Received: October 20, 2014 | Accepted: December 2, 2014 | Web Released: December 11, 2014 CL-140960

Synthesis of Oxidized Thioxanthene-type Base Amplifiers and Their Application to Photoreactive Materials

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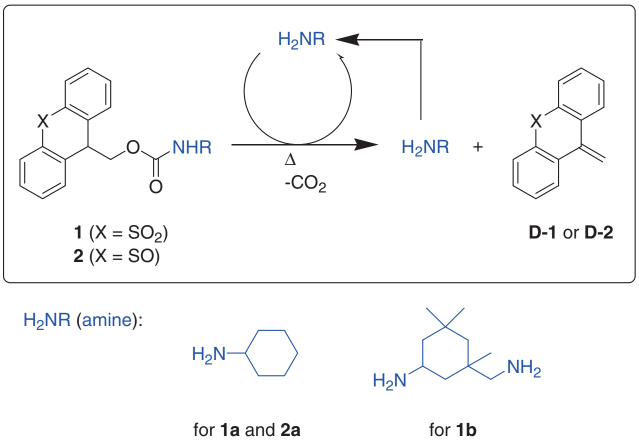
We propose base amplifiers (BAs) that are autocatalytically decomposed into base molecules by a small amount of trigger base molecules from photobase generators. We report here novel BAs having oxidized thioxanthene skeletons. It is confirmed that they are decomposed autocatalytically in solution or polymer matrix. They are applied to UV curing systems to improve their photosensitivity.

Photoreactive materials are indispensable for modern chemical industries. They are utilized in many fields such as electronics, cars, residential equipment, and other areas. To improve their photosensitivity, the concept of a proliferation reaction has been proposed by our group, where molecular catalysts themselves are generated autocatalytically by photogenerated catalysts, which is clearly distinguished from the chemical amplifications.[1] Secondary increase of the amount of catalyst would make the appearance quantum yields of photolatent catalysts greater than one. Acid amplifiers were initially developed for the concept[2] and have been applied to types of acid-reactive materials with photoacid generators.[3] However, acids generated in the proliferation reactions are problematic in that the erosion of metallic substrates could proceed.

To solve this problem, base amplifiers (BAs) have also been developed by our group.[4] Because photobase generators (PBGs) for base-reactive materials generally have low photosensitivity, BAs can be of great assistance when using photoreactive materials based on base-catalytic reactions.[4–6] 9-Fluorenylcarbamates are one of the representative BAs inspired by a protecting group of aliphatic amino groups in artificial peptide syntheses.[4a,4b,5,7] This type of BA has been integrated into various photopolymers.[8–10] In this study, we considered oxidized thioxanthenylcarbamates for designing BA molecules that were also reported as a protecting group of amino groups by Carpino et al. (Scheme 1),[11] because it would be easy for such protecting groups to change their decomposition rate by modifying the oxidation state of the sulfur atom. The sulfone-type **1** and sulfoxide-type **2** were both synthesized, in the expectation that the decomposition rate of the former would be faster than that of the latter because of the stabilization effect of the sulfone moiety on the anionic intermediate.

BAs **1** and **2** were both synthesized with 9*H*-thioxanthene as a starting compound.[12] 9*H*-Thioxanthene was oxidized again by *m*-chloroperbenzoic acid, and 9*H*-thioxanthene-10,10-dioxide for **1** was obtained with 3 equiv of the peroxide, while 9*H*-thioxanthene-10-oxide for **2** was obtained with 1.3 equiv of the peroxide. The overall yields were 29% (**1a**), 27% (**1b**), and 16% (**2a**) after four synthetic steps. These BAs were soluble in some organic solvents such as methanol, acetone, THF, and chloroform. The solubility of sulfone-type **1a** was slightly greater than that of sulfoxide-type **2a**.



Scheme 1. Autocatalytic fragmentation of BAs **1** and **2** having oxidized thioxanthene moieties.

