

Nonlinear organic reaction of carbamates as base amplifiers to proliferate aliphatic amines and their application to a novel photoreactive system

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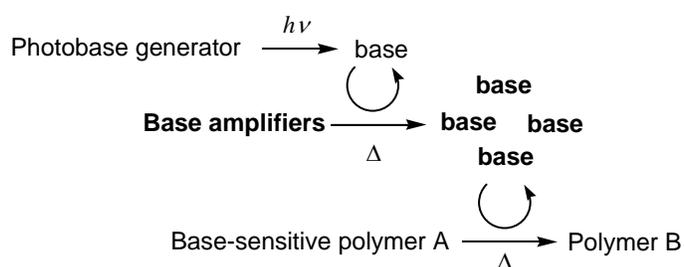
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Introduction

The photogeneration of acidic or basic species provides versatile types of photoreactive materials because these species are capable of catalyzing many organic reactions. In particular, a large number of investigations concerning acid-catalyzed systems have been reported.¹ However, only a few articles have mentioned photosensitive materials

based on base-catalyzed reactions because of relatively low quantum yields for photobase generation of a photobase generator (PBG), leading to low photosensitivity.²⁻⁶ If the concentration of a photogenerated base could be boosted by an autocatalytic process, rates of versatile base-catalyzed reactions such as eliminations, condensations and rearrangements should be enhanced considerably. This idea led us to carry out the molecular design and the synthesis of base precursors which are reasonably called base amplifiers since the generation of base molecules occurs in a manner of geometric progression.⁷⁻¹⁰ Base proliferation processes can be coupled with subsequent base-catalyzed reactions to give various types of nonlinear chemical transformations. We have focused our attention on combining a base amplifier with PBG because a tiny amount of a photogenerated base should be bred, giving rise to photosensitivity enhancement of photoreactive materials sensitized with PBG (Scheme 1).

We describe here the nonlinear chemistry of 9-fluorenyl carbamates (**1**) in the autocatalytic generation of base molecules (Scheme 2) and photosensitivity enhancement of base-sensitive photoreactive materials such as UV-curing materials (Scheme 3) and photopatterning materials (Scheme 4) by combining the base amplifiers.

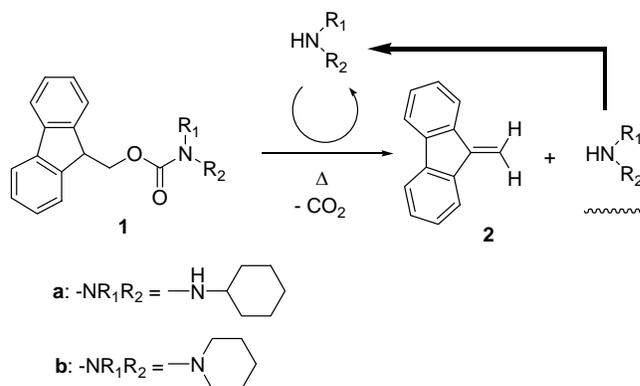


Scheme 1 Novel base-sensitive photoreactive materials enhanced by base amplifiers.

Experimental

Physical measurements

$^1\text{H-NMR}$ spectra were measured on a JEOL FX90Q. IR spectra were recorded on a JASCO FT/IR-410. Photoirradiation was carried out by a San-ei Supercure-203S Hg-Xe lamp. Film thickness was measured with a DEKTAK³ST (ULVAC Japan).



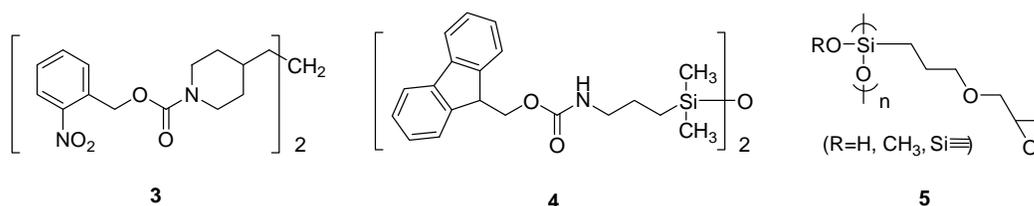
Scheme 2 Base proliferation reaction of **1**.

