Base-Amplifying Silicone Resins with Photobase-Generating Side Chains and Their Application to Negative-Working Photoresists

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Received 14 October 2014; accepted 6 December 2014; published online 00 Month 2015 DOI: 10.1002/pola.27551

ABSTRACT: To accomplish high photosensitivity of resist systems including photobase generators, we have proposed the concept of base-proliferation reactions that generate base molecules in a nonlinear manner by the action of a catalytic amount of base; however, excessive diffusion of generated base molecules is still a problem. We have designed novel functional silicone resins bearing both base-amplifying units and photobase generating units, and synthesized resins with various composition ratios. The synthesized resins are decomposed autocatalytically after UV irradiation and subsequent heating at 100 °C, which indicates progression of base-proliferation reactions.

INTRODUCTION The photolithography process is utilized for high-volume production of micropatterns for circuits or electrodes in electronic devices. Photosensitive polymers are indispensable for this process as photoresists to protect metal surfaces while being subjected to an etching process.^{1–5} To accomplish high photosensitivity, various chemical amplification systems have been developed in which photogenerated $\operatorname{acid}^{6,7}$ or $\operatorname{base}^{8-23}$ catalyses a chemical reaction in a resist film. While photosensitive materials based on basecatalysed reactions have merit for preventing erosion of metallic substrates, photobase generators generally have low quantum yields, which leads to low photosensitivity. To overcome this problem, we have proposed the novel concept of base-proliferation reactions of base-sensitive compounds, referred to as base amplifiers, that generate base molecules in a non-linear manner by the action of a catalytic amount of base.^{24–28} Photosensitive polymers bearing base-amplifying (BA) units have also been designed for photoresist formulations, taking into account the prevention of both evaporation and excessive diffusion of base molecules from resist films during post-exposure baking (PEB), referred to as "air infection."29 Nevertheless, air infection does produce amines from low-molecular-weight photobase generators. If photobase-generating (PBG) units are immobilized in a resin,

High photosensitivity (8.1 mJ cm⁻²) was recorded, and it was found that the photosensitivity is about 490 times enhanced by replacing a base-catalytic reaction system with the base-proliferation reaction system. Furthermore, a 4 \times 10 μm line-and-space pattern has been successfully fabricated using the silicone resin. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *00*, 000–000

KEYWORDS: base-amplifying unit; base-proliferation reaction; crosslinking; negative-working photoresist; photobase-generating unit; photoresists; polysiloxanes; silicone resin

not only will such infection be stopped, but also the mixing process of BA polymer with PBG molecules will be prevented. Furthermore, a siloxane polymer was applied as the main chain of the polymer, anticipating enhancement of the plasma-etching resistance by the silicone skeleton.^{30–36} However, the synthesized resins are apt to show low molecular weight because of repulsion between the bulky 9-fluorenyl-methyloxycarbonyl groups of the BA units or (2-nitro-4,5-dimethoxy)benzyloxycarbonyl groups of the PBG units. To increase the molecular weight of the resin, tetraethyl orthosilicate (TEOS) was added during the synthetic process as a spacer.

In this study, a novel photoreactive silicone resin **1** was synthesized having both BA units and PBG units, and it was found that the resins successfully functioned as negativeworking photoresists (Scheme 1). In this system, PBG units at the side chains generate primary amines that are triggered by UV irradiation. The amines catalyse autocatalytic decomposition reactions of BA units under PEB, liberating carbon dioxide and dibenzofulvene as by-products. Free amines accelerate condensation reactions between ethoxy silyl groups, leading to gelation or insolubilization of the resin.

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SCHEME 1 Chemical structure of silicone resin **1** synthesized in this study and its chemical reactions, including photodecomposition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

General

The reagents used were purchased from Tokyo Chemical Industry (Tokyo, Japan), Shin-Etsu Chemical (Tokyo, Japan), and Wako Pure Chemical Industries (Osaka, Japan). (3-Isocyanato)propyltriethoxysilane, TEOS, tetrahydrofuran (THF), benzene, and ethanol (EtOH) were used after distillation. Other chemicals were used without further purification.

¹H (²⁹Si) NMR spectra were obtained using a JEOL JNM-EX500 (JNM-EX400) spectrometer. FT-IR spectra were measured using a JASCO FT/IR-410 spectrophotometer. Measurements of melting point were performed using a Yanaco MP-S3. UV-vis spectra were measured using a JASCO V-570 spectrophotometer. Gas phase chromatography measurements were performed using a Shimadzu RID-10A detector employing THF as an eluent, and the molecular weight data were obtained relative to polystyrene standards. Photoirradiation was carried out using a San-ei Electric Hg-Xe lamp with a glass filter (UV-35 or UV-D35; AGC Techno Glass). The amount of light was measured using an Advantest TQ8210 or a Hamamatsu Photonics C8026. The film thickness was measured using a Dektak3ST (Ulvac, Japan).

