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# Benzoylformamides as new photocaged bases for photo-latent anion polymerization

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#### ABSTRACT

Benzoylformamide (BFA) derivatives are proposed as new photocaged bases with good solubility in epoxy resin. Initially their structures were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. Next, we detail their thermal stability, solubility behavior, and photolysis products. Furthermore, the model photo-latent anion polymerization (AP) of epoxide system in the presence of BFA-dBA (*N*,*N*-dibenzyl-2-oxo-2-phenylacetamide) as a photocaged base has been investigated, and excellent photopolymerization profile is obtained.

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#### 1. Introduction

In recent years, photopolymerizations have received revitalized interest as they promise a wide range of economic and ecological advantages, while photoinitiators (PIs) and photoinitiating systems (PISs) have been the subject of intense studies [1– 7]. However, the design and preparation of highly versatile PIs, which are able to initiate versatile PISs such as free radical polymerization (FRP), cationic polymerization (CP), and free radical promoted cationic photopolymerization (FRPCP), is an on-going challenge in chemical and material sciences with many applications in a wide range of industrial fields ranging from radiation curing, imaging, and optics technologies to medicine and microelectronics areas [8]. In this context, many new structures of PIs were reported recently [9–17] and exhibited a good radical initiating ability. Nevertheless, there is still room for the continuous discovery of new versatile PIs.

Indeed, the already reported photosensitive quaternary ammonium salt (QAS) [18–21], as an archetypical photocaged base, not only can liberate the amine molecules that allow for anionic polymerization of epoxides, but also immediately initiate FRP of acrylates [22–24]. However, this type of photocaged base is not soluble in monomers and common organic solvents, limiting its

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practical use in UV curing applications [25]. Improving the 32 solubility attained or meeting new or promising possibilities for 33 applications require a continuous search of new structures. 34 Following our works in the area of photocaged bases [26–31], 35 we explore here the possibility of using benzoylformamide (BFA) 36 derivatives as photocaged bases of anionic polymerization. 37

As known, photochemistry of BFA involved in photocyclization 38 or asymmetric synthesis has already been investigated in organic 39 chemistry [32-36]. Previous researchers had elucidated that the 40 photocleavage of BFA usually processed the identical pathway, 41 yielding oxazolidin-4-ones, β-lactams, and mandelic acid deriva-42 tives [37,38]. However, to the best of our knowledge, BFAs have not 43 been reported as PIs in photopolymerization. Furthermore, few 44 reports have been concerned with Norrish type II photolysis 45 products of BFAs possessing alicyclic-amine [39,40], and we 46 speculate novel heterocyclic photolytic compounds may be 47 produced. The involved mechanisms will be investigated by 48 UV-vis spectra, NMR, CG-MS, ESI-MS, and RTIR experiments. 49

#### 2. Experimental

Methyl benzoylformate (MBF, >99.0%) was provided by 51 Changzhou Tronly (China). Piperidine (PD,  $\geq$ 99.5%), 4-benzylpiperidine (BPD, 98%), morpholine (ML, 99%), pyrrolidine (PRL, 99%), 53 *N*-isopropylaniline (iPA, 99%), dibenzylamine (dBA, 98%), and 54 oxalyl chloride (98%) were purchased from Aladdin-reagent 55 (China). Bisphenol A epoxy resin (E51, Blue Star New Chemical 56

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Material) was used as received. All other chemicals used were analytical grade and used without further purification.

59 The NMR spectra were obtained on a Varian 300 MHz 60 spectrometer with CDCl<sub>3</sub> and TMS as the solvent and internal 61 standard, respectively. UV-vis absorption spectra were obtained 62 on an Agilent 8453 spectrophotometer. Thermogravimetric (TG) 63 tests were performed in the 40-500 °C range, using a TG-209 64 Netzsch thermogravimetric analyzer at a heating speed of 20 °C/ 65 min under N<sub>2</sub> atmosphere. Elemental analysis was obtained on an 66 Elementar Vario EL analyzer. Gas chromatography-mass spec-67 trometry (GC-MS) spectra were obtained from a Finnigan Voyager 68 GC-MS. Electrospray ionization mass spectra (ESI-MS) were 69 acquired on a Thermo Finnigan LCQ DECA XP ion trap mass 70 spectrometer, equipped with an ESI source. Epoxide conversions 71 were monitored by Nicolet 5700 Fourier transform infrared 72 spectroscopy.

