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

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1. Introduction

The base proliferation reaction is based on the autocatalytic decomposition of 9-fluorenyl methyloxy carbamate (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 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: propylene glycol 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 1. Concept of base proliferation reaction.

Scheme 2. Chemical structures of dendritic base amplifiers 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 polycrylates (Ac8 and Ac16), which can be conveniently synthesized in large scales thorough AMA process [5]. Gel-permiation chromatograpy 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 $1.0 \times 10^{-3}$ 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.

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 closslinking 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.

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References