Synthesis of BA Monomer 2

(3-Isocyanato)propyltriethoxysilane (6.3 g, 26 mmol) in benzene (24 mL) was dropped into a solution of 9-fluorenylmethanol (5.00 g, 26 mmol) with dibutyltin dilaurate (0.12 g, 0.19 mmol) in THF (32 mL) at 70 °C. The reaction mixture was stirred at 70 °C for 2 h, and then the solvent was evaporated. The residue was dried *in vacuo* and recrystallized from EtOH to give the BA monomer **2** in an

88% yield as a pale-yellow solid. In the case of recrystallization with cosolvents of hexane and THF, **2** was obtained in a 78% yield as a white solid. ¹H NMR (500 MHz, CDCl₃, *δ*, ppm): 0.63 (t, *J* = 8.4 Hz, 2H; -CH₂Si), 1.22 (t, *J* = 7.0 Hz, 9H; Si(OCH₂CH₃)₃), 1.64 (quint, *J* = 8.4 Hz, 2H; -CH₂CH₂CH₂-), 3.19 (t, *J* = 6.5 Hz, 2H; -NHCH₂-), 3.81 (q, *J* = 7.0 Hz, 6H; Si(OCH₂CH₃)₃), 4.20 (t, *J* = 6.5 Hz, 1H; CH of 9-fluorenyl), 4.38 (d, 2H; fluorenyl-CH₂), 5.13 (br, 1H; -O-CO-NH-), 7.2-7.7 (m, 8H; aromatic). ²⁹Si NMR (99 MHz, CDCl₃, *δ*, ppm): -45.5. FT-IR (KBr): v = 1690 (v(C=O_{carbamate})), 2970 (v(CH_{alkyl})), 3320 (v(NH)) cm⁻¹. mp: 72-74 °C.

Synthesis of PBG Monomer 3

(3-Isocyanato)propyltriethoxysilane (7.6 g, 31 mmol) in benzene (28 mL) was dropped into a solution of 6-nitroveratryl alcohol (5.4 g, 26 mmol) with dibutyltin dilaurate (0.12 g, 0.19 mmol) in benzene (32 mL) at 70 °C. The reaction mixture was stirred at 70 $\,^\circ\text{C}$ for 2 h, and then the solvent was evaporated. The residue was purified using column chromatography (TEOS/chloroform = 1/100, then chloroform) to give the PBG monomer 3 in a 78% yield (9.1 g) as a pale-yellow crystal. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 0.65 (t, J = 8.0 Hz, 2H; -CH₂Si), 1.23 (t, J = 7.0 Hz, 9H; Si(OCH₂CH₃)₃), 1.66 (quint, J = 8.0 Hz, 2H; Si-CH₂CH₂), 3.22 (t, J = 7.0 Hz, 2H; Si—CH₂CH₂CH₂), 3.73 (q, J = 7.0 Hz, 6H; Si(OCH₂CH₃)₃), 3.8 (s + s, 6H; OCH₃), 5.24 (br, 1H; NH), 5.50 (s, 2H; Ar-CH₂), 7.10 (s, 1H; aromatic), 7.70 (s, 1H; aromatic). ²⁹Si NMR (99 MHz, CDCl₃, δ , ppm): -45.8. FT-IR (KBr): v = 1330 (v(C-O-C)), 1520 (v(N-O)), 1690 $(v(C=O_{carbamate}))$, 2970 $(v(CH_{alkyl}))$, 3330 (v(NH)) cm⁻¹. Anal. calcd for C₁₉H₃₂N₂O₉Si: C, 49.54; H, 7.02; N, 6.08. Found: C, 49.49; H, 7.41; N, 6.39. mp: 56-59 °C.

