Synthesis of i- and g-Line Sensitive Photoacid Generators and Their Application to Photopolymer Systems

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We synthesized a series of i- and g-line sensitive non-ionic photoacid generators (PAGs). Photolysis and catalytic properties of the PAGs were examined. Photoreactivity of the PAGs was evaluated using UV-vis spectroscopy. The PAGs were used for photocrosslinking of epoxy-based polymers. The PAGs were also applied to positive-type photoresist materials. Sensitivity profile of the photoresists containing PAGs was affected not only by the photosensitivity of PAGs but also by the acidity of the generated acid. Post-exposure delay of the photoresists was dependent on the molecular size of the generated acid.

Keywords: photoacid generators, i-line, g-line, absorption, photoresist

1. Introduction

Photoacid generators (PAGs) are very important in the area of photo-curing (e.g. the cationic polymerization), and photoresists (e.g. the chemically amplified photoresist). [1-4] PAGs able to generate super strong acids such as $\text{CF}_3\text{SO}_3\text{H}$ or H^+SbF_6^- were applied to highly photosensitive resists. However, they usually absorb light only below 300 nm. Therefore, photosensitizers have been used when irradiation above 300 nm was necessary for photo-curing and photoresist systems. [5-6] Then, photosensitizers which effectively induce energy transfer to PAGs must be chosen. [5-6] Performances of the photosensitized system is influenced by combination of PAGs and the photosensitizers. With development of UV semiconductor lasers ($\lambda=365$ and 405 nm), the PAGs sensitive to i-, h-, or g-line are getting more important.

The demand of pattern size accuracy is increasing in photolithography manufacture. In printed wiring boards' manufactures, it is very important to produce stable patterns with the

photoresists. In chemically amplified type of the photoresists, hydrolysis reaction with acid catalyst occurs by post exposure baking (PEB). Pattern width shrinkage observed during the expose and the PEB treatment can cause a serious problem in the system. It is due to diffusion of the acid generated from the PAGs. [7]

In this study, we synthesized a series of i- and g-line sensitive non-ionic PAGs and investigated photolysis and catalytic properties of the synthesized PAGs in photoresists. These PAGs were required to absorb the light at 365 nm (i-line) and 436 nm (g-line) and to be thermally stable. PAGs having imide sulfonate units and thioxanthone moiety were synthesized. Photolysis rate of the PAGs was estimated using UV-vis spectroscopy. Photocrosslinking properties of epoxy-based polymers containing the PAGs were examined. The PAGs were applied to work in positive-type photoresists. Sensitivity profiles and post exposure delay (PED) of the photoresists were discussed in terms of the structure of the examined PAGs.

2. Experimental

2.1 Materials

N-Trifluoromethylsulfonyloxy-1,8-naphthalimide (**4a**) was purchased from Midori Kagaku.

Scheme 1. Synthesis of PAGs **4b** and **4c**.

2.1.1 Synthesis of N-nonafluorobutane sulfonyloxy-1,8-naphthalimide (**4b**)

A mixture of 1,8-naphthalic anhydride **1** (5.0 g, 25.2 mmol), hydroxylamine hydrochloride (24.5 g, 35.3 mmol), and pyridine (50 ml) was kept at 100 °C for 15 h with stirring. The reaction mixture was added to 1N hydrochloric acid (500 ml). Precipitate was filtered, washed with water, dried, and recrystallized from ethanol to obtain N-hydroxy-1,8-naphthalimide (**2**): yield 4.36 g (81.2%).

A mixture of **2** (0.6 g, 2.5 mmol), nonafluorobutanesulfonyl anhydride (1.5 g, 2.5 mmol), and toluene (10 ml) was kept at 100 °C for 1 h with stirring. The mixture was washed with 15% sodium carbonate aqueous solution, dried over anhydrous magnesium sulfate, evaporated to be dry, and recrystallized from chloroform to obtain the product **4b**: yield 235 mg (18.4%); mp 146-148 °C. ^1H NMR (270 MHz CDCl_3): δ 7.78 (t, 2H), 8.26 (d, 2H), 8.62 (d, 2H), FT-IR (KBr): 1222 (C-F), 1439 (S-O-S), 1714, 1739 cm^{-1} (C=O), MS (FAB+) 495.9 (M+H).

