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Aminimides Derived from Benzoylformic Acid Esters as Thermally Latent Base Catalysts

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ABSTRACT: As a novel thermal latent anionic initiator for lower temperature applications, a new class of aminimide, 1,1-dimethyl-1-(2-hydroxypropyl)amine benzoylformimide (BFI), was synthesized from benzoylformic acid methyl ester in 95% yield, and its thermal rearrangement behavior was studied in detail. Thermal rearrangement of BFI proved to take place on heating above 80 °C via the Curtius rearrangement mechanism, generating the corresponding isocyanate, hydroxyamine, and their further reaction products. BFI proved to catalyze the polymerization of epoxides and epoxide/thiol system on heating above 80 °C. They exhibit both the long pot life and the low-temperature rapid polymerization in the presence of BFI which supported the promising applications of BFI as an efficient thermal latent base catalyst for anionically polymerizable/curable systems.

Introduction

Latent initiators that generate active species by external stimulations such as heat and photoirradiation are important for many industrial applications such as polymerization or curing of adhesives, sealants, paints, coatings, molding resins, and so on. In the case of epoxy resin, for example, both anionic and cationic latent initiators have been extensively studied. From the practical point of view, anionic catalysts are advantageous in that they are less sensitive to impurities and moisture. Until now, derivatives of dicyandiamide, dihydrazide, and imidazole have been reported to serve as latent anionic initiators. They are solid at room temperature but melt and dissolve into the epoxy resin at elevated temperature to initiate polymerization.[1] These latent initiators of insoluble and heterogeneous type have inevasible practical drawbacks such as difficulty in preservation of uniform dispersion, use of solvents, and production of optically transparent products. Thus, miscible latent anionic initiators that dissolve in monomers and resin under ambient conditions have been paid much attention.[2] Although many cationic latent initiators such as onium salts are reported to serve as homogeneous latent initiators for epoxides,[3] only a few anionic miscible latent initiators have been reported.[4]

Among them, aminimides have been reported to undergo the thermal rearrangement by means of the cleavage of the N−N bond to produce isocyanates and tertiary amines,[5,6] and the generated amines serve as anionic initiators for epoxide. Within the authors' knowledge, some aminimides such as lactoimide,[7] propionimide,[8] valerimide,[8] adipimide,[9] and substituted benzimide[8,10,11] have been employed as thermal latent anionic initiators for epoxides,[7−10] the epoxide/acid anhydride system,[7] and the epoxide/thiol system.[11,12] However, their practical activating temperature is above 150 °C, which is not low enough for practical applications. Therefore, it is essentially important to design a new class of catalysts that exhibit activity at lower temperature.

Previously, we reported that some aliphatic aminimides exhibit initiation activity at a little lower temperature (e.g., 137.7 °C) in the polymerization of epoxide.[13] This result may suggest that the appropriate molecular design of the substituents on the aminimide can lower the temperature. We herein report a new class of aminimides from benzoylformic acid ester that shows thermal latent initiating ability at much lower temperature. Its rearrangement mechanism and its application to the polymerization of epoxide and epoxide/thiol system are also described.

Experimental Section

Materials. Benzoylformic acid methyl ester, 1,1-dimethylhydrazine, propylene oxide, methyl benzoate, 1,1-dimethylamino-2-propanol, and acetic anhydride were purchased from Tokyo Kasei Kogyo (Japan). Benzoyl isocyanate, triethylamine, and benzyl alcohol were purchased from Wako Pure Chemical Industries (Japan). Pentaerythritol tetrakis(3-mercaptopropionate) was purchased from Aldrich (Milwaukee, WI). EXA-850CRP (pure grade bisphenol A diglycidyl ether) was purchased from DIC (Japan). They were used as received.

Measurements. Nuclear magnetic resonance (NMR) spectra were recorded with a JEOL ECP300 spectrometer in $CDCl_3$ or DMSO-d_6 (300 and 75 MHz for ^1H NMR and ^{13}C NMR, respectively). IR spectra were taken on a BIO-RAD FTS-40 FTIR system using SPECAC MK II heated diamond ATR system at 25 °C. 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. Thermogravimetry/differential thermal analyses (TG/DTA) were performed on a Seiko Instruments TG/DTA 220 using ca. 1.0 mg of the samples. The decomposition temperature (T_d) was determined from the onset temperature of the weight loss observed in TG at a heating rate of 1 or 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry analyses (DSC) were performed on a Seiko Instruments DSC 220 at a heating rate of 10 °C/min under a nitrogen atmosphere.

Synthesis of 1,1-Dimethyl-1-(2-hydroxypropyl)amine Benzoylformimide (BFI). BFI was synthesized by the method described by Slagel[5] as follows: a mixture of benzoylformic acid methyl ester (13.6 g, 83.0 mmol), 1,1-dimethylhydrazine (5.00 g, 83.0 mmol),

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and propylene oxide (4.80 g, 83.0 mmol) in 2-propanol (80 mL) was stirred at 20 °C for 2 h and then at 40 °C for 48 h. The reaction mixture was concentrated by evaporation, and the residual white solid was recrystallized from methanol/ethyl acetate to obtain BFI in 95.0% yield (19.7 g, 78.9 mmol). The sample for elemental analysis was purified further by recrystallization twice from methanol/ethyl acetate; mp 104.0−105.0 °C (decomposition). IR (solid, ATR): 3225 cm^{-1} (broad, OH), 1681 cm^{-1} (s, Ph−C═O), 1571 cm^{-1} (s, −N−C═O). ^{1}H NMR ($CDCl_3$): δ 1.18 (d, 3H, CH_3, $J = 6.3$ Hz), 3.45 (m, 2H, NCH_2), 3.60 (s, 3H, NCH_3), 3.63 (s, 3H, NCH_3), 4.40 (m, 1H, CH), 5.39 (s, 1H, OH), 7.44 (m, 2H, C_6H_5), 7.56 (m, 1H, C_6H_5), 8.01 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 21.1, 52.1, 54.5, 62.6, 74.6, 128.3, 129.8, 133.4, 134.4, 168.4, 192.6. Elemental analysis Calcd for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.30; H, 7.17; N, 11.28.

