Synthesis of Phenylsulfonyl ethyl 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 phenylsulfonyl ethyl 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-phenylsulfonylethoxycarbonyl)piperidine **1** and 1,3-bis[1-(1,1-dimethyl-2-phenylsulfonylethoxy-carbonyl)-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 phenylsulfonyl ethylmagnesium 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-*d*₄ 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

Scheme 1 Base proliferation of carbamate **1**.

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-nitrobenzyloxycarbonyl-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

1. K. Ichimura, K. Arimitsu and K. Kudo, *Chem. Lett.* (1995) 551.
2. K. Ichimura, K. Arimitsu, S. Noguchi and K. Kudo, *ACS Smp. Ser.* **706** (1998) 161.
3. K. Arimitsu, K. Kudo and K. Ichimura, *J. Am. Chem. Soc.* **120** (1998) 37.
4. K. Arimitsu and K. Ichimura, *Chem. Lett.* (1998) 823.
5. E. J. Urankar, I. Brehm, Q. J. Niu and J. M. J. Fréchet, *Macromolecules* **30** (1997) 1304.
6. E. J. Urankar and J. M. J. Fréchet, *J. Polymer. Sci. Part A* (1997) 3543.
7. T. Nishikubo, E. Takehara, and A. Kameyama, *Polym. J.* **25** (1993) 421.
8. L. Field, *J. Am. Chem. Soc.* **74** (1952) 3920.
9. A. Mochizuki, T. Teranishi and M. Ueda, *Macromolecules* **28** (1995) 362.