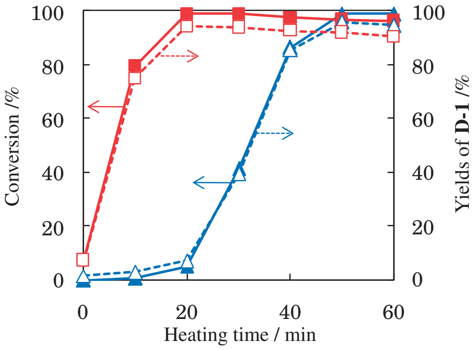


Figure 1. The consumption of **1a** (conversion, closed symbols) and the formation of **D-1** (yield, open symbols) as a function of heating time in the presence (red) and the absence (blue) of 13 mM of piperidine in 1,4-dioxane-d_8 at 100 °C.

A BA should fulfill the following three requirements.[4b] First, a BA molecule should undergo a base-catalyzed decomposition reaction to liberate a base, leading to autocatalytic decomposition. Second, the BA should be thermally stable in the absence of other base molecules under reaction conditions where both the autocatalytic decomposition and subsequent base-catalyzed reaction proceed. Third, the liberated base should be strong enough to catalyze the subsequent chemical reactions, resulting in a nonlinear chemical transformation. The thermal decomposition behavior of **1a** in 1,4-dioxane-d_8, at 100 °C, was monitored by ^{1}H NMR spectroscopy. Figure 1 shows both the consumption

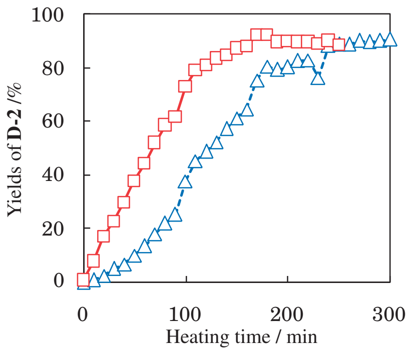


Figure 2. The formation of **D-2** from **2a** as a function of heating time in the presence (red) and absence (blue) of 13 mM piperidine in methanol-d_4 at 100 °C.

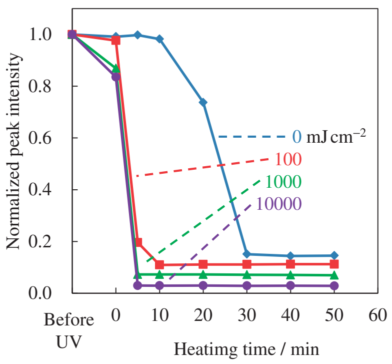
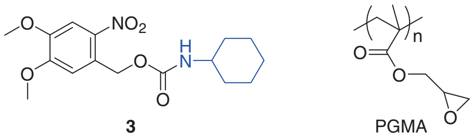


Figure 3. The consumption of **1a** as a function of heating time in polystyrene films containing 10 wt % of PBG **3** after 0–10000 mJ cm^{-2} of UV irradiation followed by postbaking at 60 °C.

of **1a** and the formation of **D-1**, and they are coincident with each other whether or not catalytic amines are contained in the systems. The decomposition reaction proceeded with the initiation of heating, and **1a** was consumed completely within 20 min in the presence of base catalysts. On the other hand, **1a** had an induction period of ca. 20 min before sigmoidal decomposition in the case of no catalysts. These results indicate that **1a** would work as a BA that is decomposed autocatalytically. An E1cB elimination could occur to release cyclohexylamines from **1a** like 9-fluorenylcarbamates,[8] and the primary amine was probably sufficient to decompose the parent molecules.