Representative procedure for synthesis of benzoylformamides except BFA-iPA: Methyl benzoylformate (10 mmol) in methanol (10 mL) was added dropwise to a stirred mixture of amine (30 mmol) and methanol (20 mL) at 55 °C and then stirred for 3 h, distilled to concentrate the solution, and crystallized in the refrigerator. The crystal was filtered, washed with cooled methanol, and dried in vacuum to give white crystals.

1-(Phenylglyoxylyl)piperidine (BFA-PD): Yield: 30.3%. <sup>1</sup>H NMR 80 81 (300 MHz, CDCl<sub>3</sub>): δ 1.54-1.58 (m, 2H), 1.69-1.73 (m, 4H), 3.28-82 3.32 (t, 2H, J = 6.0 Hz), 3.70-3.72 (m, 2H), 7.48-7.53 (t, 2H, 83 J = 6.0 Hz), 7.61–7.66 (t, 1H, J = 6.0 Hz), 7.93–7.96 (d, 2H, J = 9.0 Hz). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  24.7, 25.8, 26.6, 42.5, 84 85 47.4, 129.2, 129.7, 133.4, 134.9, 165.5, 192.0, Anal. calcd. for 86 C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>: C, 71.87; H, 6.96; N, 6.45%. Found: C, 71.59; H, 7.31; N, 87 6.36.

88 1-(Phenylglyoxylyl)-4-benzyl-piperidine (BFA-BPD): Yield: 89 39.2%. <sup>I</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.14–1.36 (m, 2H), 1.59– 90 1.64 (m, 1H), 1.78–1.82 (m, 2H), 2.54–2.56 (d, 2H, J = 6.0 Hz), 2.69– 91 2.76 (t, 1H, J = 12.0 Hz), 2.94-3.03 (t, 1H, J = 15.0 Hz), 3.50-3.54 (d, 92 1H, J = 12.0 Hz), 4.61–4.66 (d, 1H, J = 15.0 Hz),7.08–7.11 (d, 2H, 93 J = 9.0 Hz, 7.14–7.19 (t, 1H, J = 9.0 Hz), 7.23–7.27 (t, 2H, J = 6.0 Hz), 94 7.45–7.50 (t, 2H, J = 6.0 Hz), 7.58–7.63 (t, 1H, J = 6.0 Hz), 7.90–7.92 (d, 2H, J = 6.0 Hz). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  32.0, 32.7, 38.5, 95 96 41.8, 43.2, 46.6, 126.3, 128.5, 129.2, 129.7, 133.4, 134.8, 139.8, 97 165.5, 192.0. Anal. calcd. for C<sub>20</sub>H<sub>21</sub>NO<sub>2</sub>: C, 78.15; H, 6.89; N, 4.56%. 98 Found: C, 77.75; H, 7.04; N, 4.15.

991-(Phenylglyoxylyl)morpholide(BFA-MP): Yield:27.8%.<sup>1</sup>H100NMR (300 MHz, CDCl<sub>3</sub>): $\delta$  3.35–3.38 (t, 2H, J = 3.0 Hz),3.62–3.65101(t, 2H, J = 3.0 Hz),374–3.80 (m, 4H),7.46–7.51 (t, 2H, J = 9.0 Hz),1027.60–7.65 (t, 1H, J = 6.0 Hz),7.92–7.95 (d, 2H, J = 9.0 Hz).<sup>13</sup>C NMR103(300 MHz, CDCl<sub>3</sub>): $\delta$  42.0,46.6,66.9,67.0,129.2,129.8,133.4,104135.0,165.5,191.1.Anal.Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>3</sub>:C, 65.74;H, 5.98;N,1056.39%.Found:C, 65.56;H, 6.11;N, 6.25.

106 1-(Phenylglyoxylyl)pyrrolidine (BFA-PrD): Yield: 34.5%. <sup>1</sup>H 107 NMR (300 MHz, CDCl<sub>3</sub>): δ 1.89–2.02 (m, 4H), 3.40–3.45 (t, 2H, 108 J = 6.0 Hz), 3.63–3.68 (t, 2H, J = 6.0 Hz), 7.46–7.52 (t, 2H, 109 J = 9.0 Hz),7.59–7.65 (t, 1H, J = 9.0 Hz), 7.96–8.00 (d, 2H, 110 J = 9.0 Hz). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 24.3, 26.2, 45.5, 46.9, 112 129.1, 129.9, 133.0, 134.8, 165.0, 191.6. Anal. calcd. for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>: 112 C, 70.92; H, 6.45; N, 6.89%. Found: C, 70.71; H, 6.48; N, 6.35.

