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# New Anionic Photoacid Generator Bound Polymer Resists for EUV Lithography

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ABSTRACT: A new series of functionalized anionic photoacid generators (PAGs) [methacrylate substituted benzene sulfonic PAGs (such as, NO2 PAG, CF3 PAG, and F4 FAG as reference)] and perfluoro alkanesulfonic PAG (MTFB PAG), as well as corresponding PAG bound polymeric resists (HS-EA-PAG) based on hydroxystyrene (HS) and 2-ethyl-2-adamantyl methacrylate (EA), were prepared and characterized. The acid generating efficiency of PAG bound polymers was in the range of 54−81%, which agrees well with the electron withdrawing effect of the substituents. With regard to the referenced F4 PAG bound polymer with 68% acid generating efficiency and our previously reported EUVL results of F4 PAG bound polymer photoresists, these new PAG bound polymers should be effective resists for EUV lithography.

## Introduction

The microelectronic industry has made remarkable progress with the development of integrated circuit (IC) technology, which depends on the fabrication of smaller feature sizes. Although extreme ultraviolet (EUV) lithography at 13.5 nm wavelength has emerged as a promising candidate to meet the resolution requirements of the microelectronic industry roadmap,[1,2] the development of novel photoresist materials with all of the required imaging properties (high resolution, high sensitivity, and lower line edge roughness) is indispensable and one of the major subjects of current lithography research. Conventional chemically amplified resist (CAR) formulations are complex mixtures of a protected polymer matrix and a small molecule photoacid generator (PAG). This kind of PAG blended CAR materials has inherent incompatibility that can lead to PAG phase separation, PAG aggregation, nonuniform initial PAG and photoacid distribution, as well as acid migration during the postexposure baking (PEB) processes. These problems ultimately create a tradeoff between achieving the desired characteristics of high resolution, high sensitivity, and low line edge roughness through formulation changes to PAG blend CAR systems.[3] To alleviate these problems, some new perfluoroalkanesulfonate (PFAS) blend PAGs that provide strong acid, good lithographic performance, and process compatibility were developed.[4,5] However, it has been reported that the PFAS compounds with more than four consecutive CF2 units are an environmental hazard.[6,7] Ayothi et al.[8] recently reported the environmentally compatible PFAS-free PAGs for e-beam and EUV lithography. On the other hand, several systems with ionic or nonionic PAG grafting into the main-chain of the polymer have been reported.[9−17] The incorporation of anionic PAG units into the main chain of the hydroxystyrene and 2-ethyl-2-adamantyl methacrylate based polymers showed improved EUV lithographic performance, such as high PAG loading, faster photospeed and higher stability, lower outgassing, and lower line edge roughness (LER) than corresponding cationic PAG bound polymer or PAG blend polymer resists.[14−18] Herein we report the preparation of advanced anionic vinyl monomer PAGs with strong electronic withdrawing groups [methacrylate substituted benzene sulfonic PAGs (NO2 PAG, CF3 PAG)] and perfuoro alkanesulfonic PAG (MTFB PAG), as well as a series of new photoresists incorporating them in the main-chain of the polymer (Figures 1 and 2). Figure 2 also outlines the anticipated advantages of polymer microstructures incorporating PAGs in the resist backbone.

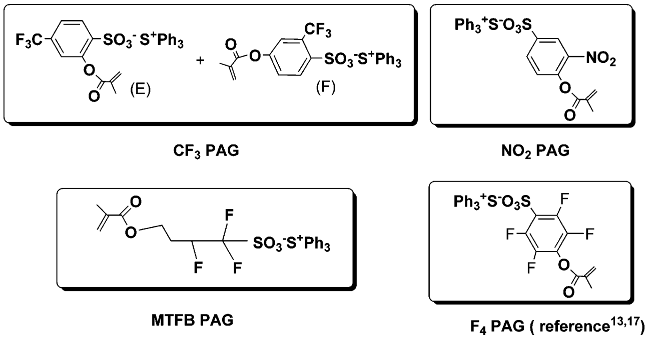

**Figure 1.** Photoacid generator (PAG) structures.

## Experimental Section

**Materials.** *m*-Trifluoromethylphenol, 2,2′-azobisisobutyronitrile (AIBN), 4-bromo-1,1,2-trifluoro-1-butene, methacryloyl chloride, and triflic acid were purchased from Aldrich. Trifluoroacetic acid (TFA), trifluoroacetic anhydride (TFAA), and acetoxystyrene were purchased from Tokyo Kasei Kogyo Co., Ltd. Japan. Methacrylic acid, sodium 4-phenosulfonate, and tetrabromophenol blue (TBPB) were purchased from ACROS ORGANICS. Triphenylsulfonium chloride 50% aqueous solution was purchased from City Chemical LLC. 2-Ethyl-2-adamantyl-methacrylate (EAMA) was supplied by AZ Electronic Materials Ltd. All chemicals and solvents were used without further purification unless otherwise noted. Tetrahydrofuran (THF) and acetonitrile were dried (over sodium, calcium hydride) before use. Hydroxystrene (HOST) was prepared by the hydrolysis of acetic acid 4-vinylphenyl ester.