Figure 2 shows the thermal decomposition behavior of **2a**, which has a sulfoxide moiety instead of a sulfone moiety. Only the formation of **D-2** was monitored in this case, and methanol-d_4 was used as the solvent. A similar decomposition behavior with **1a** could be observed where **2a** seemed to be decomposed smoothly with base catalysts, and **2a** had an induction period followed by nonlinear decomposition without the catalysts. There was a distinct difference in the decomposition rate between **1a** and **2a**. The former was decomposed more quickly than the latter. It was expected that the decomposition reaction in the latter case could be accelerated by a polar solvent, methanol, probably because the intermediate anions of the E1cB reaction could be stabilized by solvent molecules.[5b] However, **1a** in dioxane-d_8 was decomposed within a shorter time than **2a** in methanol-d_4. The difference could result from the intrinsic higher stability of the anionic intermediate from **1a** compared with the intermediate from **2a**.

Using polystyrene films containing BA **1a** and PBG **3**, the decomposition behavior of **1a** in a polymer matrix was examined (Figure 3). The chemical structure of **3** is shown in Figure 4, and **1a** was expected to be decomposed by photogenerated base molecules from **3** with the initial UV irradiation as a trigger. The normalized peak intensities of the carbonyl moiety of **1a** (1718 cm^{-1}) were plotted as a function of heating time.[13] It was found that **1a** was decomposed drastically after an induction period of ca. 10 min without UV irradiation. In contrast, more than 100 mJ cm^{-2} of irradiation decomposed **1a** almost completely within 5 min. A base-proliferation reaction of **1a** could occur by trigger bases photogenerated from **3** in a polymer matrix.



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PGMA

Figure 4. Chemical structures of PBG **3** and PGMA.

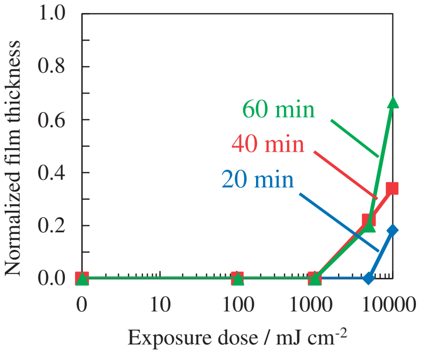
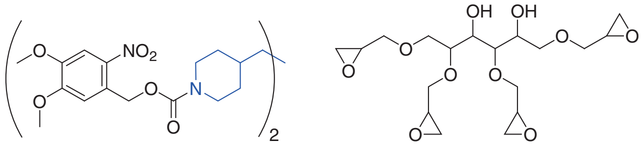


Figure 5. Photosensitivity curves of PGMA films containing 7.4 mol % of **1a** (toward epoxy groups) and 2.2 mol % of PBG **3** (toward epoxy groups) after postbaking at 100 °C for 20–60 min.

To examine the effect of the addition of **1a**, the photosensitivity was evaluated using poly(glycidyl methacrylate) (PGMA, $M_\mathrm{w} = 1.3 \times 10^4$, Figure 4) films containing **1a** and **3** with postbaking at 100 °C (Figure 5). The generated cyclohexylamines are expected to play a role in crosslinking the polymer chains, leading to insolubilization of the films. Increasing the postbaking time increased the photosensitivity, and the film remained at more than 1000 mJ cm^{-2} of UV irradiation and subsequent postbaking for 40 min. As a control experiment, no insoluble film was obtained in the case of films containing only **3** under the same postbaking condition even at 10000 mJ cm^{-2} of irradiation. These results indicate that BA **1a** could contribute to improvement of photosensitivity.

To fabricate UV curing films, a tetrafunctional epoxy resin, EX-622 and a bifunctional PBG **4** were used (Figure 6). BA **1b** is also a bifunctional molecule that was expected to achieve more efficient crosslinking than **1a** by providing one more amino groups. The hardness of the coating films was monitored by the pencil-scratch method based on JIS K5400 (Figure 7a).[14] The hardness of the pencils is arranged as follows: 6B (softest),



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EX-622

Figure 6. Chemical structures of PBG **4** and EX-622.