Base proliferation in solution

A sealed NMR tube containing a base amplifier (**1a** or **1b**) and mesitylene as an internal standard in 1,4-dioxane-*d*₈ was heated at 100 °C to be subjected to $^1\text{H-NMR}$ measurements at intervals at room temperature in the absence or in the presence of a catalytic amount of an amine.

Anionic UV-curing enhanced by a base amplifier

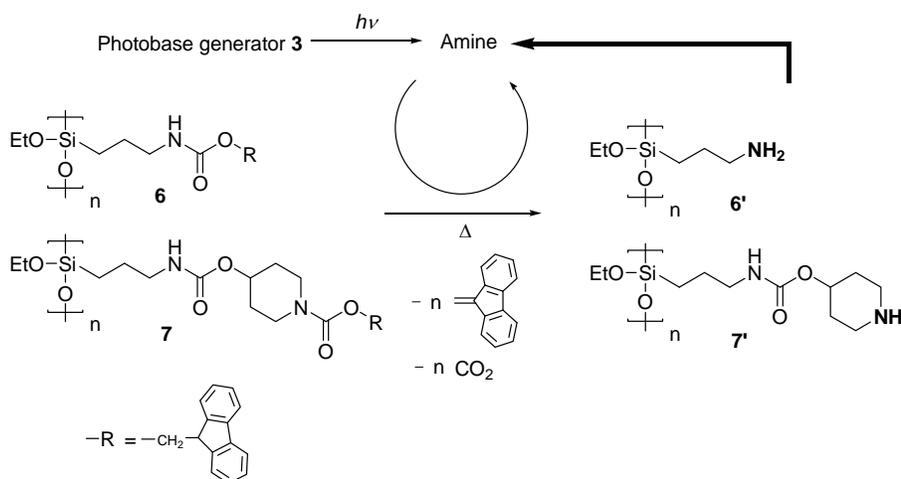
A UV-curable resin solution was prepared by dissolving a silicone resin **5** (0.33 g/1 mL), **3** as PBG (10 wt% relative to **5**) and base amplifier **4** (40 wt% relative to **5**) in chloroform. The solution was coated on silicon wafers, and the coated films of *ca.* 4 μm in thickness were baked at 100 °C for 1 min, exposed to UV light and postbaked at 100 °C.



Scheme 3 Chemical structures of anionic UV-curing materials.

Photosensitivity determination of photopatterning materials based on base-amplifying polymers

A 1-methoxypropyl-2 acetate solution of **6** ($M_w=4600$, $M_w/M_n=1.4$) or **7** ($M_w=4800$, $M_w/M_n=1.1$) containing **3** as PBG (10 wt% relative to the resin) was spin-coated on a silicon wafer and prebaked at 100 °C for 1 min to give 0.7 μm -thick film. The film was exposed to 254 nm light. Subsequently, the film was baked at 100 °C for 4, 6, and 8 min on a hot stage, dipped in a 2 wt% aqueous solution of lactic acid for 1 min, and followed by measurement of residual film thickness to give photosensitivity curves.



Scheme 4 Photobase-catalyzed reactions of photopatterning materials **6** and **7**.

Results and discussion

Base proliferation in solution

Base amplifiers should fulfill the following requirements.^{7,8} First, a base amplifier should undergo a base-catalyzed decomposition to liberate a base, leading to its autocatalytic decomposition. Second, a base amplifier should be thermally stable in the absence of a base under reaction conditions that advance both the autocatalytic decomposition and the subsequent base-catalyzed reaction. Third, the liberated base should be strong enough to catalyze subsequent chemical reactions. Consequently, we designed carbamates **1a** and **1b** as base amplifiers (Scheme 2).⁸ These carbamates were isolated as thermally stable crystals.