Synthesis of 1,1-Dimethylamino-2-propyl *N*-Benzoylcarbamate (3). Benzoyl isocyanate (**1**) (0.62 g, 4.2 mmol) was added dropwise to a *n*-hexane (10 mL) solution of 1,1-dimethylamino-2-propanol (**2**) (0.52 g, 5.0 mmol) at room temperature under a nitrogen atmosphere. Within a few minutes, a white precipitate began to form as the progress of the reaction, which was identified as a urethane from its IR spectrum. After stirring at room temperature for 24 h, the reaction mixture was concentrated by evaporation, and the residual white solid was recrystallized from ethyl acetate/*n*-hexane to obtain **3** in 77% yield (0.81 g, 3.2 mmol). The sample for elemental analysis was purified further by recrystallization twice from ethyl acetate/*n*-hexane; mp 79.0−80.0 °C (decomposition). IR (solid, ATR): 1765 cm^{-1} (s, NH−CO−O), 1697 cm^{-1} (s, Ph−C═O). ^{1}H NMR ($CDCl_3$): δ 1.27 (d, 3H, CH_3, $J = 6.3$ Hz), 2.16 (s, 6H, NCH_3), 2.59 (dd, 1H, NCH_2, $J = 12.9$, 8.7 Hz), 2.15−2.21 (1H, NCH_2), 5.10 (m, 1H, CH), 7.41 (m, 2H, C_6H_5), 7.51 (m, 1H, C_6H_5), 7.77 (m, 2H, C_6H_5), 8.80 (s, 1H, OH). ^{13}C NMR ($CDCl_3$): δ 18.5, 45.8, 64.2, 70.0, 127.6, 128.7, 132.7, 133.3, 150.7, 165.5. Elemental analysis Calcd for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.03; H, 7.17; N, 11.17.

Synthesis of 1,1-Dimethyl-1-(2-acetoxypropyl)amine Benzoylformimide (4). The synthesis of **4** was performed by the acetylation of the hydroxy group in BFI as follows: a dichloromethane (30 mL) solution of BFI (3.00 g, 12.0 mmol), acetic anhydride (2.45 g, 24.0 mmol), and triethylamine (1.21 g, 12.0 mmol) was refluxed for 24 h. The reaction mixture was concentrated and dried at 40 °C for 6 h under reduced pressure (0.23 mmHg). After washing the residual paste with *n*-hexane, the white solid thus obtained was recrystallized from ethyl acetate to obtain **4** in 51.8% yield (1.80 g, 6.22 mmol) as white crystals. The sample for elemental analysis was purified further by recrystallization twice from ethyl acetate; mp 100.0−101.0 °C (decomposition). IR (solid, ATR): 1740 cm^{-1} (s, CH_3−C═O), 1681 cm^{-1} (s, Ph−C═O), 1604 cm^{-1} (s, N^{-}−C═O). ^{1}H NMR ($CDCl_3$): δ 1.27 (d, 3H, CH_3, $J = 6.6$ Hz), 1.99 (s, 3H, C(O)−CH_3), 3.35 (s, 3H, NCH_3), 3.49 (s, 3H, NCH_3), 3.69 (dd, 1H, NCH_2, $J = 13.5$, 8.1 Hz), 4.14 (dd, 1H, NCH_2, $J = 13.5$, 0.9 Hz), 5.49 (m, 1H, CH), 7.38 (m, 2H, C_6H_5), 7.48 (m, 1H, C_6H_5), 7.98 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 19.1, 21.1, 54.1, 54.3, 65.8, 69.3, 128.2, 129.8, 133.1, 134.7, 169.0, 169.6, 192.8. Elemental analysis Calcd for $C_{15}H_{20}N_2O_4$: C, 61.63; H, 6.90; N, 9.58. Found: C, 61.59; H, 7.13; N, 9.55.

Synthesis of 1,1-Dimethyl-1-(2-hydroxypropyl)amine Benzimide (5). Similar to the case of BFI, **5** was prepared from methyl benzoate (10.9 g, 80.0 mmol), 1,1-dimethylhydrazine (4.80 g, 80.0 mmol), and propylene oxide (4.60 g, 80.0 mmol) in 81.0% yield (14.4 g, 64.8 mmol); mp 122.0−122.5 °C (lit.[5] 122−125 °C). T_d: 186.2 °C (TG/DTA, at a heating rate of 10 °C/min). IR (solid, ATR): 3220 cm^{-1} (broad, OH), 1609 cm^{-1} (s, −N−C═O), 1570 cm^{-1} (s, −N−C═O). ^{1}H NMR ($CDCl_3$): δ 1.17 (d, 3H, CH_3, $J = 6.3$ Hz), 3.05 (dd, 1H, NCH_2, $J = 12.6$, 1.5 Hz), 3.43 (dd, 1H, NCH_2, $J = 12.6$, 9.9 Hz), 3.55 (s, 3H, NCH_3), 3.57 (s, 3H, NCH_3), 4.37 (m, 1H, CH), 6.92 (s, 1H, OH), 7.20−7.32 (3H, C_6H_5), 7.78 (m, 2H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 20.8, 50.8, 54.8, 62.8, 75.7, 127.1, 127.8, 129.7, 137.7, 169.9.

Thermal Decomposition Studies by Cryo-Trap GC-MS. Gas chromatographic−mass spectrometric (GC-MS) analyses were performed on a Thermoquest GCQ GC-MS system equipped with Frontier laboratories UA5 (MS/HT)-30M-0.25F GC column and liquid nitrogen cryo-trap. The samples were heated at 120 °C for 3 min, and the volatile fractions were directly trapped by liquid nitrogen and were analyzed by GC-MS. Sample temperature: 120 °C; split flow: 40 mL/min (He gas); split ratio: 1/40; GC heating profiles: 50 °C for 5 min and then 300 °C at a heating rate 10 °C/min; ionization voltage: 70 eV.

