 cm^{-1} in the IR spectra.

reports on the photoinduced polymerization of the epoxide/thiol system using aminimides such as 4-nitrobenzimides,[22,23] the present BFI-catalyzed system exhibits remarkably faster polymerization in much lower temperature, indicating the highly active nature of BFI as a photobase catalyst for the epoxide/thiol system. Considering the highly active nature of BFI as a thermal latent base catalyst,[26] it was supported that BFI serves as an efficient photo/thermal latent dual-base catalyst.

Photoinitiated Radical Polymerization of Acrylic Monomers with BFI

It has been reported that both benzoylformic acid esters[27–32] and benzoylformic acid amide[33] serve as photoradical initiators. Because BFI also has benzoylformic acid moiety, it is expected that BFI exhibits photoradical activity. As mentioned earlier, the proposed photoreaction mechanism of BFI also implies free radical intermediates such as products via the hydrogen abstraction by the triplet nitrenes and/or the ketyl radicals (Scheme 2). Thus, the ability of BFI as an initiator for the photoinitiated radical polymerization of vinyl monomers was evaluated. In this study, 2-hydroxyethyl methacrylate (HEMA) was chosen because of its low volatility and good ability to solubilize BFI. A homogeneous mixture of HEMA (both as received and after purification, 10 mmol) and BFI (0.040 mmol) was subjected to the polymerization under the UV irradiation of 5 J cm^{-2}. From both the purified and unpurified monomers, tough transparent film was obtained which was hardly soluble in organic solvents such as tetrahydrofuran, chloroform, toluene, and N,N-dimethylformamide.

The conversion of HEMA in the photopolymerization with BFI was monitored by the FTIR measurements. For example, a homogeneous mixture of HEMA (without purification, 10 mmol) and BFI (0.040 mmol) was subjected to the UV irradiation and the conversion of HEMA was monitored by the variation of the peak intensity of the vinyl group at 1635 cm^{-1} in the IR spectra. It was found that the smooth conversion of HEMA took place in the presence of BFI under the UV irradiation [Fig. 10(a)]. On the other hand, the consumption of HEMA was very slow in the presence of **1** [Fig. 10(e)] or without any initiators [Fig. 10(d)]. Thus, the possibility of the anionic mechanism in the polymerization of HEMA/BFI

could be excluded. These results also indicate that the initiating species are not generated from amine or HEMA. Furthermore, the consumption of HEMA took place slower if TEMPO was added as a radical trapping agent, where the increased amount of TEMPO remarkably suppressed the polymerization [Fig. 10(a–c)]. Accordingly, the polymerization of HEMA most probably proceeds in the photoinitiated radical mechanism in the presence of BFI. Furthermore, as shown in Figure 10(b), it was found that the activity of BFI is high enough compared to commercial initiators such as benzophenone, benzoylformic acid methyl ester, and 1-hydroxycyclohexyl phenyl ketone. The high activity of BFI might be due to the aminimide structure, because the activity of benzoylformic acid methyl ester was a little lower than BFI which
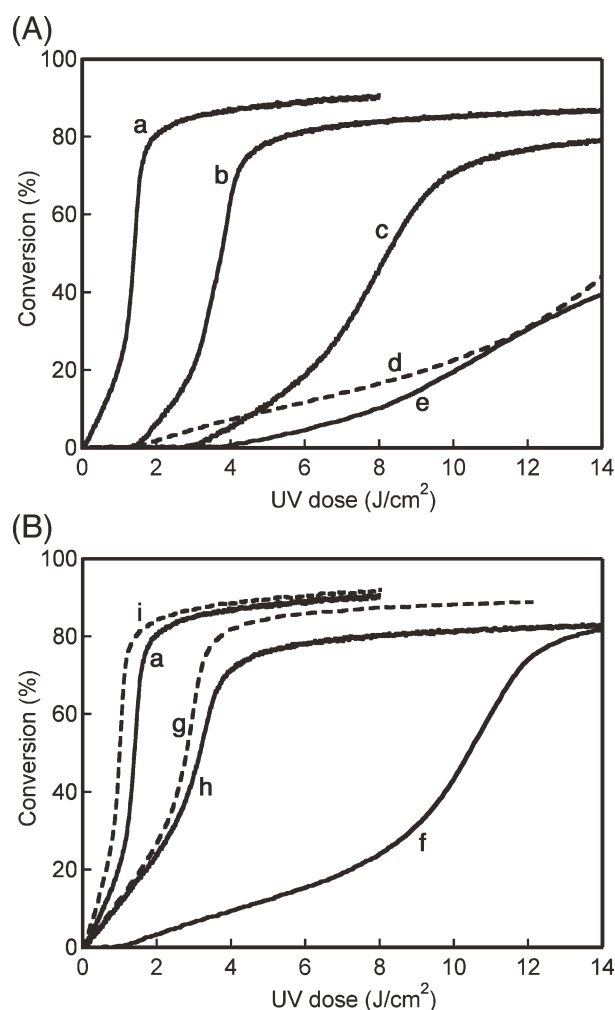

FIGURE 10 Conversions of the vinyl group in the photoinitiated radical polymerization of HEMA (10 mmol) in the presence of various additives: (a) BFI (0.040 mmol), (b) BFI (0.040 mmol) and TEMPO (0.020 mmol), (c) BFI (0.040 mmol) and TEMPO (0.040 mmol), (d) without initiators, (e) **1** (0.040 mmol), (f) benzophenone (0.040 mmol), (g) benzoylformic acid methyl ester (0.040 mmol), (h) benzoylformic acid methyl ester (0.040 mmol) and **1** (0.040 mmol), and (i) 1-hydroxycyclohexyl phenyl ketone (0.040 mmol).

was also not improved by addition of **1** [Fig. 10(h)]. The mixture of HEMA and BFI exhibits a long pot life (e.g., more than 1 year at room temperature) in dark. These results indicate that BFI also serves as an efficient photoradical initiator.

CONCLUSIONS

An aminimide having a benzoyl substituent, BFI, was found to generate both base and radical species by the photoirradiation. The decomposition of BFI takes place smoothly by the irradiation of UV light, and a tertiary amine and a diamide (i.e., the dimer of benzoylformic acid amide) were detected in the degraded products. BFI exhibits high photo/thermal dual-base activity in the polymerization of epoxide/thiol system. The activity of BFI as a photoradical initiator was also evaluated in the polymerization of 2-hydroxyethyl methacrylate, in which the polymerization takes place fast enough compared to the conventional photoradical initiators. These results support the promising applications of BFI both as an efficient photo/thermal dual-base catalyst and photoradical initiators for polymerization and curing systems. The applications of BFI as a base/radical hybrid catalyst that can be utilized for both the base-catalyzed and radical polymerization systems (e.g., a combination of epoxides and acrylates) are currently being investigated.

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