Base proliferation reactions of the carbamates in solution were monitored by ¹H-NMR spectroscopy. For instance, Fig.1 shows both the consumption of **1a** and the formation of dibenzofulvene (**2**) in the presence and absence of a catalytic amount of cyclohexylamine. Carbamate **1a** disappeared immediately with a sigmoidal time conversion curve in the presence of cyclohexylamine to form

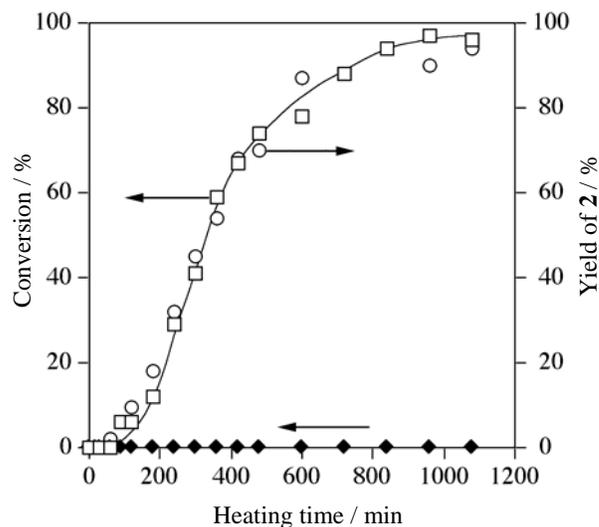


Fig. 1 The consumption of **1a** (70 mmol dm^{-3}) (□) and the formation of dibenzofulvene (**2**) (○) as a function of heating time in the presence of cyclohexylamine (11 mmol dm^{-3}), as well as the conversion of **1a** in the absence of cyclohexylamine (◆) in 1,4-dioxane-*d*₈ at $100 \text{ }^\circ\text{C}$.

2 quantitatively. On the other hand, **1a** was thermally stable in the absence of cyclohexylamine under the conditions that advance the autocatalytic decomposition reaction. Carbamate **1b** behaved quite similarly except for the difference in gradients of sigmoidal-shaped conversion curves and thermal stability. For qualitative discussion, half lifetimes for the disappearance of the base amplifiers and gradients in the curves are listed in Table 1.

Table 1 Parameters of the nonlinear thermolysis of **1a** and **1b**.

BA ^a	Amine	Conc.(mmol/dm ³)		Half lifetime (min)	Gradient (%/hr)
		BA	Amine		
1a	Cyclohexylamine	70	0	>1080	--
	Cyclohexylamine	70	11	300	12
1b	Piperidine	69	0	260	42
	Piperidine	69	13	78	38

^aBA, Base amplifier

Since the gradient (%/hr) defined as the level of the disappearance of the base amplifiers corresponds to an autocatalytic decomposition rate in the presence of a catalytic amount of an amine, the results indicate that the base proliferation rate of **1a** slower than **1b**, reflecting the weaker basicity of cyclohexylamine when compared to piperidine.

Anionic UV-curing behavior

Epoxy resins have been extensively used as base-sensitive precursors in coating technologies¹¹, while UV-curable organic-inorganic hybrids have received much attention because cured films have unique properties such as good flexibility and scratch-resistance.¹² This situation led us to examine novel UV-curable organic-inorganic hybrids utilizing base-catalyzed reactions enhanced by base amplifier **4** which proliferates a diamine incorporating a disiloxane structure to improve curing efficiency (Scheme 3).^{13,14} In addition, the disiloxane structure of the diamine is expected also to lead to enhancing mechanical properties of cured films because the content of Si-O-Si bonds in UV-cured films increases considerably as a result of the base proliferation reaction of **4**. To examine the effect of the involvement of the base proliferation reaction, **4** was added to UV-curable organic-inorganic hybrids composed of silicone resin **5** bearing epoxy groups and 10 wt% of **3** as PBG. Silicone resin **5** is expected to be cured in the presence of **3** upon UV irradiation and after post-exposure baking, owing to both the crosslinking reaction of epoxy groups with the photogenerated amine and the photobase-catalyzed hydrolytic condensation of RO-Si units of **5** to form branched Si-O-Si bonds.