Thermal Decomposition Studies by IR. IR spectra of the samples after the heat treatment were taken on a real-time FTIR system (BIO-RAD FTS-40) using heated ATR (SPECAC MK II heated diamond ATR system) equipped with a hot stage (115 °C) under a nitrogen atmosphere.

DSC Onset Temperature Measurement. BFI (0.10 g) and benzyl alcohol (0.40 g) were stirred at room temperature to obtain a homogeneous transparent mixture. A portion of this sample (5.0 mg) was placed in an aluminum pan and completely sealed. The thermal profiles were measured by DSC.

Thermal Decomposition Studies by ^{1}H NMR Spectra. The conversion of BFI was estimated by the ^{1}H NMR spectra as follows: a sealed NMR tube containing BFI in DMSO-d_6 (0.13 M) was heated at 80, 100, or 120 °C in an oil bath, and the NMR spectra were measured after designated period. The conversion of BFI was elucidated from the relative intensity of the peak for the $N^{+}(CH_3)_2$ protons with respect to that of the residual protons of DMSO-d_6. On assuming that the thermal decomposition takes place via the first-order kinetic equation

$$d[\mathrm{BFI}]/dt = k[\mathrm{BFI}]$$

the first-order kinetic coefficient (k) was calculated from the slope of the graph for ln[BFI] vs time.

Polymerization Studies of Epoxide with BFI. EXA-850CRP (3.44 g, 100 mmol) and BFI (0.500 g, 20.0 mmol) were stirred at 50 °C for 10 min to obtain a transparent homogeneous mixture, and its polymerization behavior was monitored by DSC and IR measurements as follows:

DSC Measurements: A portion of this mixture (7.5 mg) was placed in an aluminum pan and completely sealed. The polymerization profile was monitored by DSC under a nitrogen atmosphere, where the temperature of the sample was raised rapidly from 40 to 100 °C at a heating rate of 100 °C/min, and then the temperature was held at 100 °C for 240 min. Subsequent heating cycles were monitored for determining the glass transition temperature (T_g) from −20 to 200 °C at a heating rate of 10 °C/min.

IR Observations: The mixture was placed on the ATR stage, and its surface was protected with a cover glass. The real-time IR spectra were measured at 100 °C. The conversion was estimated from the changes of the peak intensity of the epoxide (910 cm^{-1}) with respect to that of the benzene ring (1506 cm^{-1}) in EXA-850CRP.

Polymerization Studies of Epoxide/Thiol with BFI. BFI (2.50×10^{-2} g, 1.00×10^{-4} mol) and benzyl alcohol (1.08×10^{-1} g, 1.00×10^{-3} mol) were stirred at room temperature to obtain a homogeneous transparent mixture. Then, EXA-850CRP (6.88×10^{-1} g, 2.00×10^{-3} mol) and pentaerythritol tetrakis(3-mercaptopropionate) (4.89×10^{-1} g, 1.00×10^{-3} mol) were added to the solution to obtain a transparent homogeneous mixture (**M1**). The polymerization behavior of **M1** was monitored by DSC and IR measurements as follows:

DSC Measurements: A portion of **M1** (5.0 mg) was placed in an aluminum pan and completely sealed. The polymerization profile was monitored by DSC at a heating rate of 10 °C/min under a nitrogen atmosphere. Likewise, a mixture consisting of benzyl alcohol (1.00×10^{-3} mol), EXA-850CRP (2.00×10^{-3} mol),

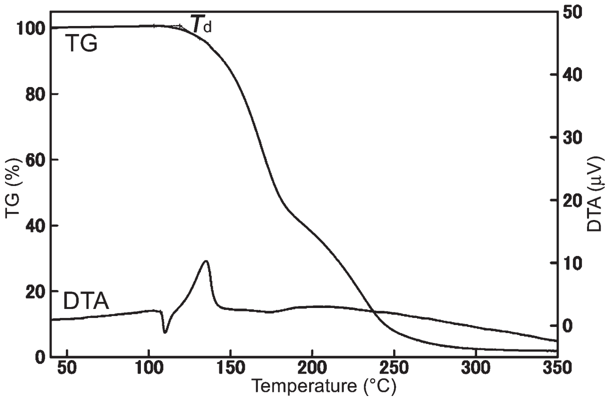
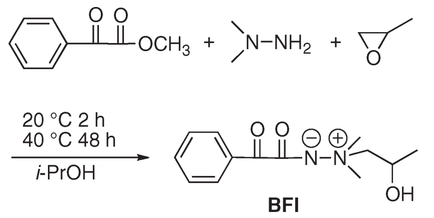


Figure 1. TG/DTA profiles of BFI at a heating rate of 10 °C/min.

Scheme 1. Synthesis of BFI



and pentaerythritol tetrakis(3-mercaptopropionate) (1.00 × 10^{-3} mol) (i.e., without BFI) and that of benzyl alcohol (1.00 × 10^{-3} mol), EXA-850CRP (2.00 × 10^{-3} mol), pentaerythritol tetrakis(3-mercaptopropionate) (1.00 × 10^{-3} mol), and **2** (1.00 × 10^{-4} mol) in place of BFI were also subjected to the DSC measurements to evaluate the role of BFI. The isothermal DSC measurement of **M1** was carried out by heating this mixture (7.5 mg) from 40 to 80 °C rapidly (i.e., at a heating rate of 100 °C/min) and then the keeping the temperature at 80 °C.

IR Observations: **M1** was placed on the ATR stage, and the surface of the sample was protected with a cover glass. The real-time IR spectra were measured at 80 °C. The conversion was estimated from the changes of the peak intensities of both the thiol (2571 cm^{-1}) and the epoxide (913 cm^{-1}) with respect to that of the ester (1738 cm^{-1}) in pentaerythritol tetrakis-(3-mercaptopropionate).