2.1.2 Synthesis of N-perfluorooctane sulfonyloxy-1,8-naphthalimide (**4c**)

The product **4c** was synthesized by the reaction of **2** (1.0 g, 4.7 mol) with perfluorooctanesulfonyl anhydride (1.3 g, 4.7 mmol) according to the same procedure for the preparation of **4b**: yield 426 mg (13.1%); mp

165-166 °C. ^1H NMR (270 MHz CDCl_3): δ 7.84 (t, 2H), 8.31 (d, 2H), 8.67 (d, 2H), FT-IR (KBr): 1222 (C-F), 1442 (S-O-S), 1707, 1737 cm^{-1} (C=O), MS (FAB+) 659.7 (M+H).

Scheme 2. Synthesis of PAGs **7** and **10**.

2.1.3 Synthesis of nonafluorobutanesulfonyl acid 1,3,6-trioxo-3,6-dihydro-1H-11-thia-2-azacylopenta[a]anthracene-2-yl ester (**7**)

2-Oxa-11-thiacyclopenta[a]anthracene-1,3,6-trione (**5**) was prepared according to the literature. [8]

A mixture of **5** (0.5 g, 1.7 mmol), hydroxylamine hydrochloride (1.72 g, 1.7 mmol), and pyridine (20 ml) was kept at 100 °C for 15 h with stirring. The mixture was further mixed with 1N hydrochloric acid (200 ml). The precipitate was filtered, washed with water, dried, and recrystallized from ethanol to obtain 2-hydroxy-11-thia-2-azacylopenta[a]anthracene-1,3,6-trione (**6**): yield 0.43 g (76.6%).

A mixture of **6** (0.5 g, 1.7 mmol), nonafluorobutanesulfonyl anhydride (1.0 g, 1.7 mmol), and toluene (50 ml) was stirred at 25 °C for 1 h. The mixture was washed with 15% sodium carbonate aqueous solution, dried over anhydrous magnesium sulfate, evaporated to be dry and recrystallized from chloroform to obtain the product **7**: yield 91.6 mg (9.3%); mp 241-245 °C. ^1H NMR (270 MHz DMSO): δ 7.64 (d, 1H), 7.88 (m, 2H), 7.97 (d, 1H), 8.3 (d, 1H), 8.8 (d, 1H), FT-IR (KBr): 1212, 1245 (C-F), 1458 (S-O-S), 1591, 1642, 1757 cm^{-1} (C=O), MS (FAB+) 579.5 (M+H).

2.1.4 Synthesis of nonafluorobutanesulfonic acid 8-isopropyl-1,3,6-trioxo-3,6-dihydro-1H-11-thia-2-azacylopenta[*a*]anthracen-2-yl ester (**10**)

Product **10** was synthesized according to the same procedure as the preparation of **7** using 5-isopropyl-thiosalicylic acid [9-10] as a starting material. Total yield: 1.2%. mp 215-217 °C. ¹H NMR (270 MHz CDCl₃): δ 1.31 (d, 6H), 3.07 (m, 1H), 7.61 (s, 2H), 7.93 (d, 1H), 8.46 (s, 1H), 9.06 (d, 1H), FTIR (KBr): 1214, 1236 (C-F), 1445 (S-O-S), 1598, 1631, 1758 cm⁻¹ (C=O), MS (FAB+) 621.2 (M+H).

2.2 Characterization

FT-IR, UV, and ¹H NMR measurements were performed using JASCO FTIR/410, SHIMADZU 2400PC, and JEOL JNM-GX270 spectrometers, respectively.

The films for photocrosslinking experiments were prepared by spin coating on Si wafer with cyclohexanone solution containing 8.8 wt% poly (glycidyl methacrylate) (Mn=80000 or 140000) and 2.5 x 10⁻² mol% PAGs. The film was baked at 90 °C for 30 sec. Irradiation was performed by a USHIO UM-102 high-pressure Hg lamp (100 W) through a filter (ASAHI SPECTRA CO. λ=365 nm filter or λ=436 nm filter) at the room temperature. Light intensity was measured by ORC UV-M02 photometer (ca. 12.0 W/m² at 365 nm or 12.0 W/m² at 436 nm). PEB was carried out on Koike Precision Instrument HM-15G hot plate at 100 °C for 5 min. Development was performed by a dip mode using tetrahydrofuran as a developer for 10 min at room the temperature. Film thickness of the polymer films was obtained using Nanospec/AFT M3000.

