A Novel Negative-working Photoimaging Material Based on a Base-amplifying Silicone Resin Tethering Phenylsulfonylethyl Groups

Satoru Inoue,[1] Koji Arimitsu,*[1] Yoshimoto Abe,[1] and Kunihiro Ichimura[2,3]
[1] *Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science,*
2641 Yamazaki, Noda 278-8510
[2] *Center of Advanced Photopolymers, Faculty of Science, Toho University, Chiba 274-8510*
[3] *Research Center for Materials with Integrated Properties, Toho University, Chiba 274-8510*

(Received August 1, 2007; CL-070819; E-mail: arimitsu@rs.noda.tus.ac.jp)

We have developed a base-sensitive silicone resin tethering phenylsulfonylethyl units as base-amplifying groups showing high thermal stability. The resin underwent a base proliferation reaction autocatalytically to generate amino groups on its side chains, which accelerated the base-catalyzed hydrolytic condensation of residual ethoxysilyl units in its main chain. Furthermore, a film of the resin sensitized with a photobase generator provided a negative-working photoimaging material with a high sensitivity.

We have proposed the concept of base proliferation to improve the photosensitivity of photopolymers composed of a photobase generator (PBG) and a base-labile polymer.[1] Our concept involves the base-catalyzed autocatalytic fragmentation of an organic compound (referred to as a base amplifier) to generate newborn base molecules. A small amount of photogenerated base triggers a base proliferation reaction of the base amplifiers in the base-sensitive polymer film, leading to the enhancement of the base-catalyzed reactions of the polymer, resulting in the photosensitivity enhancement of the photopolymer. We have already developed base-reactive silicone resins tethering 9-fluorenylmethylcarbamoyl units as base-amplifying groups.[2] These resins sensitized with PBG provide negative-working photoresists that show a high sensitivity of 2.5 mJ/cm^2 in light at 254 nm and 8.1 mJ/cm^2 in light at 365 nm. This is because the base-catalyzed decomposition of the silicone resin proceeds autocatalytically to generate newborn amino groups in the side chains, leading to an enhancement of the base-catalyzed hydrolytic condensation reactions of the residual alkoxysilyl units in the main chains to form a cross-linked network. However, because a resin film containing PBG decomposes on heat treatment at 100 °C for a period of 20 min without UV-irradiation, the thermal stability of these resins is relatively low.[3] The thermal stability of these resins depends on their side chains, i.e., the 9-fluorenylmethylcarbamoyl units. On the other hand, we have also reported on phenylsulfonylethyl carbamates as base amplifiers having a high thermal stability compared with 9-fluorenylmethyl carbamates.[4] Here, we report on the photosensitivity characteristics of a novel base-amplifying silicone resin **1** having phenylsulfonylethylcarbamoyl groups, which shows autocatalytic fragmentation to form amino groups in its side chains (Scheme 1).

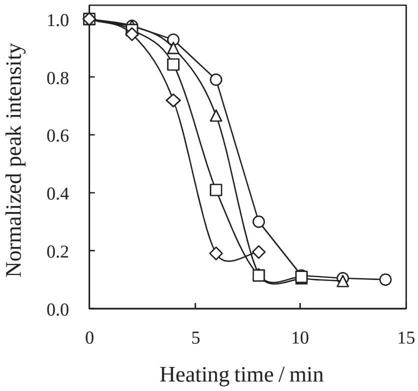
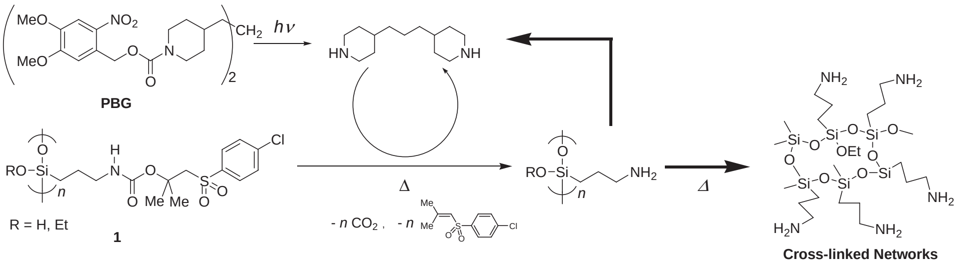


Figure 1. Time courses of the thermal decomposition of films of **1** containing 10 wt % PBG after irradiation at 365 nm with an exposure dose of 0 mJ/cm^2 (○), 10 mJ/cm^2 (△), 100 mJ/cm^2 (□), and 1000 mJ/cm^2 (◇), after being heated to 140 °C.

The silicone resin **1** was prepared by the acid-catalyzed hydrolytic polycondensation of the corresponding monomer, which was synthesized from the reaction of 3-isocyanatopropyltriethoxysilane with 1-(4-chlorophenylsulfonyl)-2-methylpropan-2-ol.[5] The GPC chromatogram of **1** showed that resin **1** was an oligomer ($M_w = 4000$, $M_w/M_n = 1.1$). The DSC thermogram of **1** showed a glass-transition temperature (T_g) and a decomposition temperature (T_d) of $T_g = 67\,°C$ and $T_d = 177\,°C$. These results indicate that **1** has sufficient thermal stability for photoimage formation.