**Characterization.** The NMR was performed on a JEOL500 spectrometer with DMSO-$d_6$ or $CDCl_3$ and TMS as the solvent and internal standard, respectively. Elemental analyses were

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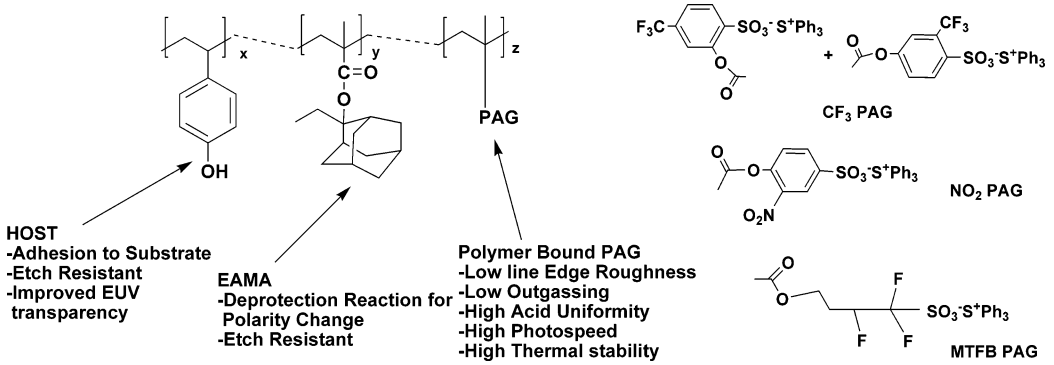


**Figure 2.** Design of polymer microstructures for EUV lithography.

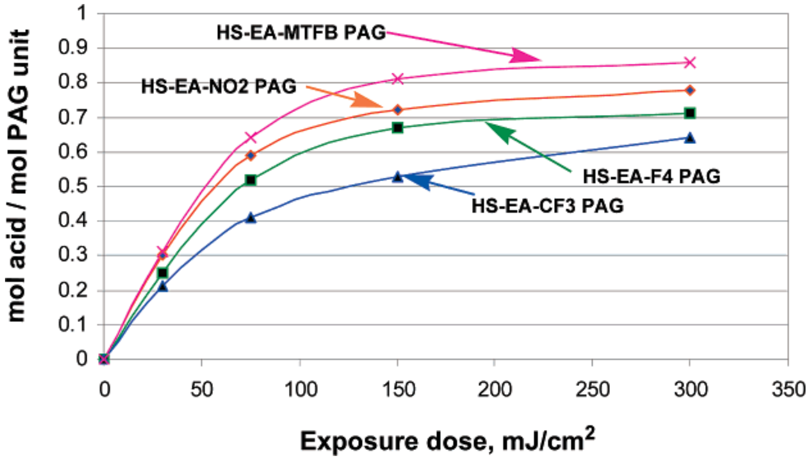


**Figure 3.** Acid generation efficiency vs exposure doses.

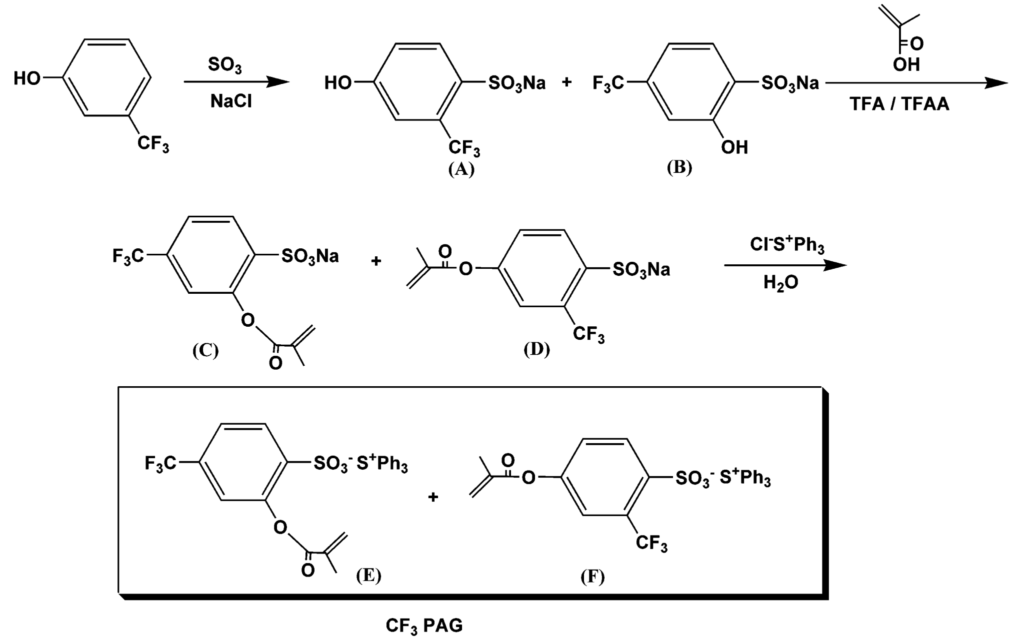
performed at Atlantic Microlab Inc., Atlanta, GA. UV−vis absorption spectra were obtained on a Varian CARY 300 Bio UV-visible spectrophotometer. Gel permeation chromatography (GPC, Waters Breeze software) was performed with THF as the eluent. The molecular weights of polymers were calculated with respect to polystyrene as narrow $M_w$ standards. Thermal analysis was performed on a TA instrument, Hi-Res TGA 2950 Thermogravimetric Analyzer 7, and differential scanning calorimetry (DSC 2920) under a nitrogen atmosphere at a heating rate of 10 °C/min. TGA was used to determine the decomposition temperature ($T_d$, at 5% weight loss). For acid generating measurements, a 254 nm UV lamp (model R 52 G UVP lnc) was used. The thickness of the films was measured with a Woollam variable angle spectroscope ellipsometer. Film thicknesses were in the range of 110−130 nm.