Results and Discussion

Synthesis of 1,1-Dimethyl-1-(2-hydroxypropyl)amine Benzoylformimide (BFI). The synthesis of BFI was performed by using equimolar amount of benzoylformic acid methyl ester, 1,1-dimethylhydrazine, and propylene oxide by the method for β-hydroxyaminimides described by Slagel[5] (Scheme 1). The reaction took place smoothly to give BFI in 95.0% yield by recrystallization from methanol/ethyl acetate.

Thermal Decomposition Behavior of BFI. In the TG/DTA measurement of BFI at a heating rate of 10 °C/min (Figure 1), the decomposition temperature (T_d) was observed at 119.0 °C, which is significantly lower than those reported for aliphatic aminimides (156.2−212.1 °C).[13] From the melting point measurement of BFI, the irreversible melting behavior was observable at 104.0−105.0 °C. Thus, the endothermic peak starting from 107.0 °C in the DTA experiment is most probably not due to the simple melting, but ascribable to the irreversible chemical reaction.

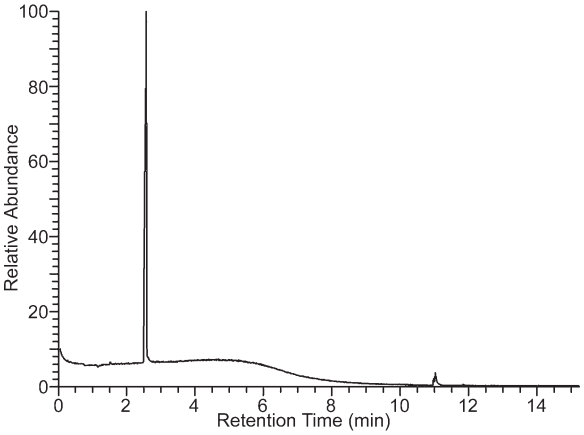
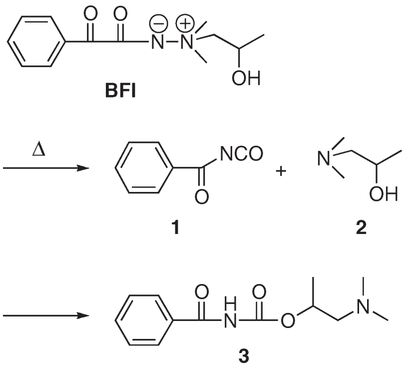


Figure 2. GC profiles of the volatile fractions obtained by the pyrolysis of BFI at 120 °C for 3 min.

Scheme 2. Plausible Thermal Rearrangement Reaction of BFI



It has been reported that some aminimides undergo thermal cleavage of the N−N bond to produce the corresponding isocyanates and tertiary amines via the Curtius-type rearrangement.[6] In the case of β-hydroxyaminimides, the generated β-hydroxyamines and isocyanates are reported to react further to give the corresponding urethanes.[5] Therefore, the reaction of BFI would also proceed in a similar rearrangement process as shown in Scheme 2.

Identification of Products Obtained by the Thermal Rearrangement of BFI. To support the reaction mechanism indicated in Scheme 2, the identification of thermal rearrangement products from BFI was carried out using the GC-MS measurement and the IR spectroscopic analyses. In the GC-MS measurement of the volatile fractions obtained after the pyrolysis of BFI at 120 °C for 3 min, a main peak was observed at a retention time of 2.58 min (Figure 2), which was identified as **2** from its MS spectrum in comparison with that of the authentic sample. Thus, it was clearly supported that BFI generates **2** by the N−N bond cleavage in the rearrangement reaction.

In the time-course FT-IR spectra of the samples obtained by heating BFI at 115 °C under nitrogen, we could monitor the progress of the rearrangement process (Figure 3a). After heating for 2 min, a peak at 1588 cm^{-1} attributable to the carbonyl group in the aminimide ($N^{-}C{=}O$) decreased, and new peaks appeared at 1771 and 1735 cm^{-1}. The peak at 1771 cm^{-1} is attributable to the carbonyl group in the urethane (**3**), as confirmed by the IR spectrum of the authentic sample (**3**). Also in the FT-IR spectrum of the sample after heating **3** at 115 °C for 20 min, the peak for the carbonyl group in the urethane decreased and a new absorption peak at 1733 cm^{-1} appeared, suggesting that **3** also decomposes under the conditions for the rearrangement of BFI. Accordingly, the thermal cleavage of the N−N bond in BFI takes place to give **3** via **1** and **2**. In this case, however, **1** could not be detected probably because **1** reacts immediately with the hydroxy group in **2**.

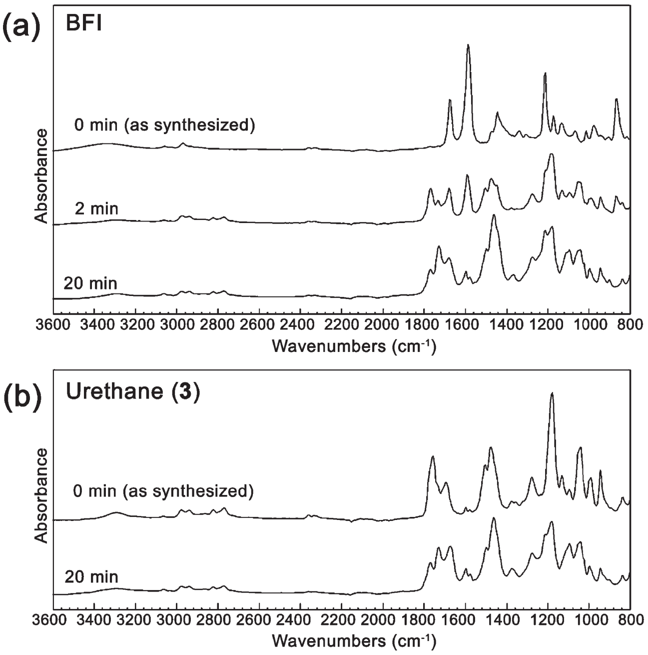


Figure 3. FT-IR spectra of samples obtained by heating BFI (a) and a urethane (**3**) (b) at 115 °C under nitrogen.