113N,N-Dibenzyl-2-oxo-2-phenylacetamide(BFA-dBA):Yield:11442.8%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 3.86 (s, 4H), 7.18–7.37 (m,11510H), 7.43–8.01 (m, 5H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 50.1, 128.6,116129.0, 130.2, 131.5, 133.6, 134.3, 170.6, 194.9. Anal. calcd. for117 $C_{22}H_{19}NO_2$ : C, 80.22; H, 5.81; N, 4.25%. Found: C, 80.11; H, 5.94; N,1184.16.

*N*-Isopropylbenzoylformanilide (BFA-iPA): To a CH<sub>2</sub>Cl<sub>2</sub> solution
(20 mL) of benzoylformic acid (3.00 g, 30.0 mmol) prepared from
methyl benzoylformate by basic hydrolysis with aqueous NaOH
solution (quantitative) was added catalytic amount of DMF

(1 drop) and oxalyl chloride (1.9 mL, 22.0 mmol). The reaction 123 mixture was stirred for 4 h at room temperature until generation of 124 gases stopped and then cooled to 0 °C. To this was added a solution 125 of N-isopropylanilin (3.2 mL, 29.9 mmol) and Et<sub>3</sub>N (7.0 mL, 126 50.2 mmol). The reaction mixture was stirred at room temperature 127 for 1 h and then quenched by adding water. Organic materials were 128 extracted 3 times with ethyl acetate, and then the combined 129 extracts were washed successively with a 5% HCl aqueous solution 130 and saturated NaCl solution, dried over anhydrous MgSO<sub>4</sub>. 131 evaporated to give the corresponding product, and recrystallized 132 from ethyl acetate to give colorless crystals. Yield: 35.4%. <sup>1</sup>H NMR 133  $(300 \text{ MHz}, \text{CDCl}_3)$ :  $\delta 1.22 - 1.24 (d, 6H, I = 6.0 \text{ Hz}), 5.01 - 5.15 (m, 1H, 1)$ 134 I = 6.0 Hz), 7.05–7.78 (m, 10H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  21.2, 135 47.0, 128.8, 129.1, 129.4, 131.2, 133.8, 134.2, 135.7, 166.8, 136 190.0. Anal. Calcd for C17H17NO2: C, 76.38; H, 6.41; N, 5.24%. 137 Found: C, 75.89; H, 6.50; N, 5.16. 138

Photodecomposition of BFA-dBA: First, BFA-dBA in acetonitrile  $(1 \times 10^{-4} \text{ g/mL})$  was put into a quartz cell. Next, the photodecomposition was carried out by optical cable-directed UV lamp (RW-UVA- $\Phi$ 200U, Runwing Co. China) over time (0 min, 1 min, 2 min, 3 min), then UV-vis spectra were measured.

Photoinitiated thermal anion polymerization: Mixtures of BFAdBA ( $5 \times 10^{-4}$  mol) and a commercial epoxide E51 (1 g) were spread on KBr plates. The mixtures were irradiated on the UV curing machine for 10 min. In all photochemical experiments, the optical cable-directed UV lamp operating in the 200–400 nm range (RW-UVA- $\Phi$ 200U, Runwing Co., China) was used as the irradiation source, and the light intensity at the surface level of the cured samples was 20 mW/cm<sup>2</sup> measured by a UV-radiometer (type UV-A, Photoelectric Instrument Factory, Beijing Normal University). Then some of the mixtures were baked at high temperature. The results were observed visually and measured quantitatively by FT-IR spectra.

#### 3. Results and discussion

In this paper, we endeavor to synthesize BFAs possessing alicyclic-amine in order to test the photochemical characteristics. Furthermore, their Norrish type II photolysis products may involve basic heterocyclic compounds, which is of particular current interest as they can be exploited in the design of new photocaged bases. Hence, BFAs 1–5 (Scheme 1) with different amide substituents were successfully synthesized from methyl benzoylformate (MBF) by transesterification reaction with secondary amine (Scheme 2a) [41]. Due to the weak basicity of *N*-isopropylanilin, transesterification reaction with MBF was difficult, but BFA-iPA can be prepared according to the literature (Scheme 2b) [42]. The structures of BFAs 1–6 were confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis.

Thermal stability is one of the important parameters of photocaged bases. When the stability of the initiator is very low, the pot life may be short, making the system less useful. Indeed, the observed order of thermal stability for BFAs is BFA-BPD



Scheme 1. Structures of the benzoylformamides (BFAs) 1-6.

