Synthesis of Novel Monodispersed Dendritic Base Amplifiers to Apply to Negative-tone Photoresists

Ken'ichi Aoki^{a,b,*}, Tsutsumu Hashimoto^a and Kunihiro Ichimura^c

^a Graduate School of Chemical Sciences and Technology,
Tokyo University of Science, Tokyo 162-8601, Japan

^b Faculty of Science, Tokyo University of Science, ^c Soan Lab
k-aoki@rs.tus.ac.jp

Keywords: dendrimer, base amplifier, base proliferation reaction, photoresist

1. Introduction

The base proliferation reaction is based on the autocatalytic decomposition of 9-fluorenyl methoxycarbamate (Fmoc) derivatives called “base amplifiers”, which can release newborn amines in a non-linear manner as shown in scheme 1[1]. We have recently begun to synthesized novel types of dendritic base amplifiers having multiple Fmoc units at the

Scheme 1. Concept of base proliferation reaction.

surface of the molecules, aiming at the efficient diffusion of the catalytic amine species in photoresist films.[2,3] However, our previous works on the dendritic base-amplifiers focused on low-molecular-weight (three- or four-armed) [3] and/or polydispersed hyper-branched base amplifiers ($M_w/M_n > 1.5$) [2]. We discuss herein the synthesis of novel monodispersed ($M_w/M_n < 1.07$) dendritic base amplifiers in a convenient manner, applying to the negative-tone photoresist systems with high photosensitivity by the combination of conventional photobase generator (PBG) and epoxy resins.

2. Method

Monodispersed dendritic base amplifiers (**BA8** and **BA16** in scheme 2) were synthesized

through Michael addition of *N*-(2-mercapto)-9-fluorenylmethylcarbamate (**Fmoc-SH**) [4] to the dendritic polyacrylates. The dendritic base amplifiers of **BA8** and **BA16**, a conventional photobase generator (**PBG**) [1-3] and poly(glycidyl methacrylate) (**PGMA**, $M_w = 1.30 \times 10^4$, $M_w/M_n = 2.4$) were dissolved in mixture solvent (chloroform: propyleneglycol methylether acetate (**PGMEA**) = 1:1, v/v), and spin-cast onto glass substrates. The films were exposed to 365 nm UV light, heated at 100 °C, and developed with **PGMEA**.

Scheme 2. Chemical structures of dendritic base amplifiers of **BA8** and **BA16** used in this study.

3. Results and Discussion

Dendritic base-amplifiers having 8- and 16-terminal Fmoc units (**BA8** and **BA16**) were conveniently prepared through Michael addition of **Fmoc-SH** to corresponding dendritic polyacrylates (**Ac8** and **Ac16**), which can be conveniently synthesized in large scales thorough AMA process [5]. Gel-permeation chromatography analysis revealed that the base-amplifying dendrimers exhibited $M_w = 4.29 \times 10^3$, $M_w/M_n = 1.04$ for **BA8** and $M_w = 8.95 \times 10^3$, $M_w/M_n = 1.07$ for **BA16**, respectively, indicating that both of the dendrimers are sufficiently monodispersed.

Spin-cast films composed of **BA**(*n*) (*n* = 8 and 16), **PBG** and **PGMA** were exposed to UV light (365 nm), followed by post-exposure baking (PEB) at 100 °C for 15 min. Each film became insoluble in organic solvent (**PGMEA**) during the process due to the occurrence of the base proliferation and the subsequent crosslinking reactions of the epoxy resins (**PGMA**). The photosensitivity curves were constructed by tracing the residual film thickness after exposure and PEB, which are summarized in Figure 1. It was found that each film began to insoluble at the lower exposure dose as the increase in the number of the terminal functional groups from *n* = 3 to 16. The photosensitivity of each film is estimated to be 90 mJ cm⁻² for **BA8** and 17 mJ cm⁻² for **BA16** in a concentration of Fmoc units of 1.0×10^{-3} mol g⁻¹. We have previously reported that the three- and four-armed base amplifiers (**BA3** and **BA4**) hardly give rise to base amplifying reaction [3] at the PEB temperature of 100 °C, exhibiting 1000 (**BA3**) and 1200 mJ cm⁻² (**BA4**) in photosensitivity, while the 16-terminal hyper-branched base-amplifier (**HB-BA16**) [2] with wide molecular weight distribution ($M_w/M_n > 1.5$) required larger exposure dose (160 mJ cm⁻²) for the insolubilization compared with the monodispersed **BA16**.

The effect of the dendrimerization of the base amplifiers on the photosensitivity is likely to arise mainly from following two factors: One is the local concentration of the Fmoc units to serve the efficient base proliferation reactions at the surface of the molecules. The other is the formation of monodispersed dendritic polyamines as the result of the base amplifying reaction, which can promote efficient crosslinking reaction of the epoxy resin in films.

Figure 1. Photosensitivity curves of the photoresist films composed of PBG, PGMA and dendritic base amplifiers of **BA3** (●), **BA4** (×), **BA8** (○) and **BA16** (+). Concentration of Fmoc units: 1.0×10^{-3} mol g⁻¹. PEB condition: 15 min. at 100 °C.

As a consequence, the monodispersed dendritic base-amplifier of **BA16** exhibits excellent photosensitivity, which is *ca.* 50 times higher than that of **BA3** and *ca.* 10 times higher than that of the polydispersed **HB-BA16**.

In summary, base-amplifying and following crosslinking reactions of epoxy resins were accelerated in films by using the novel monodispersed base amplifiers, which contributes to the practical application of the negative-tone photoresists with excellent photosensitivity.

Acknowledgements

This study was supported by Grants-in-Aid for Scientific Research (K. A.; No. 23710134).

References

- (a) K. Arimitsu, M. Miyamoto and K. Ichimura, *Angew. Chem. Int. Ed. Engl.*, **39**, 3425 (2000). (b) K. Ichimura, *Chem. Rec.*, **2**, 46 (2002). (c) K. Arimitsu and K. Ichimura, *J. Mater. Chem.*, **14**, 336 (2004).
- K. Aoki, R. Sakurai and K. Ichimura, *J. Photopolym. Sci. Technol.*, **20**, 277 (2007).
- K. Aoki, R. Sakurai and K. Ichimura, *Macromol. Chem. Phys.*, **210**, 1303 (2009).
- Y. Miura, T. Arai and T. Yamagata, *Carbohydr. Res.*, **210**, 1303 (1996).
- (a) K. Aoki and K. Ichimura, *Chem. Lett.*, **38**, 990 (2009). (b) K. Aoki and K. Ichimura, *Bull. Chem. Soc. Jpn.*, **84**, 1215 (2011).