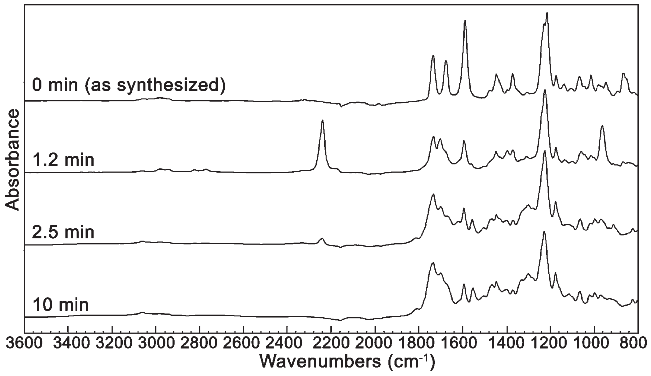


Figure 4. FT-IR spectra of the sample obtained after heating the acetylated BFI (**4**) at 115 °C for 0, 1.2, 2.5, and 10 min under nitrogen.

To detect **1**, the acetylated BFI (**4**) was synthesized from BFI and its thermal rearrangement behavior was monitored by the FT-IR spectra (Figure 4). After 1.2 min at 115 °C, a strong absorption peak appeared at 2241 cm^{-1} attributable to **1**. This result supported that BFI generates **1** by the thermal rearrangement process. After the prolonged reaction period, the peak at 2224 cm^{-1} gradually decreased and disappeared completely after 10 min, indicating that the acyl isocyanate (**1**) is highly reactive and decomposes also in the absence of **2**.

Thermal Decomposition of Urethane (3). As mentioned above, **3** produced by the reaction of **1** and **2** also decomposes under the conditions for the rearrangement of BFI. When the crystals of **3** was heated above its melting point at 79.0–80.0 °C, the irreversible chemical reaction takes place. As is also clear from its TG/DTA measurements at a heating rate of 1 °C/min, **3** exhibited an endothermic peak with an onset temperature at 80 °C and T_d at 86.8 °C (Figure 5).

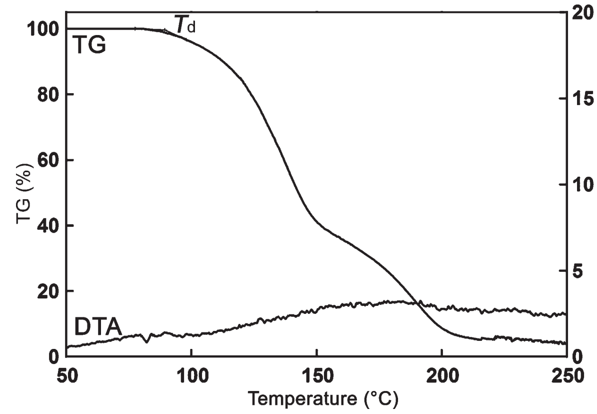


Figure 5. TG/DTA measurement of **3** under nitrogen at a heating rate of 1 °C/min.

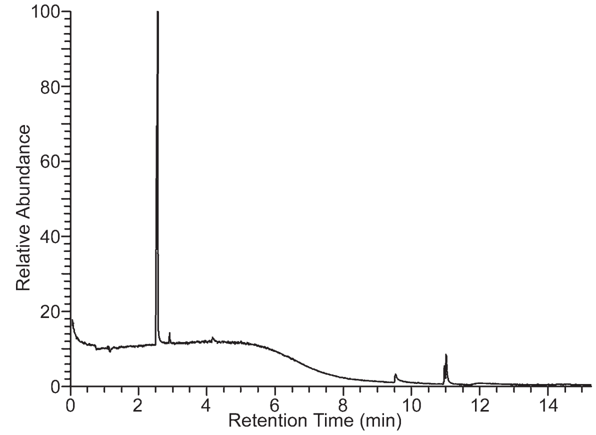
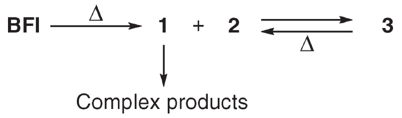


Figure 6. GC profile of volatile fractions obtained by heating the urethane (**3**) at 120 °C for 3 min.

Scheme 3. Thermal Decomposition Mechanism of BFI



As mentioned above, urethanes are known to be cleaved on heating to produce the corresponding isocyanates and alcohols.[14] This bond cleavage mechanism would also work in the case of **3** which can be attributed to the weight loss observed in the TG analysis above its T_d. The decrease of the residual weight in the TG analysis may suggest that the generated **2** volatilized under the measurement conditions. To clarify this, GC-MS measurement of **3** was carried out in the same manner to BFI. Figure 6 shows GC profile of the volatile fractions obtained by the treatment of **3** at 120 °C for 3 min. The MS spectrum of the main peak at 2.56 min was identical to that of the authentic **2**. Thus, it was confirmed that **3** also generates **2** by the thermal decomposition process.

In general, the bond dissociation of urethanes is often applied to industrial processes, and the urethanes are classified as "blocked isocyanates". The dissociation temperature of "blocked isocyanates" ranges from 120 to 250 °C, which is affected largely by the substituents. Especially, the electron-withdrawing substituents on the nitrogen atom tend to lower the dissociation temperature.[14] Accordingly, the lower dissociation temperature of **3** (86.6 °C) is most probably due to its electron-withdrawing carbonyl substituent on the nitrogen atom.

