Synthesis of Phenylsulfonylethylene Carbamates as a Base Amplifier and Their Applications to Photopolymer Systems

Mana Miyamoto, Koji Arimitsu and Kunihiro Ichimura*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Keywords: base proliferation reaction, base amplifier, autocatalytic reaction, photopolymer

The concept of acid proliferation to enhance the photosensitivity of a chemically amplified photoresist was proposed in our laboratory.[1] The concept involves the acid-catalyzed decomposition of an organic compound termed as an acid amplifier, which releases another strong organic acid, leading to the autocatalytic decomposition. The addition of the acid amplifier to a chemically amplified photoresist which consists of a photoacid generator and an acid-labile polymer resulted in the enhancement of photosensitivity.[2-4]

Photoimaging materials based on base-sensitive polymers catalyzed by photogenerated bases have been reported.[5-7] But the number of this type of works have been limited when compared acid-sensitive photopolymer systems probably because of their low photosensitivity. In this context, the concept of base proliferation is needed to improve their photosensitivity in a manner similar to acid proliferation-type photopolymer systems.

Our recent efforts have been focused on the development of base amplifiers which are susceptible to a base-catalyzed β-elimination to release another base molecules, leading to the autocatalytic decomposition. In this communication, we report a novel base proliferation of phenylsulfonylethylene carbamates, which are referred to as a base amplifier and combined with a base-sensitive polymer to present a way to enhance the photosensitivity of this kind of photopolymers.

We designed 1-(1,1-dimethyl-2-phenylsulfonylethyleneoxycarbonyl)piperidine 1 and 1,3-bis[1-(1,1-dimethyl-2-phenylsulfonylethyleneoxycarbonyl)-4-piperidinyl]propane 2 as base amplifiers. Both of them were anticipated to be decomposed autocatalytically by the action of a base catalyst, leading to the base proliferation (Scheme 1). They were synthesized by the Grignard reaction of phenylsulfonylethylmagnesium bromide with acetone to give 1,1-dimethyl-2-phenylsulfonylethanol-1[8], which was subsequently treated with p-nitrophenyl chloroformate, followed by piperidine and 1,3-dipiperidinylpropane, respectively, in the presence of 1-hydroxybenzotriazole.[9]

The thermal decomposition behavior of 1 in methanol-d4 sealed in a tube was studied by NMR spectroscopy. The decomposition was induced by 13 mmol dm⁻³ of piperidine at 100 °C, while no change was observed in the absence of piperidine.

Figure 1 Chemical structures of compounds used in the photopolymer system.

at the same temperature. The consumption of 1 took place abruptly after heating for about 80 min to display a sigmoidal time conversion course. This indicates that 1 is decomposed autocatalytically to proliferate piperidine molecules.

To examine the effect of the carbamates on the improvement of photosensitivity of a base-sensitive polymer, 2 as a base amplifier was added to poly(glycidyl methacrylate) (PGMA) as a base-labile polymer sensitized with 1,3-bis(2-nitrobenzylxycarbonyl-4-piperidinyl)propane 3 as a photobase generator which are known to react readily with epoxides (Figure 1). The carbamate 2 was used in place of 1 here, taking notice of the volatility of piperidine generated from 1. A photopolymer solution was prepared by dissolving PGMA (8 wt %), the carbamate 2 (20 wt % relative to the polymer) and 3 (10 wt % relative to the polymer) in 2-methoxyethyl acetate. The polymer solution was spin-coated on silicon wafers and prebaked on a hot-plate at 130 °C for 60 sec to give a thin film of 0.32 mm in thickness. Thin films were exposed to UV light, followed by heating at 130 °C for 15 min to be subjected to the development with 2-methoxyethyl acetate.

Figure 2 shows the addition effect of 2 on the photosensitivity curves of PGMA films containing 3. The sensitivity is defined as the irradiation time required for the reduction of normalized film thickness by half. The presence of 2 gave rise to the improvement of photosensitivity by about 3 times. The results suggest that the proliferation of base molecules takes place in the polymer film to bring about the cross-linking of the polymer effectively.

In conclusion, we designed and synthesized novel compounds as a base amplifier which accelerates the photoinduced insolubilization of PGMA. The present preliminary experiments support that the incorporation of the base proliferation in base-sensitive photopolymer systems is a promising way to enhance photosensitivity of this sort of polymers.

Figure 2 The characteristic curves of PGMA films containing 10 wt % of the photobase generator 3 in the absence (●) and in the presence of 20 wt % of 2 (○).

References