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Scheme 2. Synthesis of BFAs 1-6.

174 (246.6 °C) > BFA-iPA (188.6 °C) > BFA-MP (172.2 °C) > BFA-PD 175  $(168.6 \ ^{\circ}C) > BFA-PrD$   $(164.6 \ ^{\circ}C) > BFA-dBA$   $(139.2 \ ^{\circ}C)$  (Fig. 1, 176 Table 1). Noting that the initial decomposition temperatures of 177 all BFAs are above 135 °C, we conclude the BFAs have good thermal 178 stability at room temperature. Among the BFAs studied, BFA-BPD is 179 the most stable one, while BFA-dBA has the worst thermal stability. 180 In the paper, we focus on the photochemistry properties of BFAs. 181 Actually, since the thermal stability of BFAs is quite different, this 182 may be used for thermal latent anion polymerization of epoxy 183 resin, and detailed research is worthy of further exploration.

Introducing the amide group to benzoyl skeleton drastically 184 changes the solubility behavior of the BFAs. Of these photocaged 185 186 bases, liquid BFA-PrD is readily soluble in the bisphenol A epoxy 187 resin E51, BFA-PD, BFA-BPD, BFA-MP, BFA-iPA and BFA-dBA 188 showed moderate solubility after adequate mixing at 50 °C. Thus, 189 BFA derivatives as photocaged base exhibit sufficient solubility in 190 E51, and may provide a promising future for its practical use in UV 191 curing applications.

192The absorption spectra of the investigated BFAs in chloroform193are given in Fig. 2. All BFAs exhibit similar absorption character-194istics with maxima at 286 nm and 355 nm, and a tail over 400 nm,195exhibiting a red shift compared with that of the parent compound,196methyl benzoylformate (MBF,  $\lambda_{max} = 255$  nm), due to the presence197of the amide substituents on the benzoyl skeleton.



Fig. 1. Thermogravimetric profiles of BFAs with heating rate at 20 °C/min under N<sub>2</sub>.

Table 1Thermal stability of BFAs.

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BFA	BFA-PD	BFA-BPD	BFA-MP	BFA-PrD	BFA-iPA	BFA-dBA
TG(oC) <sup>a</sup>	168.6	246.6	172.2	164.6	188.6	139.2
A Determined by thermogravimetric analysis as the point of 5% weight loss						

<sup>a</sup> Determined by thermogravimetric analysis as the point of 5% weight loss.



Fig. 2. UV-vis absorption spectra of BFAs in chloroform (1  $\times$  10<sup>-4</sup> g/mL).

In the paper, BFA-dBA was selected here for the model 198 mechanistic investigation i.e. this photocaged base was character-199 ized both by the UV absorption properties and photopolymeriza-200 tion (see below). As shown in Fig. 3, photolysis of BFA-dBA in 201 chloroform was investigated by UV-vis spectroscopy. BFA-dBA 202 exhibits a strong UV absorption with molar extinction coefficients 203 of  $1.52 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup> at 288 nm, which is attributed to the 204  $\pi$ - $\pi$ \* transition: the maximum at 368 nm with molar extinction 205 coefficients of 7.38  $\times$  10<sup>1</sup> L mol<sup>-1</sup> cm<sup>-1</sup> can be explained by the *n*-206  $\pi^*$  transition. Furthermore, distinct decreases in absorption bands 207 at 288 nm and 368 nm were observed with prolonged irradiation 208 time. 209

The photolysis products formed from irradiated BFA-dBA in 210 chloroform were identified by <sup>1</sup>H NMR, followed by GC-MS and 211 ESI-MS assisted product analysis. From Fig. 4, most proton signals 212 in BFA-dBA weakened after 30 min irradiation, meanwhile new 213 protons  $H_a$  (10.0 ppm),  $H_b$  (8.3 ppm), and  $H_c$  (4.8 ppm) appeared. 214 According to the literature [43], we can speculate that the above-215 mentioned new protons should correspond to -CHO in benzalde-216 hyde and -CH=N- and -CH<sub>2</sub>-Ph in N-benzylidenebenzylamine, 217 respectively. Normalized by an internal standard peak at TMS, the 218 ratios of the photolysis products were calculated by the internal 219 standard method. As shown in Scheme 3, after 30 min irradiation, 220 the yields of benzaldehyde and N-benzylidenebenzylamine were 221 48.5% and 21%, respectively. Due to a superposition with the parent 222



Fig. 3. UV–vis spectral changes of BFA-dBA in chloroform  $(1\times 10^{-4}\,g/mL)$  being irradiated over time.