The photoresist films for measurement of photosensitivity were prepared by coating on Cu substrate with cyclohexanone solution containing 30 wt% photoresist resin. The concentration of the PAGs was 2.9 x 10⁻¹ mol/g (photoresist resin). The film thickness was 10 μm. The UV irradiation was carried out with JAPAN SCIENCE ENGINEERING MA-1200 super high-pressure Hg lamp (500 W) using 365 nm pass-filter, 365 nm cut-filter, and non-filter. PEB was carried out for 10 min at 100 °C with KATO CLN-22DP clean-oven. The film was developed in a dip mode using 0.75 wt% Na₂CO₃ aqueous solution for

1 min at 25 °C. The line widths of the photoresist were measured using OLYMPUS BX-60 optical microscope.

The photoresist films to check the post exposure delay effect were prepared by coating on a PET film with cyclohexanone solution containing 30 wt% photoresist resin. The concentration of PAGs was 5.8 x 10⁻¹ mol/g (photoresist resin). The film thickness was 10 μm. The photoresist films were laminated on Cu substrate at 120 °C with TAISEI-LAMINATOR VAIL-700. The UV irradiation was carried out with JAPAN SCIENCE ENGINEERING MA-1200 super high-pressure Hg lamp (500 W). To check the post exposure delay effect, the exposed film was kept at 25 °C in the dark. PEB was carried out for 10 min at 120 °C with KATO CLN-22DP clean-oven. The film was developed in a dip mode using 0.75 wt% Na₂CO₃ aqueous solution for 1 min at 25 °C. The line widths of photoresist were measured using OLYMPUS BX-60 optical microscope.

3. Results and Discussion

The structure of the PAGs examined in this study is shown in Scheme 3. The characteristics of the PAGs are shown in Table 1. PAGs **4a-c** absorbed the light at 365 nm. PAGs **7** and **10** were able to absorb the light at 365 and 436 nm. These PAGs were thermally stable (Td: 174-227 °C).

Scheme 3. Structures of PAGs used.

UV-vis spectra of **4a** and **7** are shown in Fig. 1. PAG **7** absorbed lights below 490 nm because of imide with thioxanthone moiety.

Table 1. Characteristics of PAGs.

	Td (°C)	ϵ (365 nm) CH ₃ CN	ϵ (436 nm) CH ₃ CN	pK _a ^{a)}	Molecular size ^{b)} (Å ³)	Structural energy gap by N-O bond cleavage (kJ/mol)
4a	174	380	- ^{c)}	-5.2	79	862.7
4b	193	463	- ^{c)}	-5.0	154	832.6
4c	208	537	- ^{c)}	-4.7	244	830.9
7	227	856	4530	-5.0	154	754.3
10	199	381	4030	-5.0	154	717.5

^{a)} The acidity of acid generated from PAGs.

^{b)} Molecular size of acid generated from PAGs calculated from molecular orbital theory (RH/PM3).

^{c)} Negligibly low.

Fig. 1 UV-vis spectra of **4a** and **7** in acetonitrile. [4a] = 3.16×10^{-5} M, [7] = 3.40×10^{-5} M.

Figure 2 shows UV-vis spectral changes of **7** in acetonitrile on irradiation at 365 nm. Efficient photolysis of **7** was observed by irradiation with 365 nm light. The photolysis of **7** and **10** occurred on irradiation not only at 365 nm but also at 436 nm.