UV-Curing was achieved by exposing the coated films of **5** containing **3** and **4** to UV light, followed by annealing. The chemical transformations of **4** and **5** in curable coatings were followed by means of FT-IR spectroscopy. The hardness of the coatings was monitored by the pencil scratch method. The pencil-hardness was evaluated by scratching UV-cured coatings with pencils, the

hardness of which is arranged as follows: 6B (softest), 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H, 7H, 8H, and 9H (hardest).

FT-IR spectral changes of UV-cured films provided valuable information concerning the base proliferation reaction of **4** and the crosslinking reaction of **5**. Normalized peak intensity of the absorption band at 908 cm^{-1} due to the epoxy ring of **5** was 0.6 after heating a UV-exposed film without **4** at $100\text{ }^{\circ}\text{C}$ for 60 min. The film was too soft to evaluate the pencil-hardness so that the hardness was of a level lower than 6B. On the other hand, as given in Fig. 2, $\nu_{\text{C}=\text{O}}$ of **4** at 1690 cm^{-1} disappeared abruptly, whereas the peak intensity at 908 cm^{-1} decreased effectively down to 0.45, resulting in a level of 3H after heating for 60 min. These results indicate that the enhancement of the UV-curing efficiency arises from the base proliferation reaction of **4** to lead to the sufficient hard coating.

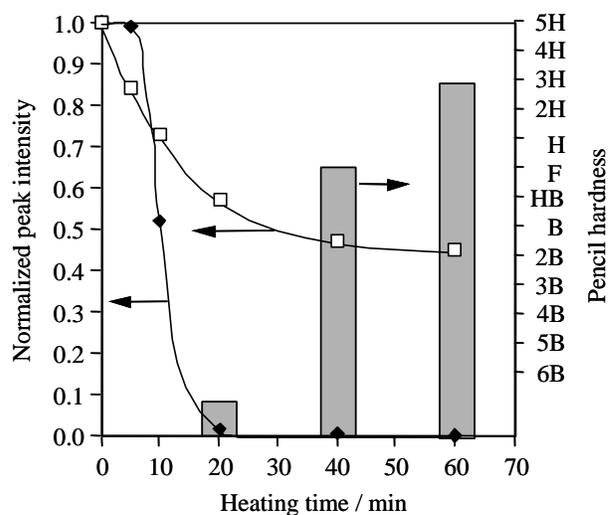


Fig. 2 Time courses of the decomposition of base amplifier **4** (◆) and epoxy groups (□) of silicone resin **5** sensitized with **3** as a photobase generator in the presence of 40 wt% of **4** at $100\text{ }^{\circ}\text{C}$ with initial UV irradiation. Gray rectangles mean pencil-hardness of coating films.

Photosensitivity characteristics of photopatterning materials

The base amplifiers clearly contributed to enhancement of the photosensitivity of the base-sensitive photoreactive materials as described above. However, these systems have several problems in creating innovative photoimaging materials with much higher photosensitivity and resolution. Firstly, amine molecules generated from the base amplifiers will be vaporized from a polymer film when the film containing the base amplifiers is heated, unless we choose suitable amines as basic species produced from the base amplifiers. Secondly, although the photosensitivity increases with an increase in the number of doped base amplifiers, a large number of base amplifiers will lead to lower resolution power because of excessive diffusion of basic species generated from the base amplifiers. Thirdly, increasing the doped base amplifiers as additives cannot maintain the thermal properties of the base polymer itself. Fourthly, almost all the base-reactive polymers reported contain epoxy groups as base-labile functional groups that react with amine molecules generated from the base amplifiers, leading to a decrease in the turnover of a base-catalyzed reaction. To overcome the above problems, we developed novel base-sensitive polymers **6** and **7** tethering base-amplifying units (Scheme 4), which causes base-catalyzed elimination reactions to lead to a polarity change in the polymer.^{15,16} These polymers sensitized with PBG should be suitable for photopatterning.