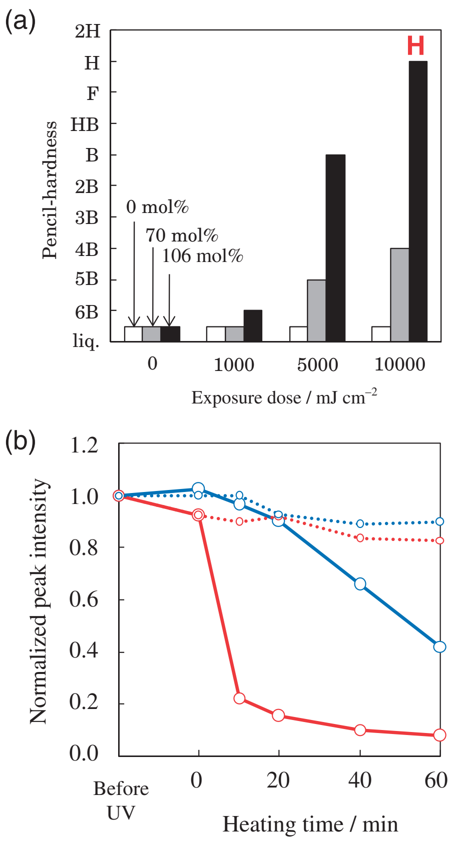

Figure 7. (a) Pencil-hardness of EX-622 coating films containing 10 mol % of **4** and 0, 70, or 106 mol % of **1b** as a function of exposure dose of 365 nm-light. Postbaking was performed at 60 °C for 20 min. (b) Changes in peak intensities of carbonyl moieties of **1b** (red) and epoxy moieties of the resin (blue) in FT-IR measurements as a function of heating time with (solid line) and without (dotted line) 5000 mJ cm^{-2} of UV irradiation. Postbaking was performed at 60 °C.

5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, and 9H (hardest). In the absence of BA **1b**, the resin mixtures retained their viscous liquid states. In contrast, increasing the exposure dose increased the pencil-hardness in the cases of resins containing 70 and 106 mol % of **1b**, which indicated that the generated diamines could contribute to the formation of crosslinking networks. Dark reactions did not proceed without UV irradiation. It was confirmed that the phototriggered base-proliferation reactions were achieved with these BA and PBG molecules. The maximum pencil-hardness of H was obtained using 106 mol % of **1b** with 10000 mJ cm^{-2} of irradiation and subsequent postbaking at 60 °C for 20 min. Figure 7b shows that the peak intensity of carbonyl groups of **1b** decreased dramatically by heating at 60 °C for 10 min,[13] and that the peak intensity of the epoxy moieties of EX-622 also decreased gradually in the case of the irradiated film. This clearly indicates that both the autocatalytic decomposition of **1b** and the subsequent crosslinking reaction between resins and diamines from **1b** proceeded.

In conclusion, novel BAs **1** and **2** having oxidized thioxanthene moieties were designed and synthesized. It was confirmed that they were decomposed autocatalytically in the presence of trigger base molecules, and that the decomposition rate could be changed by the oxidation state of the sulfur atom of the thioxanthene. An improvement in photosensitivity of PGMA films and the efficient UV curing of EX-622 resins was achieved by integrating **1a** or **1b** as BAs. They could be applied to other anionic UV curing systems.

Supporting Information is available electronically on J-STAGE.

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12 9*H*-Thioxanthene was obtained by reduction of thioxanthone in a high yield. For the synthetic procedure of BAs **1** and **2** in detail, see Supporting Information.

13 The carbonyl groups of PBGs would also contribute to the peak intensity around 1720 cm^{-1}.

14 JIS K5400 defined by Japanese Industrial Standards is a simple method to test the scratch hardness of coatings. In this test, pencils in a range of 6B to 9H hardness grade are used. The pencil is moved scratching over the surface of the coating at a 45° angle with a constant pressure.