Electron Beam-Induced Reactions of a Sulfonium Salt in the Solid State for Chemically Amplified Electron Beam Resists; Comparison with Photolytic Reactions

Seong-Yun Moon, Yasunari Maekawa,* and Masaru Yoshida

Department of Material Development, Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, 1233 Watanuki, Takasaki, Gunma 370-1292, Japan

Keywords: sulfonium salt, photoacid generator, electron beam, deep UV, resist

1. Introduction

The electron beam (EB) resist system [1] has attracted great attention as a candidate for future lithography with its high resolving capacity, as compared with optical lithography which has resolution limitation due to its wavelength. High sensitivity in photoresists can be achieved by the incorporation of a chemical amplification concept, in which a photoacid generator (PAG), such asonium salts, decomposes to yield strong acids which amplify photochemical reactions in the resist films [2]. However, the current sensitivity and resolution are not sufficient for EB lithography, because onium salts were optimized for optical sources such as a UV light or an excimer laser. From such a point of view, it is important to explore organic compounds that are highly susceptible to EB to develop high performance EB resists.

Sulfonium salts that produce strong Brønsted acids on photolysis by UV irradiation have been widely employed as PAG for chemically amplified photoresists. Direct photolysis of sulfonium salts in the matrix (solvents or polymers) was known to mainly proceed through a cationic mechanism by phenyl cation intermediates [3]. On the other hand, an EB-induced reaction is recognized to proceed predominantly through the ionization process, which is different from a photoreaction through the excited state, because the potential energy of EB is much higher than the ionization potential of sulfonium salts. The EB irradiation of sulfonium salts in the matrix ionizes the matrix to offer electrons and radical cations, and then the salts that have scavenged the released electron generate phenyl radicals as an intermediate species [4]. Upon the EB irradiation, even though the intermediate species is different, the final products are the same as those in photolysis (Scheme 1).

Though the matrix effect is known to be an important characteristic in EB-induced reactions, no study has yet been reported for sulfonium salts in the solid state that are directly ionized by EB. We have recently found that an EB irradiation of triphenylsulfonium methanesulfonate 1 in the solid state provides a new benzene-substituted sulfonium salt [5]. This paper describes difference in the EB-induced and photochemical reactivities of 1 in the solid on the basis of product analysis.

2. Experimental

2.1. Materials and Instruments

All the chemicals used for synthesis of the sulfonium salt 1 were purchased from Aldrich Chemical Company. The high performance liquid chromatography (HPLC) system for quantitative analysis of EB-induced products consisted of a pump (Hitachi, L7100), a UV detector (Hitachi, L7400, operated at \( \lambda = 235 \) nm), and a column (Showa Denko, Shodex ODSpak F511, packed with 5 µm octadecyl-bonded siloxanes). The eluent passing the column at 40 °C with a flow rate of 1 mL/min was a mixture of 10 mL pH 2 buffer solution (Kishida, Osaka), 20 mL H2O and 90 mL acetonitrile.

2.2. Synthesis

The introduction of methanesulfonate into the anionic moiety of sulfonium salt enables us to analyze the structure of EB-induced products by \(^1\)H and \(^13\)C NMR. The sulfonium salt 1 comprising the anionic methanesulfonate moiety was synthesized.
by condensation of diphenyl sulfoxide with benzene in the presence of a 1:10 mixture of phosphorus pentoxide in methanesulfonic acid [6]. After the reaction was performed at ca. 70 °C, the reaction product diluted in distilled water was salted out with sodium methanesulfonate and extracted with methylene chloride (MC). The pale yellow product 1 was obtained in a yield of 57%. The structure of the salt was confirmed by $^1$H and $^{13}$C NMR, HPLC, and UV-visible spectroscopy.

3. Results and Discussion

Fine powder 1 (0.07 g) was charged into a hollow with 10 mm diameter and 1 mm thickness of a glass plate. The samples, which were covered with a Kapton film (12 µm thickness) and placed on the water-cooled copper metal plates, were irradiated with EB of 1 MeV-0.5 mA (0.616 µC cm$^{-2}$s$^{-1}$) using a cascade type electron accelerator (Dynamitron) in an atmosphere of argon and air. Direct photolysis of 1 in the solid state was performed in the similar manner as above. The sample 1 (0.07 g) was charged into a hollow with 30 mm diameter and 0.1 mm thickness of a quartz plate and then superposed with another quartz plate. The sample 1 between two plates was exposed stepwise in the dose range of 0 to 200 J/cm$^2$ at 254 nm light.

