Photochemistry of Imino Sulfonate Compounds and
Their Application to Chemically Amplified Resists

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Compounds that generate strong acids upon irradiation are of interest in microlithography. The chemistry of onium salts that photochemically generate strong acids has been studied by Crivello [1], and the application of onium salts to lithography has been described by Ito and coworkers [2]. The onium salts have several disadvantages, e.g., poor solubility in organic solvents and the presence of undesirable elements such as arsenic or antimony which affect device characteristics. Synthesis of nitrobenzyl esters of sulfonic acids and their applications to lithography have been studied by Reichmanis and coworkers [3]. Recently we have reported that imino sulfonate compounds can form sulfonic acids on photolysis [4]. Negative-type and positive-type photoresists using the photolysis of imino sulfonates have been reported [5,6]. In this paper we report an application of imino sulfonates (1 - 4) to the chemically amplified resist system. Since poly(p-tert-butoxycarbonyloxystyrene) (PBOS) is converted to a phenolic polymer by thermolysis and the temperature of onset of deprotection of tert-butoxycarbonyl (t-BOC) groups from PBOS decreases in the presence of acids, upon postbake the exposed PBOS containing photoacid generating compounds becomes soluble in aqueous alkaline solutions. Thus PBOS is particularly useful to study the application of imino sulfonates to the chemically amplified resist system.

p-tert-Butoxycarbonyloxystyrene and its corresponding polymer (PBOS) were synthesized according to the literature [7]. 9-Fluorenylideneimino p-toluenesulfonate (1) was prepared from p-toluenesulfonyl chloride and 9-fluorenone oxime: mp. 160 °C. Syntheses of 1,2,3,4-tetrahydro-1-naphthylideneimino p-toluenesulfonate (2), 1-phenylethylideneimino p-toluenesulfonate (3), and 1,2,3,4-tetrahydro-1-naphthylideneimino methanesulfonate (4) were reported elsewhere [4]. Thermogravimetric analysis

was performed at a heating rate of 10 °C per minute for the dynamic measurements, while isothermal curves were obtained at 75-102 °C. The N₂ flow rate was held constant at 50 cc per minute. The solutions of polymers containing imino sulfonates were coated onto quartz plate. The film thickness was in the range of 0.5-1.0 μm. The photochemical reactions were carried out with 313 or 254 nm light. The quantum yields (φ) for the photolysis of imino sulfonates in polymer films were determined as the number of moles of decomposed imino sulfonate per einstein of light absorbed by the imino sulfonate. The amounts of photoreacted imino sulfonates were determined by HPLC.

Table 1. Characteristics of selected imino sulfonates

Imino sulfonate	λ (log ε) ^{a)}		T _d (°C) ^{b)}
<u>1</u>	254 (4.73)	313 (3.51)	248
<u>2</u>	254 (4.18)	313 (1.41)	250
<u>3</u>	235 (4.09)	313 (0.30)	177
<u>4</u>	254 (4.13)	313 (1.40)	190

a) In dichloromethane at room temperature.

b) Temperature of onset of decomposition.

Scheme 1

Imino sulfonates are generally synthesized from a sulfonyl chloride and an oxime derived from ketones. Thus imino sulfonates showing a proper region of light absorption are easily obtained. On irradiation with UV light the cleavage of -O-N= bonds of imino sulfonates and the subsequent abstraction of hydrogen atoms lead to the formation of sulfonic acids accompanying the formation of azines, ketones, and ammonia. The intermediary imine is known to be easily hydrolyzed to a carbonyl compound (Scheme 1). The absorption peaks and the temperature of onset of thermal decomposition (T_d) of the selected imino

sulfonates are shown in Table 1. 1-4 showed λ_{max} around 254 nm where the molar extinction coefficients are very high. Although 2-4 did not show significant absorption peaks above 300 nm, 1 showed a shoulder peak at 313 nm, log ϵ being 3.51. The T_d values of 1-4 were 177 - 250°C, being comparable to those of 2,6-dinitrobenzyl esters of sulfonic acids [3]. Thermal stability under lithographic processing conditions is a key requirement that photoacid generating compounds must satisfy.

The quantum yields (ϕ) for the photolyses of 1 and 2 in films of poly(methyl methacrylate) (PMMA), Poly(butyl methacrylate) (PBMA), and PBOS with 313 or 254 nm light are shown in Table 2. The ϕ values did not strongly depend on the wavelength of irradiation light, the structures of imino sulfonates, and the polymer matrices. The content of imino sulfonate in polymer films did not significantly affect ϕ values.

Table 2. Quantum yields (ϕ) for the photolyses of 1 and 2 in polymer films

Polymer matrix	Imino sulfonate content (mol %)	ϕ			
		<u>1</u>		<u>2</u>	
		254 ^{a)}	313 ^{a)}	254 ^{a)}	313 ^{a)}
PMMA	3.0	0.35	0.16	0.17	0.17
PBMA	3.0	0.14	0.10	0.28	0.26
PBOS	6.5	0.10	0.11	-	-
PBOS	25	0.11	0.19	-	-

a) Wavelength of irradiation light.

Figure 1 shows the dynamic thermogravimetric analysis (TGA) scans of PBOS and exposed PBOS containing 4.4 or 15 mol% of 1. It is clear that the photochemical formation of acids in the polymer matrix results in a sharp decrease in the temperature required to remove the t-BOC groups. The activation energy for the deprotection of t-BOC groups of the exposed PBOS containing 4.5 mol% of 1 was 25 Kcal/mol in the temperature range of 75-102°C. This value was higher than that for the deprotection of t-BOC groups of poly(p-tert-butoxycarbonyloxy- α -methylstyrene) with p-toluenesulfonic acid [3].

Figure 2 shows the sensitivity curves of PBOS containing 3.3 mol% of 1. The normalized thickness remaining after postbake at 130°C for 10 min is plotted as a function of 313 nm exposure dose. The system functioned as a positive-type resist when the development was carried out with n-propanol/DMF=95/5 (v/v). When chloroform was used as a developer, it functioned as a negative-type photoresist. Thus, imino sulfonates are useful photoacid generating compounds which can be applied to the chemically amplified resist systems.

Fig.1 TGA scans of PBOS (—) and exposed PBOS containing 4.4 mol% (---) or 15 mol% (·····) of 1.

Fig.2 Exposure response curves for PBOS containing 3.3 mol% of 1: postbaked at 130 °C for 10 min. Developer: (●) CHCl₃, (○) n-propanol/DMF=95/5 (v/v).

References

1. J. V. Crivello, *Polym. Sci. Technol.*, **29** (1984), 351.
2. C. G. Willson, H. Ito, J. M. J. Frechet, T. G. Tessier, F. M. Houlihan, *J. Electrochem. Soc.*, **133** (1986), 1181.
3. T. X. Neenan, F. M. Houlihan, E. Reichmanis, J. M. Kometani, B. J. Bachman, and L. F. Thompson, *Proc. SPIE Int. Soc. Opt. Eng.*, **1086** (1989), 2.
4. M. Shirai, T. Masuda, M. Tsunooka, and M. Tanaka, *Makromol. Chem., Rapid Commun.*, **5** (1984), 689.
5. M. Shirai, T. Masuda, H. Ishida, M. Tsunooka, and M. Tanaka, *Eur. Polym. J.*, **21** (1985), 781.
6. M. Shirai, N. Katsuta, M. Tsunooka, and M. Tanaka, *Makromol. Chem.*, **190** (1989), 2099.
7. J. M. J. Frechet, E. Eichler, H. Ito, C. G. Willson, *Polymer*, **24** (1983), 995.