TABLE 1 Syntheses of copolycondensation resins 1 using monomers 2, 3 and TEOS^a



Run	Resin	Monomer [g (mmol)]			Yield	<i>M</i> w ^b	PDI ^c	Ratio ^d		
		2	3	TEOS	(g)	(10 ³)		1	т	п
1	1a	2.27 (5.12)	0.02 (0.05)	0	1.6	2.4	1.2	99	1	0
2	1b	2.27 (5.12)	0.07 (0.15)	0	1.8	2.1	1.2	97	3	0
3	1c	2.27 (5.12)	0.12 (0.27)	0	1.9	2.5	1.2	95	5	0
4	1d	2.27 (5.12)	0.28 (0.60)	0	1.8	2.1	1.2	90	10	0
5	1e	2.27 (5.12)	0.59 (1.28)	0	2.1	2.2	1.3	80	20	0
6	1f	1.90 (4.28)	0.10 (0.23)	0.94 (4.51)	1.9	6.0	1.4	33	1	66
7	1g	1.80 (4.06)	0.21 (0.45)	0.94 (4.51)	1.9	6.3	1.4	30	4	66
8	1h	1.60 (3.60)	0.42 (0.90)	0.94 (4.51)	1.9	5.6	1.4	32	7	61

^a Mole ratios were as follows: runs 1–5: HCl/(**2** + **3**) = 0.12–0.15, H₂O/ (**2** + **3**) = 0.25–0.29, runs 6–8: HCl/(**2** + **3**) = 0.105, H₂O/(**2** + **3**) = 8.0. ^b Polystyrene standard. ^c Polydispersity index.

^d Each ratio was estimated using ¹H NMR and/or UV-vis spectroscopy.

General Polycondensation Procedure with BA Monomer 2, PBG Monomer 3, and TEOS to form Silicone Resin 1

BA monomer **2**, PBG monomer **3** and TEOS were dissolved in EtOH (4.2 g for runs 1–5 and 3.3 g for runs 6–8) and stirred for 10 min at 0 $^{\circ}$ C. Aqueous hydrochloric acid was

added to the solution, stirred at room temperature for another 10 min, and then stirred at 70 °C for 1–1.5 h under flowing N₂ (300–360 mL min⁻¹). The residue was dissolved in THF, and dropped into hexane or cyclohexane to give the silicone resins as a pale-yellow or white solid.



FIGURE 1 Time courses for the decrease in peak area (carbonyl groups): (a) **1e** with (25 or 10 mJ cm⁻²) and without irradiation and (b) **1a–1e** with 10 mJ cm⁻² of irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 2 Time courses for the decrease in peak area (carbonyl groups): (a) **1h** with (50, 25, or 10 mJ cm⁻²) and without irradiation and (b) **1f–1h** with 10 mJ cm⁻² of irradiation. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

For resin **1h**, remaining silanol groups were capped with trimethylchlorosilane. Trimethylchlorosilane (0.23 g, 2.1 mmol) in THF (10 mL) was dropped into a solution of **1h** (0.30 g) with triethylamine (0.21 g, 2.1 mmol) in THF (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 20 min. After filtration, the solvent was evaporated. The residue was dissolved in THF, and dropped into cyclohexane to give the capped **1h**.

Base-Catalyzed Decomposition Behavior

A solution of silicone resin **1** (0.1 g) in chloroform (1 mL) was spin cast onto a hydrophobized Si substrate, and prebaked at 100 °C for 1 min. The time course of the FT-IR spectra of the film of **1** was monitored with heating at 100 °C after 365 nm light irradiation. The normalized peak intensity was calculated as the ratio of the peak intensity of the carbonyl group absorption band to the intensity of the peak before UV irradiation.

Sensitivity Determination

A solution of silicone resin **1** (0.1 g) in chloroform (1 mL) or in propylene glycol monomethyl ether acetate (0.5 mL) was spin cast onto a hydrophobized Si substrate, and prebaked at 100 °C for 1 min. The film of **1** was exposed to 365 nm light irradiation and subsequent heating at 100 or 120 °C. Development of the film was performed with chloroform for 30 s to obtain photosensitivity curves. The normalized film thickness was calculated as the ratio of the film thickness after the developing process to the thickness before UV irradiation.

Fabrication of Micropatterns

A solution of silicone resin **1e** containing 20% PBG units in chloroform was spin cast onto a hydrophobized Si substrate, and prebaked at 100 °C for 1 min. UV exposure was conducted through a photomask with 365 nm light (110 mJ cm⁻²). After PEB at 100 °C for 25 s and subsequent development with benzene, a micropatterned film on the substrate was obtained.

RESULTS AND DISCUSSION

Syntheses of Copolymers 1 Using 2, 3, and TEOS

Table 1 shows the synthetic results for resins **1a-1h**. Composition ratios were varied between BA, PBG and TEOS units.