Figure 3 shows the photolysis rate of **4a-c**, **7**, and **10** in acetonitrile on irradiation at 365 nm. Although the molar extinction coefficient (ϵ) at 365 nm of **4a-c**, **7**, and **10** was almost the same, the photoreactivity of **7** and **10** was higher than **4a-c**. The result was coincided with the expected energy [11] in excited state (Table 1). The energy is defined as structural energy gap between before and after bond cleavage. The structural energy gap indicates bond stabilization energy. Ortica et al. reported that photolysis of the PAGs occurred through heterolytic cleavage of N-O bond. [12] We calculated the energy gap of N-O bond cleavage using CIS/6-31G//CIS/PM3. Since the energy of **4a** and **10** were 862.7 kJ/mol and 717.5

kJ/mol, respectively, photoreactivity of **10** was higher than **4a**.

Fig. 2 UV spectral change of **7** in acetonitrile on irradiation at 365 nm. [7] = 3.40×10^{-5} M.

Fig. 3 Photolysis of PAGs in acetonitrile on irradiation at 365 nm.

(●): **4a**, (×): **4b**, (◇): **4c**, (■): **7**, (▲): **10**.

Figure 4 shows the photolysis rate of **7** and **10** in acetonitrile on irradiation at 365 and 436 nm. The ϵ values at 436 nm of **7** and **10** were higher

than those at 365 nm because of imide with thioxanthone moiety as chromophore. (Table 1.) Therefore, the photoreactivities of **7** and **10** for 436 nm light were higher than those for 365 nm light.

Fig. 4 Photolysis of PAGs **7** and **10** in acetonitrile on irradiation.

(■): PAG **7** in acetonitrile on irradiation at 365 nm.
(▲): PAG **10** in acetonitrile on irradiation at 365 nm.
(□): PAG **7** in acetonitrile on irradiation at 436 nm.
(△): PAG **10** in acetonitrile on irradiation at 436 nm.

The photocrosslinking properties of poly (glycidyl methacrylate) (PGMA) containing the **4a-c**, **7**, and **10** were investigated. Figure 5 shows the photocrosslinking properties of PGMA containing **4a-c** on irradiation at 365 nm. Although the photolysis rate of **4a-c** was almost the same (Fig. 4), the photocrosslinking efficiency of PGMA containing **4a** and **4b** was higher than that containing **4c**. This is due to the strength of the acid produced by the PAGs. Therefore, the photocrosslinking properties of PGMA were strongly affected by the acidity of acid generated from the PAGs. Figure 6 shows the photocrosslinking properties of PGMA containing **4a** and **10** on irradiation at 365 and 436 nm. The photocrosslinking efficiency of PGMA containing **10** on irradiation at 365 nm was higher than PGMA containing **4a**. This is due to photoreactivity of PAGs at 365 nm (Fig. 3). The photocrosslinking properties of PGMA containing PAGs were dependent on not only the acidity of acid generated from PAGs but also the photoreactivity of PAGs. Moreover, the photocrosslinking efficiency of PGMA containing **10** on irradiation at 436 nm became still higher than on irradiation at 365 nm

because ϵ value of **10** at 436 nm was higher than at 365 nm. (Table 1) Since **4a** did not absorb the light at 436 nm, photocrosslinking of PGMA containing **4a** did not occur.

Fig. 5 Insolubilization of PGMA (Mn=140000) film containing PAGs on irradiation at 365 nm followed by PEB at 100 °C for 5 min. Developer: THF for 10 min.
(●): **4a**, (×): **4b**, (◇): **4c**.

Fig. 6 Insolubilization of PGMA (Mn=80000) film containing PAGs on irradiation followed by PEB at 100 °C for 5 min. Developer: THF for 10 min.

(●): PGMA film containing **4a** irradiated at 365 nm.
(▲): PGMA film containing **10** irradiated at 365 nm.
(○): PGMA film containing **4a** irradiated at 436 nm.
(△): PGMA film containing **10** irradiated at 436 nm.

PAGs **4a** and **10** were blended with “SONNE LRUV”, a positive type photoresist from Kansai Paint. The photosensitivity of two types of photoresist was measured. The photosensitivity defined the lowest exposure dose which can form L/S=20/20 μm pattern of photoresist after development. The UV irradiation was carried out with a super

high-pressure mercury lamp using 365 nm pass-filter, 365 nm cut-filter, and non-filter. The results are shown in Table 2. The photoresist containing **4a** on irradiation through 365 nm cut-filter showed no reaction because **4a** did not absorb the light at 400 nm or longer wavelength. On the other hand, photosensitivity of the photoresist containing **10** on irradiation through 365 nm cut-filter was 800 J/m². Therefore, the photosensitivities of the photoresists containing **4a** and **10** on irradiation without filter were 2000 J/m² and 600 J/m², respectively. The photoresist containing **10** showed high photosensitivity.