The thermal decomposition behavior of films of **1** contain-



Scheme 1. The phototriggered base proliferation reaction of **1** leading to a cross-linked network.

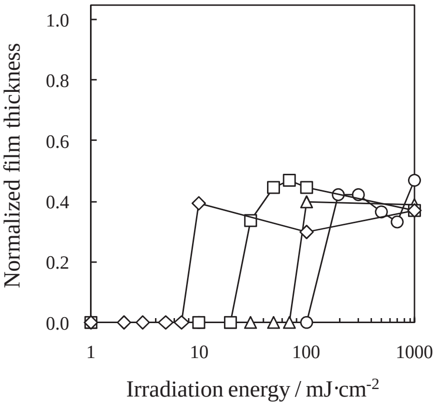


Figure 2. Photosensitivity curves of films of **1** composed of 10 wt % PBG exposed to light at 365 nm and heated to 140 °C for a period of: 6 min (○), 7 min (△), 8 min (□), and 9 min (◇).

ing PBG was evaluated using UV absorption measurements.[5] The progress of the base proliferation reaction of **1** results in the elimination of its aromatic rings, which are immediately vaporized. This enables us to examine the decomposition of films of **1** by monitoring the changes in the UV absorption spectra due to the loss of the aromatic rings of **1**. The data shown in Figure 1 were obtained by plotting the peak intensity of the absorption band at 230 nm from a film of **1** containing PBG as a function of heating time. The peak intensity decreased immediately, displaying an *S*-shaped conversion curve. An *S*-shaped conversion curve means that there was a progression of the base proliferation reaction of **1**, even in the film state. The data in Figure 1 also show that the induction period depended on the UV-irradiation energy. This means that the base proliferation reaction of **1** was triggered by photogenerated bases.

The base proliferation reaction of **1** gives rise to the autocatalytic formation of amino groups in its side chains. These amino groups accelerate the base-catalyzed hydrolytic condensation reactions of the residual ethoxysilyl units in its main chain to form a cross-linked network. Consequently, resin **1** may be insoluble in organic solvents. Films of **1** sensitized with PBG after irradiation with light at 365 nm and a heat treatment were developed using chloroform. The residual film thickness was measured to obtain the photosensitivity curves.[5] Films for sensitivity determination were about three times as thick as films used in Figure 1 and were thermally stable during the conditions to determine sensitivity. As shown in Figure 2, negative-type photosensitivity curves were obtained. It is clear that the photosensitivity, which was defined as the irradiation energy required for the reduction of a normalized film thickness by a value of 0.4, was influenced by the heating period. As shown in Table 1, the exposure dose was reduced to 10 mJ/cm^2 when the film was heated to 140 °C for a period of 9 min. These results show that the base proliferation reaction of **1** proceeded effectively to proliferate amino groups, leading to the enhancement of the base-catalyzed hydrolytic condensation reaction of the residual ethoxysilyl groups of **1**, resulting in the formation of an insoluble resin. Resin **1** sensitized with PBG exhibited a higher photosensitivity compared with conventional photoresists that rely on base-catalyzed reactions.[6]

Table 1. Sensitivity of films of **1** containing 10 wt % PBG[a]

Run	Heating periods[b]/min	Sensitivity[c]/mJ·cm^{-2}
1	6	200
2	7	100
3	8	30
4	9	10

[a]Films of **1** developed with chloroform. [b]Films of **1** heated to 140 °C. [c]Sensitivity is defined as the irradiation energy required for the reduction of the normalized film thickness by a value of 0.4.

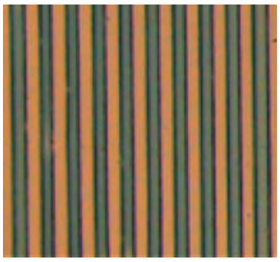


Figure 3. Lithographic image of a 10-μm line and space film of **1** sensitized with 10 wt % PBG.

Microphotopatterning was carried out in a preliminary evaluation.[5] A 1.0-μm thick film of **1** containing 10 wt % PBG was exposed to light at 365 nm with a dose of 300 mJ/cm^2, heated to 130 °C for a period of 10 min, and developed with chloroform for a period of 30 s. A clear negative-tone image with a 10-μm line and space resolution was obtained, as shown in Figure 3, although further optimization is needed.

In summary, we have developed a thermally stable base-amplifying silicone resin **1** having phenylsulfonylethyl units. Films of resin **1** underwent base proliferation reactions that were triggered by a small amount of photogenerated amine molecules. Combining this resin with PBG provided a negative-working photoimaging material. In addition, the photosensitivity increased with increasing heating period, and the exposure dose was reduced to 10 mJ/cm^2 for a film of **1** heated to 140 °C for a period of 9 min. This system showed a higher photosensitivity compared with conventional photoimaging materials utilizing base-catalyzed reactions.

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