In the cases of **1a-1e** using BA monomer **2** and PBG monomer **3**, molecular weights of 2100–2500 were obtained (runs 1–5). It was found that the copolycondensation ratio was approximately proportional to the amount of load of the monomers, estimated by ¹H NMR and/or UV-vis spectroscopy. The resins were found by ²⁹Si NMR to take T^2 and T^3 structures.³⁷ H₂O and HCl were added as accelerating reagents for the hydrolysis polycondensation; however, the molecular weight was not increased sufficiently. In contrast, it was found that introduction of TEOS units led to an increase in the resulting molecular weight of **1f-1h** to 5600–6300 (runs 6–8). The TEOS units could act as a spacer between the bulky BA and PBG units. These polymers also had T^2 and T^3 structures, recorded by ²⁹Si NMR.³⁷

Decomposition Behavior of the Copolymers

The synthesized photobase-sensitive resin should fulfil the following requirements. First, the resin should be readily decomposed by base catalyst to produce amino groups in its side chain. Second, these amino groups are strong enough bases to catalyse the β -elimination reaction at BA units to form more amino groups, leading to autocatalytic decomposition. Third, the resin should be thermally stable in the absence of base, at least under the same reaction conditions, to enhance the autocatalytic decomposition initiated by photogenerated base. Among the synthesized resins, 1e, which contained 20% PBG units, was spin cast and a film of 0.9 µm in thickness was prepared on a hydrophobized Si wafer. Irradiation with 365 nm light (25 mJ cm⁻²) did not influence the peak intensity of the carbonyl band very much in the FT-IR spectral measurement (Supporting Information Fig. S1). In contrast, subsequent heating at 100 °C decreased the intensity. This result implied that BA units in the resin were decomposed by amines photogenerated from PBG units. The normalized peak intensity plotted against heating time is shown in Figure 1 for resin 1e. The induction period, defined as the heating time required to begin decomposition of the urethane bonds, was about 30 min with 25 mJ cm^{-2} of irradiation energy [Fig. 1(a)]. Lowering the irradiation energy to 10 mJ cm $^{-2}$ slightly increased the period. Without UV irradiation, decomposition occurred after an induction period of about 40 min. The decomposition behaviour was sigmoidal, which



FIGURE 3 Illustration of the procedure for photosensitivity determination and chemical changes in a film of **1**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

indicated exponential increase of amino groups in the resin, as becomes a base-proliferation reaction, during PEB. The proportion of PBG units also influenced the decomposition behaviour of the resins, comparing between **1a** and **1e**. The induction period decreased in the order 1% > 20% > 10% > 5% > 3% [Fig. 1(b)]. In the case of the 1% PBG unit, the amount of photogenerated amines would not be adequate to trigger the base-proliferation reaction. Except for this case, decreasing the amount of PBG units increased the decomposition rate. Because PBG units are not decomposed by amine catalysts, they do not contribute to base-proliferation reactions. The

density of the BA units was found to be a key factor for effective reaction during PEB. A similar decomposition behavior was observed in measurements using films of resins **1f-1h** synthesized from BA monomer **2**, PBG monomer **3**, and TEOS (0.7–0.9 μ m in thickness, Fig. 2). The induction periods of these films (50–120 min) were longer than those of films of **1a–1e**, and a higher heating temperature (110 °C) was required. Nevertheless, the carbonyl groups decomposed in a non-linear manner, and the induction period decreased with increasing irradiation energy. Resin **1g** containing 4% PBG units reacted more sensitively than resin **1h** containing 7% of



FIGURE 4 Photosensitivity curves (a) of films of 1c-1e after heating for 15 min and (b) of a film of 1d. The PEB temperature was 100 °C.

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FIGURE 5 (a) Photosensitivity curves of films of **1h** after heating at 120 °C for 60 min, or at 100 °C for 15 min. (b) Photosensitivity curve of a film of **1h** after capping silanol groups with trimethylchlorosilane, heating at 120 °C for 60 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the units. This shows that the ratio of BA units to PBG units was crucial for an effective decomposition reaction.

Photosensitivity Determination

Evaluation of photosensitivity was performed with films of resins **1c-1e**, and **1h** (0.9 μ m, Fig. 3). After 365 nm light irradiation and PEB at 100 °C, the film was developed using chloroform for 30 s. The thickness of the remaining film was measured and plotted as normalized film thickness against UV irradiation energy. Figure 4(a) shows photosensitivity curves for films of resins **1c**, **1d**, and **1e**. These curves indicate that the resins functioned as negative-working resists that were insolubilized by increasing irradiation energy.

A film having a lower fraction of PBG units showed higher sensitivity. The sensitivity was improved by increasing the heating time [Fig. 4(b)]. These results would be because of promotion of the base-proliferation reaction. With heating for 30 min at 100 °C, high photosensitivity (8.1 mJ cm⁻²) was accomplished using resin **1d** containing 10% PBG units.³⁸ The normalized film thickness was about 0.4, probably because carbon dioxide and dibenzofulvene could be removed during PEB and subsequent development.