On the basis of these results, we believe that the decomposition of BFI proceeds in the mechanism as shown in Scheme 3. The isocyanate (**1**) and the amine (**2**) are generated by the Curtius-type rearrangement of BFI. Then, the generated **1** and **2**

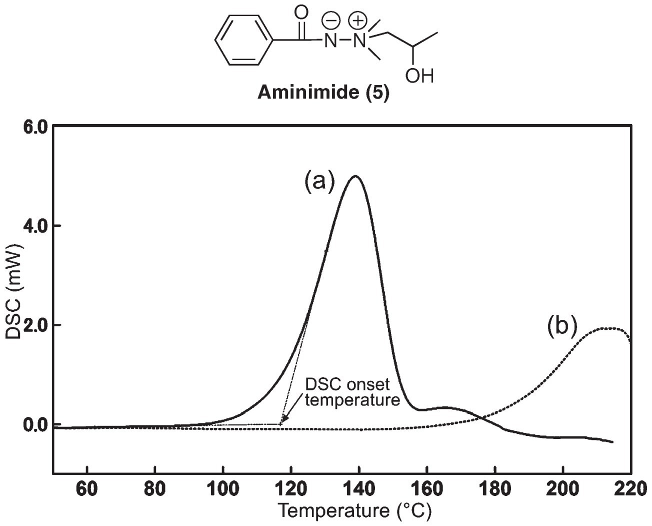


Figure 7. DSC profiles of (a) BFI and (b) aminimide (**5**) in benzyl alcohol (20 wt % solution) at a heating rate of 10 °C/min.

produce **3**, and **3** is in equilibrium with its dissociated form, **1** and **2**. Because **1** is susceptible to degrade into complex products due to its high reactivity, we could detect **2** as the sole identifiable product.

Thermal Decomposition Behavior of BFI in Alcohol Solution. To estimate the thermal decomposition behavior of BFI in solution, benzyl alcohol was used as a solvent because of the good solubility of BFI and its high boiling point. Figure 7 shows DSC profiles of 20 wt % solution of BFI in benzyl alcohol and that of aminimide without acyl moieties (**5**).[10]

In the DSC measurement of the BFI solution, an exothermic peak with an onset temperature of 116.9 °C was observed, which was close to the T_d of BFI determined by TG/DTA (119.0 °C). Therefore, the exothermic peaks observed in this experiment are most probably ascribable to the thermal rearrangement reaction to give **1** and **2** and the subsequent addition reaction of **1** and alcohol moieties in **2** and/or the solvent. In comparison, the aminimide (**5**) exhibits the onset of the exothermic peak at 190.0 °C, which is significantly higher than that of BFI. This result clearly indicates that the α-acyl substituent in BFI does lower the temperature required for the rearrangement of aminimides.

Kinetic Studies of Thermal Decomposition of BFI. As mentioned above, the DSC profile indicates that the decomposition of BFI occurs above 80 °C. So as to perform the quantitative analyses of this thermal decomposition, the kinetic studies were performed using NMR measurements at 80−120 °C. Figure 8 shows representative time-course ^{1}H NMR spectra of BFI heated at 100 °C. As the progress of the reaction, the intensity of the peaks for $N^+(CH_3)_2$ (3.39 and 3.51 ppm) and N^+CH_2 (3.41−3.82 ppm) of the aminimide decreased, while peaks at 2.02 and 2.50 ppm attributable to $N(CH_3)_2CH_2$ moieties in **2** and **3**, respectively, newly appeared. This result is in good accordance with the idea that the decomposition of BFI generates **2** and **3**, as shown in Scheme 3. Similar experiments were carried out at 80 and 120 °C. From the peak intensity of the protons in the N^+CH_3, the conversion of BFI was determined, and the time−conversion curves at 80, 100, and 120 °C were plotted as shown in Figure 9a. From the kinetic plots of these conversion curves (Figure 9b), the thermal decomposition of BFI can be fitted well by the first-order kinetic equation (i.e., d[BFI]/dt = k[BFI]). This result is in accordance with the preceding reports in which the thermal decomposition of the aminimides follows the first-order kinetic equation.[8,9,15] The kinetic coefficients (k) of the rearrangement of BFI at 80, 100, and 120 °C were estimated as 1.8×10^{-5}, 4.4×10^{-4}, and 3.0×10^{-3} s^{-1}, respectively. These values are significantly larger than that of aminimides without α-acyl moieties (i.e., the kinetic coefficient of 1,1-dimethyl-1-(2-hydroxypropyl)amine propionimide was reported as 6.4×10^{-5} s^{-1} at 150 °C).[8]

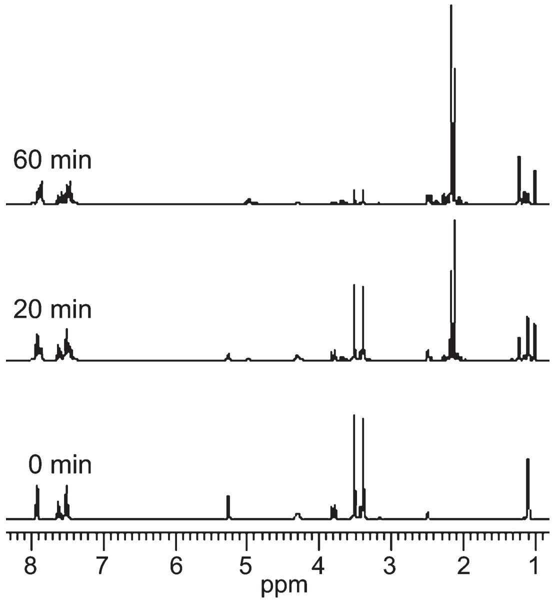


Figure 8. ^{1}H NMR spectra of BFI in DMSO-d_6 after heating at 100 °C for 0, 20, and 60 min.