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Fig. 4. <sup>1</sup>H NMR spectral changes of BFA-dBA (a) before and (b) after 30 min irradiation.



Scheme 3. Photolysis products of BFA-dBA in chloroform on excitation at 365 nm.

molecule BFA-dBA, the signals of N-dibenzylamine are difficult to 223 224 detect by NMR. Moreover, GC–MS study of the photolysis products 225 confirmed the formation of benzaldehyde (M' = 106) and N-226 benzylidenebenzylamine (M' = 195). Astonishingly, basic photoly-227 sis compounds from irradiated BFA-dBA were detected by pH-228 indicator paper. Since GC-MS failed to detect an amine compound, 229 ESI-MS was employed to probe photogenerated base in Fig. 5. It 230 should be noticed that the detection of protonated dibenzylamine 231  $dBA^+$  (m/z = 198.2) after irradiation was direct evidence for the 232 formation of dBA from BFA-dBA, and thus BFA-dBA also can act as a 233 novel photocaged base. We speculate that the photolysis of BFA-234 dBA may undergo Norrish type II elimination reaction, and the 235 photolysis products of BFA-dBA are identified as benzaldehyde, N-236 benzylidenebenzylamine, N-dibenzylamine and some unknown 237 substances. Taking the foregoing points into consideration, the 238 photolysis products of BFA-dBA can be listed in Scheme 3.

239 This BFA-dBA also can provide a promising future for its 240 application to photolatent amine-catalytic ring-opening polymerization (ROP) of epoxide systems. The chemical transformation in 241 242 an E51 film containing BFA-dBA was followed by monitoring the 243 characteristic band of the epoxide ring at 915 cm<sup>-1</sup> in FT-IR spectra 244 to obtain some information concerning the photo-latent amine 245 catalytic reaction (Fig. 6). After UV-exposure of 10 min, no 246 alteration of the spectral shape (Fig. 6, curve 2) was observed 247 after 60 min at room temperature compared to the pristine E51 248 (Fig. 6, curve 1), suggesting that the crosslinking of the epoxide is 249 not essentially induced before post-exposure baking. When the 250 film was heated at 120 °C after UV-exposure, the peak intensity of the epoxide at 915 cm<sup>-1</sup> gradually decreased over time (curve 251 252 3-4). This situation is visualized by plotting the decreased peak

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Fig. 5. The protonated N-dibenzylamine from irradiated BFA-dBA in chloroform (0.01 mmol/L) detected by ESI-MS.



Fig. 6. IR spectra of E-51 thermally cured by irradiated BFA-dBA (pristine E51 - 1, the spectral shape for 60 min at room temperature after UV-exposure of 10 min - 2, bakes at 120 °C for 20 min - 3, 250 min - 4).



Fig. 7. Conversion vs. time curves for photo-latent amine-catalytic reaction of E51 heating at 120 °C after UV-exposure of 10 min with the light intensity of 20 mW/ cm<sup>2</sup>. Experimental conditions: BFA-dBA =  $5 \times 10^{-4}$  mol, E51 = 1 g.

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area as a function of heating time, as given in Fig. 7. No marked
spectral alteration was observed within 9 min, but the absorption
band of epoxide abruptly decreased thereafter, and 80% conversion
was obtained after 100 min baking. These results indicate that the
crosslinking reaction of E51 can be induced by the photogenerated
dibenzylamine from BFA-dBA.

#### 259 4. Conclusions

260 Benzovlformamides (BFAs) derivatives as novel photocaged bases were designed and synthesized. Initially their structures were 261 confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and elemental analysis. Next, we 262 detail their thermal stability, solubility behavior and photolysis 263 264 products. The results show that BFAs have good thermal stability at 265 room temperature and exhibit sufficient solubility in epoxy resin 266 E51. Meanwhile, photolysis products of BFA-dBA are identified as 267 benzaldehyde, N-benzylidenebenzylamine, N-dibenzylamine and 268 some unknown substances. Furthermore, the model photo-latent 269 anion polymerization (AP) of epoxide system in the presence of 270 BFA-dBA (N, N-Dibenzyl-2-oxo-2-phenylacetamide) as a photo-271 caged base has been investigated, and 80% conversion was obtained 272 at 100 min baking after UV-exposure of 10 min. This photodecom-273 position reaction is of particular interest as it is can facilitate the 274 design of new photocaged bases with very promising properties.

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