The EB-induced and photochemical reactions of 1 in the solid state were monitored by HPLC, as shown in Fig. 1. When the sulfonium salt 1 was irradiated with a dose of 752 µC/cm$^2$ under argon gas, five major peaks appeared in the HPLC profile (Fig. 1a). Four of the products were assigned to be the same products as those by photolysis of sulfonium salts in solutions and polymer films from the previous reports [3]. The peak at 3.6 min was the sole product that has not been observed either by photolysis in both a solution and a polymer film nor by EB irradiation in a solution. While the other four peaks increased with increase in the exposure, the new peak reached the maximum at 806 µC/cm$^2$ (Fig. 1a) and again began to decrease at further exposure doses (Fig. 1b). This new peak was assigned to be three regio-isomers of a benzene-substituted sulfonium salt 2 by HPLC, UV, GC-MS, and $^1$H and $^{13}$C NMR analyses (Scheme 1). Methanesulfonic acid 7 was observed in $^1$H and $^{13}$C NMR spectra as a sole reaction product from the anionic moiety when 1 and the

![Scheme 1. Photolytic and EB-Induced Products of Sulfonium Salts.](image)

![Fig. 1. HPLC profiles of the EB and UV light-irradiated 1. EB: (a) 806 µC/cm$^2$, (b) 2690 µC/cm$^2$, UV: (c) 85.3 J/cm$^2$.](image)
new salt decomposed in nearly quantitative yields (> 95 %) with an irradiation dose of 2690 µC/cm². Fig. 1c shows the HPLC profile after the exposure of 1 in the solid state at 85.3 J/cm² under deep UV of 254 nm. The four peaks in the chromatogram are assigned to be the same photolytic products 3-6 as those in the matrix photoreactions [3]. Though the new salt 2 was also observed in the HPLC, the peak intensity was much smaller during the whole course of photolysis than that in the EB-induced reaction of 1.

The quantitative analysis of the EB-induced and photochemical reactions of 1 in the solid state was carried out. The concentration of each product at each dose is evaluated by the peak area in HPLC profiles and the molar extinction coefficient from UV-visible spectra. The results are exhibited in Figs. 2 and 3 as plots of the relative concentration of the products on the basis of initial concentration of 1 ([1]₀) against the exposure dose.

As can be seen in Fig. 2, 1 decomposed in the solid state with the conversion of more than 80 % at EB dose of 2149 µC/cm². The new salt 2 was accumulated at an early stage, and reached the maximum concentration (25 % among all the products) at 806 µC/cm² and then gradually decomposed to the final products, 3, 4, 5 and 6. As shown in Fig. 3, the concentration of 1 also decreased exponentially with increasing the dose of UV irradiation and about 80 % of 1 decomposed at 200 J/cm². The salt 2 was also accumulated during UV exposure. However, the relative concentration of 2 reached only 3 % among all the products at 150 J/cm² as a maximum concentration. This maximum concentration of 2 upon UV exposure is the eighth of that with EB irradiation.
Therefore, the formation of the new salt 2 is very efficient in the reaction of 1 initiated by EB irradiation, compared with the initiation via the UV excitation.

Judging from the comparison of the EB-induced reaction with the photochemical one, most of the salt 2 must generate through the specific path for EB-induced reaction. As previously reported, direct photolysis of sulfonium salts mainly generate phenyl cation via singlet state to give substitution products such as 4, 5, and 6. However, phenyl cation, which reacts with 1 to give 2, should be ruled out as an intermediate due to the repulsion between the cationic moiety of 1 and the phenyl cation. Therefore, at present, the most probable intermediate for the generation of 2 is the phenyl radical that reacts with the starting sulfonium salt 1. Further studies on the detailed mechanism are currently in progress.

4. Conclusion

The EB irradiation of the sulfonium salt 1 in the solid state offers a new benzene-substituted sulfonium salt 2. The new product 2 was accumulated as an intermediate product at an early stage, and then it gradually decomposed to final products. On the basis of product analysis, upon EB irradiation, the content of the product 2 with the maximum concentration at the exposure dose of 806 µC/cm\(^2\) was 25 % of all the EB-derived products, while the maximum concentration of 2 was only 3 % of all the UV-derived products upon UV irradiation at 150 J/cm\(^2\), indicating that the new salt forms in peculiar mechanism for EB-induced reactions. The EB-induced decomposition of 1 in the solid is considered to proceed through the radical mechanism by a phenyl radical intermediate.

References