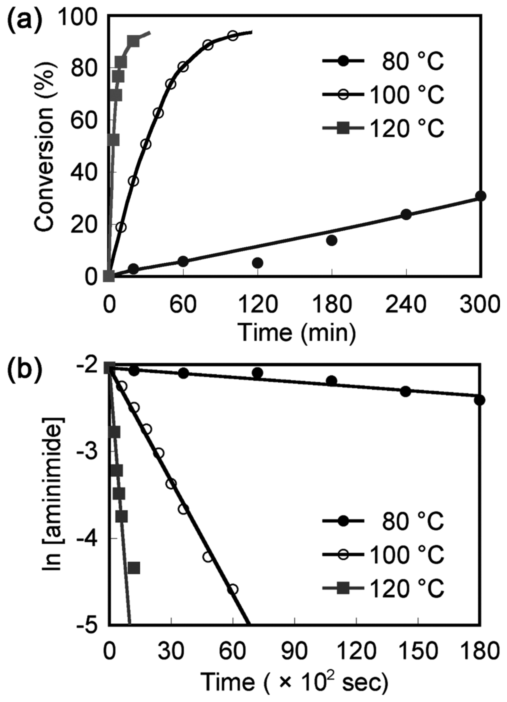


Figure 9. (a) Time−conversion curves of a DMSO-d_6 solution of BFI (0.13 M) at 80, 100, and 120 °C and (b) their kinetic plots.

Mechanistic Consideration for High Activity of BFI. On the basis of the results obtained from the analyses of the thermal rearrangement products and the preceding reports on the rearrangement of some aminimides, the benzoyl cation is the most plausible intermediate in the Curtius-type rearrangement of BFI (Scheme 4). To explain the high activity of BFI

Scheme 4. Plausible Rearrangement Mechanism of BFI

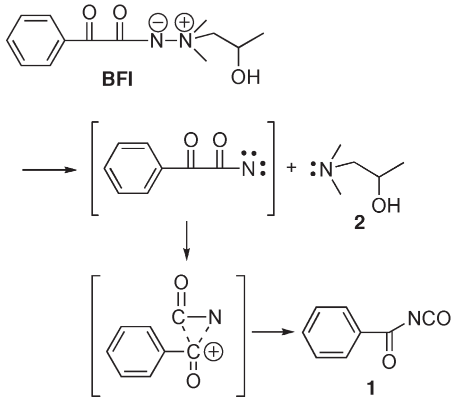
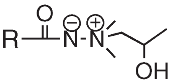


Table 1. $D(R^+-H^-)$ and T_d of Aminimides Having the Corresponding Substituents

R	$D(R^+$–$H^-)$ [a] (kcal/mol)	Td [b] (°C) of 
PhCO	212	119.0
$Me_2C(OH)$	220	162.1 [c]
Me_3C	233	166.6 [c]
Ph	294	186.2
Me	313	209.9 [c]

[a] See ref 19. [b] Estimated by TG/DTA (heating rate: 10 °C/min). [c] See ref 13.

at low temperature, we focused the thermodynamic stability of the carbocation in form of the migrating group.[16]

In the Curtius-type 1,2-rearrangement reactions, it is reported that the rate of the rearrangement increases as a function of the thermodynamic stability of the carbocationic form of the migrating groups.[17] In the case of BFI, it is assumed that migrating group is the benzoyl cation that has been reported to be significantly more stable than alkyl or aryl cations.[18] Because heterolytic bond dissociation energies $[D(R^+-H^-)]$[18,19] would be informative to compare the thermodynamic stability of carbocations, they were compared with T_d of aminimides bearing the corresponding substituents (Table 1 and Figure 10). Although more detailed studies should be performed for the precise discussion on the relationship of T_d and $D(R^+-H^-)$ by also taking the steric factors into consideration,[12,13,20] it is apparent that the lower $D(R^+-H^-)$ value results in the lower T_d of the corresponding aminimides.

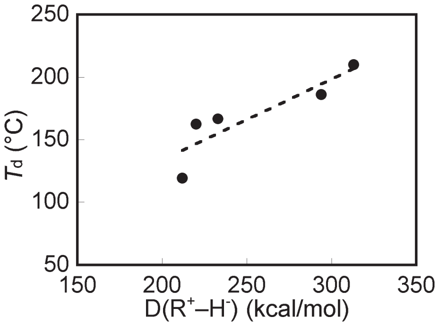


Figure 10. Relationship between $D(R^+-H^-)$ and T_d of aminimides possessing the corresponding substituents $(R-CON^--N^+(CH_3)_2-CH_2CH(CH_3)OH)$.

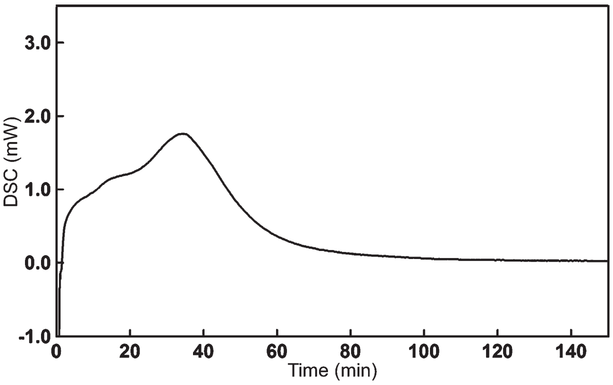


Figure 11. Isothermal DSC profile of bisphenol A diglycidyl ether containing BFI (20 mol %) at 100 °C.

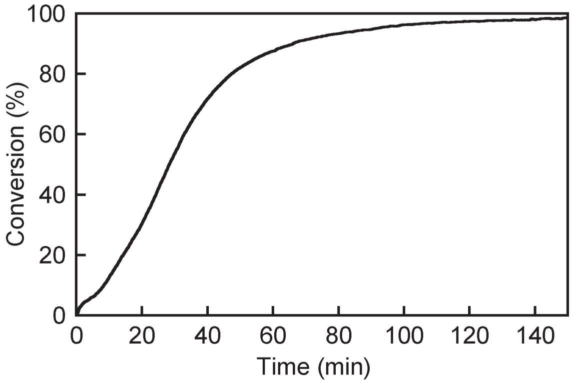


Figure 12. Time–conversion curve of bisphenol A diglycidyl ether containing BFI (20 mol %) measured by the real-time IR measurements at 100 °C.