Table 2. Photosensitivity of photoresist. (J/m²)

	Non-filter ^{a)}	365nm ^{b)} cut-filter	365nm ^{c)} pass-filter
4a	2000	- ^{d)}	2000
10	600	800	3000

^{a)} Light intensity: ca. 98.0 W/m² at 365 nm.

^{b)} Light intensity: ca. 124.5 W/m² at 405 nm.

^{c)} Light intensity: ca 73.0 W/m² at 365nm.

^{d)} Not detected.

Fig. 7 SEM photographs of line and space images of photoresist containing 5.8×10^{-1} mol/g (photoresist resin) PAGs on irradiation and baked at 120 °C for 10 min. Exposure dose: 500 J/m², L/S = 20/20 μm. PAG: (a) **4a**, (b) **4b**

Fig. 8 SEM photographs of line and space images of photoresist containing 5.8×10^{-1} mol/g (photoresist resin) PAGs on irradiation and baked at 120 °C for 10 min. PEB was carried out after 24 h on irradiation. Exposure dose: 500 J/m², L/S = 20/20 μm. PAG: (a) **4a**, (b) **4b**

Figure 7 shows the SEM photographs of line and space images of the photoresist after PEB and development immediately after irradiation. Line shapes of the photoresist was not affected by the used PAGs. Figure 8 shows the SEM photographs of line and space images of the photoresist irradiated, left for 24 h, and baked at 120 °C for 10 min. The shrinkage of the photoresist pattern was observed using **4a** (Fig. 8 (a)). On the other hand, the photoresist pattern was not affected by the interval time between irradiation and PEB (Fig. 7 (b) and Fig. 8 (b)) by using **4b**. This is due to lower diffusion rate of nonafflic acid generated from **4b** than that of triflic acid generated from **4a**. Therefore, PEB time was dependent on the molecular size of the generated acid.

4. References

1. M. Shirai, M. Tsunooka, *Bull. Chem. Soc. Jpn.*, **71** (1998) 2483.
2. F. M. Houlihan, E. Chin, O. Nalamasu, J. M. Kometani, T. X. Neenan, A. Pangborn, *Proc. SPIE.*, **2195** (1994) 137.
3. M. L. Schilling, H. E. Katz, F. M. Houlihan, J. M. Kometani, S. M. Stein, O. Nalamasu *Proc. SPIE.*, **2195** (1994) 182.
4. J. V. Crivello, J. H. W. Lam, *J. Polym. Sci. Polym. Chem. Ed.*, **17** (1979) 1047.
5. J. V. Crivello, J. H. W. Lam, *J. Polym. Sci. Polym. Chem. Ed.*, **17** (1979) 1059.
6. J. V. Crivello, M. Sangermano, *Polym. Preprints.*, **42** (2001) 783.
7. S. L. Ablaza, J. F. Cameron, G. Xu, W. Yueh, *J. Vac. Sci. Technol. B.*, **18** (2000) 2543.
8. W. Fischer, *Helv. Chim. Acta.*, **74** (1991) 1119.
9. G. B. Guise, W. D. Ollis, J. A. Peacock, J. S. Stephanatou, J. F. Stoddart., *J. Chem. Soc. Parkin Trans. I.*, (1982) 1637.
10. K. Mitra, M. E. Pohl, L. R. MacGillivray, C. L. Barnes, K. S. Gates, *J. Org. Chem.*, **62**, (1997) 9361.
11. K. Kawamura, F. Sasaki, *J. Photopolym. Sci. Technol.*, **14** (2001) 265.
12. F. Ortica, J. C. Scaiano, G. Pohlers, J. F. Cameron, A. Zampini, *Chem. Mater.*, **12** (2000) 414.