In the case of **1h** film having TEOS units, 400 mJ cm⁻² of irradiation energy was required with heating for 15 min (Fig. 5). In contrast, the film was insolubilized without



FIGURE 6 Sensitivity curves of films of resin **4** having blank/PBG units (blank:PBG = 74:26, \bigcirc) and resin **5** having BA/PBG units (BA:PBG = 82:18, •). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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FIGURE 7 (a) Negative-tone micropatterns of a film of **1e** containing 20% PBG units after UV irradiation at 110 mJ cm⁻² through a photomask, PEB at 100 °C for 25 s and development with benzene for 30 s. (b) 10×10 , 6×10 , and $4 \times 10 \mu$ m line-and-space patterns. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

irradiation after heating for 60 min at 120 °C, probably because of a condensation reaction between the remaining ethoxy silyl groups or silanol groups. Trimethylchlorosilane was then used to cap the remaining silanol groups. A photosensitivity of 30 mJ cm⁻² for the resin film was accomplished by heating for 60 min at 120 °C. TEOS units could contribute to increasing the value of the normalized film thickness to about 0.6, although the units would decrease the density of PBG and BA units, leading to low photosensitivity.

To evaluate the effect of the base-proliferation reaction by BA/PBG units on the photosensitivity, an additional experiment was performed (Fig. 6).39 Instead of BA units, blank units having amines capped by 9-fluorenyloxycarbonyl groups were combined with PBG units. The ratio of blank/ PBG units of the resulting resin 4 was 74/26. This resin does not undergo the base-proliferation reaction, while the PBG units generate primary amines. The corresponding resin 5 was also synthesized in a similar manner where the ratio of BA/PBG units was 82/18. UV irradiation towards films of these resins (0.8-0.9 µm in thickness) was performed using a Hg-Xe lamp without a glass filter, followed by PEB at 100 °C for 20 min. The film was developed using chloroform for 30 s. It took 240 s to obtain the value of 0.31 of normalized film thickness in the case of resin ${\bf 4}.$ On the other hand, it took just 0.49 s in the case of resin 5, where the value was 0.47. Interestingly, the photosensitivity of resin 5 was ca 490

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times enhanced compared with resin **4**, even though resin **5** has a smaller amount of PBG units than resin **4**. This would strongly demonstrate that introducing base-proliferation reactions to photoresist systems is a powerful approach for enhancement of the photosensitivity of materials consisting of base-reactive polymers and PBGs.

These resins could be applied to fabricate micropatterns, and a demonstration was performed. A film of resin **1e** (film thickness: 0.9 μ m) containing 20% PBG units was used. Irradiation with 365 nm light (110 mJ cm⁻²) followed by PEB at 100 °C for 25 s successfully gave 10 \times 10, 6 \times 10, and 4 \times 10 μ m line-and-space patterns, where development with benzene for 30 s was performed (Fig. 7).

CONCLUSIONS

Base-proliferation reactions in which BA units are decomposed autocatalytically using a base catalyst can be integrated in a photoresist system with a photobase generator, as required for enhancement of photosensitivity. Silicone resins bearing both BA units and PBG units were synthesized. TEOS was utilized as a spacer unit, resulting in relatively high molecular weights. The BA units in these resins were found to be decomposed abruptly after an induction period, which indicated autocatalytic decomposition triggered by amines generated from PBG units. High photosensitivity, 8.1 mJ cm⁻², was accomplished using a film of the resin containing 10% PBG units with PEB for 30 min at 100 °C. To our great delight, the potential ability of the base-proliferation reaction was clearly shown by comparison between resins having blank/PBG or BA/PBG units, which showed about 490 times enhancement of photosensitivity. Finally, a negative-tone relief image with 4 \times 10 μ m line-and-space pattern was successfully fabricated, which was comparable to a conventional acid-amplifying resist.

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38 In this work, photosensitivity was defined as the irradiation energy or time for remaining more than 30% of the film thickness.

39 Synthetic procedures for resins **4** and **5** are shown in Supporting Information. For sensitivity determination, a solution of resin **4** or **5** (0.1 g) in chloroform (1 mL) was spin cast onto a Si substrate, and prebaked at 100 °C for 1 min. The film of **1** was exposed to UV light irradiation and subsequent heating (PEB) at 100 °C for 20 min. Development of the film was performed with chloroform for 30 s to obtain photosensitivity curves. The normalized film thickness was calculated as the ratio of the film thickness after the developing process to the thickness before UV irradiation.