Thermal Polymerization of Epoxide Catalyzed by BFI. The polymerization behavior of epoxides in the presence of BFI was evaluated by the isothermal DSC and the IR measurements using pure bisphenol A diglycidyl ether (EXA-850CRP) as an epoxide monomer. A mixture of BFI (20 mol %) and the epoxide was heated using DSC at 100 °C (Figure 11), in which an exothermic peak attributable to the polymerization of the epoxide is observable at the early stage of the polymerization. The conversion of epoxide reached 90% at 65 min (Figure 12), indicating that the polymerization proceeds smoothly at 100 °C. The T_g of the product after the DSC experiment was 84.4 °C, which supported that the current system formed the cross-linked product. The pot life of the mixture of BFI and the epoxide is more than 3 weeks at 25 °C. That is, no significant increase of the viscosity of this mixture was observed during that period. These results strongly support that BFI is quite suitable for the thermal latent catalyst of epoxides that can be used under mild polymerization conditions.

Thermal Polymerization of the Epoxide/Thiol System by BFI. The BFI-catalyzed polymerization behavior of the epoxide/thiol system was likewise evaluated from the DSC measurements using pure bisphenol A diglycidyl ether (EXA-850CRP) and pentaerythritol tetrakis(3-mercaptopropionate) as monomers, using benzyl alchol as a solvent. A homogeneous mixture of the epoxide (2.00×10^{-3} mol), thiol (1.00×10^{-3} mol), BFI (1.00×10^{-4} mol), and benzyl alcohol (1.00×10^{-3} mol) was subjected to the measurement of DSC at a heating rate of 10 °C/min. As references, a mixture of epoxide, thiol, benzyl alcohol, and **2** instead of BFI and that of epoxide, thiol, and benzyl alcohol

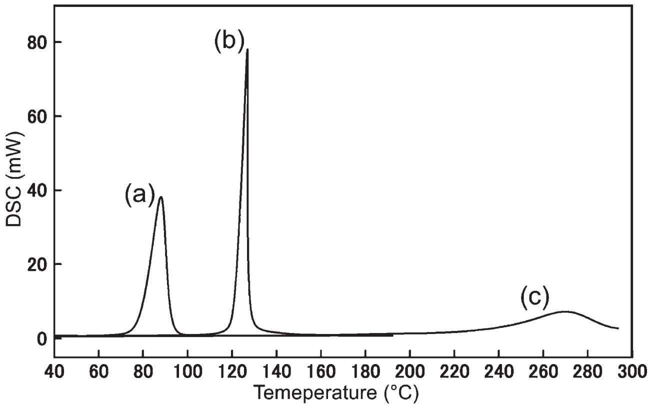


Figure 13. DSC profiles of epoxide/thiol system with **2** (a), with BFI (b), and without catalyst (c) at a heating rate of 10 °C/min.

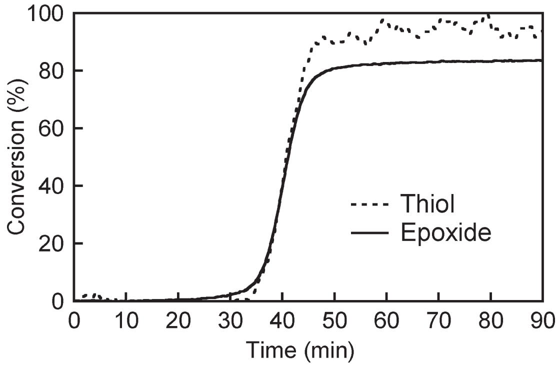


Figure 14. Time−conversion curves of the epoxide/thiol system with BFI measured by the real-time IR measurements at 80 °C.

(without BFI) were also subjected to the DSC analyses. Figure 13 shows the DSC curves for these mixtures.

In the presence of **2**, the polymerization of epoxide and thiol takes place at 78.7 °C (Figure 13a). However, the curing reaction of this mixture gradually takes place also at room temperature, which prevents the use of **2** as the thermal latent catalyst. On the other hand, the polymerization takes place at 121.1 °C in the presence of BFI (Figure 13b). It is of note that the epoxide/thiol system exhibited a long pot life in the presence of BFI (i.e., more than 2 weeks at room temperature). These results also indicate that BFI is quite suitable for the thermal latent catalyst of the epoxide/thiol system.

In addition, from the isothermal DSC measurements of the mixture of the epoxide, thiol, BFI, and benzyl alcohol at 80 °C, the exothermic peak was complete by 55 min. Likewise, the IR measurements of this mixture at 80 °C further supported that the conversion of both the thiol and the epoxide (Figure 14) was complete by 55 min, indicating that their polymerization takes place smoothly under the examined conditions.

Conclusions

A novel aminimide, 1,1-dimethyl-1-(2-hydroxypropyl)amine benzoylformimide (BFI), was synthesized from benzoylformic acid methyl ester, 1,1-dimethylhydrazine, and propylene oxide in 95% yield, and its thermal rearrangement behavior was studied in detail by TG/DTA, IR, GC-MS, ^{1}H NMR, and DSC analyses. BFI was found to decompose above 80 °C via the Curtius-type rearrangement to generate benzoyl isocyanate, 1,1-dimethylamino-2-propanol, and their further reaction products. BFI prove to catalyze the thermal polymerization of epoxide and the epoxide/thiol system above 80 °C, while the homogeneous mixture of BFI and epoxy resin could be stored at ambient temperature for at least 2 weeks without significant increase of the viscosity. The characteristics of BFI in both the long pot life and the low-temperature rapid polymerization indicate its promising application to the efficient thermal latent base catalyst for the polymerization and curing of epoxide and epoxide/thiol resin.

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