A film of **6** sensitized with **3** was exposed to 254 nm light, followed by heating at 100 °C to be subjected to the development with a 2 wt% aqueous solution of lactic acid and the rinse with water to give photosensitivity curves. As shown in Fig. 3, the thin film functions as a positive-working photoresist whose photosensitivity is markedly affected by post-exposure baking (PEB) period. Judging from the fact, base-catalyzed hydrolytic condensation of residual ethoxysilyl units of **6** is negligible. An exposure dose was reduced down to 0.7 mJ/cm² when the film was heated at 100 °C for 8 min. This is because the base proliferation reaction of **6** proceeds effectively. A film of **7** sensitized with **3** provided a positive-working photoresist in a same way as described for the film of **6**. These results are summarized in Table 2. A film of **7** doped with **3** shows higher sensitivity when compared with that of **6** containing **3**. It arises from the fact that basicity of **7'** is stronger than that of **6'**. The present systems exhibited two order magnitude higher sensitivity when compared with conventional photoimaging materials relying on a base-catalyzed reaction.^{5,6}

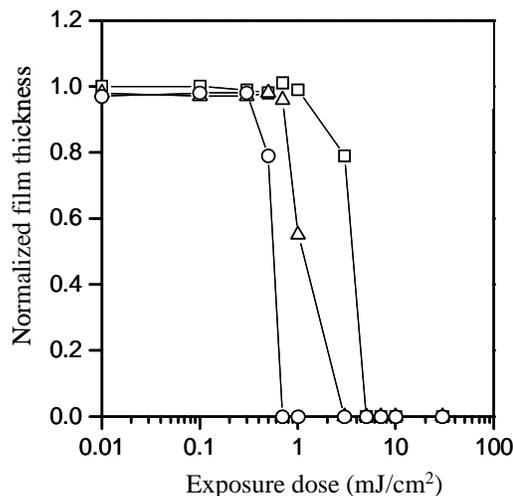


Fig. 3 Photosensitivity curves of films of **6** sensitized with **3** heated at 100 °C for 4 min (\square), 6 min (\triangle), and 8 min (\circ).

Table 2 Photosensitivity of films of **6** and **7**.^a

Polymer	PEB Period (min) ^b	Sensitivity (mJ/cm ²) ^c
6	4	5
	6	3
	8	0.7
7	4	1
	6	0.7
	8	0.3

^aThe films are sensitized with 10 wt% of **3**. ^bPEB: 100°C.

^cExposure: 254 nm light.

Microphotopatterning was carried out as follows. A thin film consisting **6** (or **7**) and 10 wt% of **3** as PBG was exposed to 254 nm light of an exposure dose of 15 mJ/cm² (or 1.5 mJ/cm²) through a photomask. Subsequently, the film was baked at 100 °C for 3.5 min (or 4 min) and developed with a 2 wt% aqueous solution of lactic acid for 1 min. Our preliminary evaluation obtained positive-tone images, resolving 10 μm line-and-space (L&S) patterns for **6** and 3 μm L&S patterns for **7**. Further optimizations of exposure as well as developing conditions should be needed for improving photoresist performances including resolution power.

Conclusion

We developed base amplifiers for the first time to improve the photosensitivity of photoreactive materials utilizing base-catalyzed reactions. The base proliferation was demonstrated by base-catalyzed decomposition of base amplifiers **1a** and **1b** in solution, which resulted in a nonlinear fragmentation to produce amine molecules. Combining a base amplifier with an epoxy resin containing PBG opened a way to anionic UV-curing. Furthermore, we developed novel base-amplifying polymers **6** and **7** for photopatterning. These polymers displayed the base proliferation reactions even base-amplifying units are covalently attached to polymer main chains. Polymers **6** and **7** sensitized with **3** provided positive-working photoresists developable with an aqueous acidic solution. The present systems exhibited two order magnitude higher sensitivity when compared with conventional photoimaging materials utilizing base-catalyzed reactions.

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