**1. Synthesis of Photoacid Generators (PAGs). 1.1. Triphenylsulfonium Salt 2-(Methacryloxy) 4-Trifluoromethyl Benzenesulfonate (E) and Triphenylsulfonium Salt 4-(Methacryloxy) 2-Trifluoromethyl Benzenesulfonate (F) (CF3 PAG).** Triphenylsulfonium salt 2-(methacryloxy) 4-trifluoromethyl benzenesulfonate (**E**) and triphenylsulfonium salt 4-(methacryloxy) 2-trifluoromethyl benzenesulfonate (**F**) (CF3 PAG) were prepared as shown in Scheme 1.

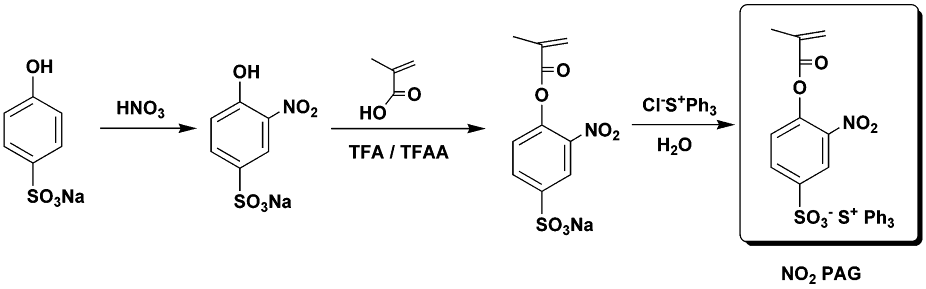
2-Hydroxy-4-trifluoromethylbenzenesulfonic acid (**A**) and 4-hydroxy-2-trifluoromethylbenzenesulfonic acid (**B**) were prepared as per the literature method, yield 63% (**A**/**B** = 7:3),[19] characterized by $^1$H NMR (25 °C, DMSO-$d_6$, ppm) $\delta$ 7.56 (d, $J$ = 8.3 Hz, 1H); 7.36 (d, $J$ = 8.3 Hz, 1H); and 7.30 (d, $J$ = 8.3 Hz, 1H) for **A** and 7.66 (d, $J$ = 8.3 Hz, 1H); 7.15 (d, $J$ = 8.3 Hz, 1H); 7.10 (d, $J$ = 8.3 Hz, 1H) for **B**. Intermediates (**A** and **B**, 0.01 mol) were next reacted with methacrylic acid (0.012 mol) in trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) as the media, under a nitrogen atmosphere overnight. On removing the solvent, followed by washing with diethyl ether, the sodium 4-(methacryloxy) trifluorobenzenesulfonate (**C**/**D** = 4:1) was obtained in 51% yield, characterized by $^1$H NMR (25 °C, DMSO-$d_6$, ppm) $\delta$ 7.92−7.96 (m, 2H); 7.55 (b, 1H); 5.98 (s, 1H); 5.61 (s, 1H); 1.81 (s, 3H) for **C** and 7.84 (d, $J$ = 7.5 Hz, 1H); 7.79 (dd, $J$ = 7.5 and 1.7 Hz, 1H); 7.60 (d, $J$ = 1.7 Hz, 1H); 6.33 (s, 1H); 5.80 (s, 1H); 2.00 (s, 3H) for **D**. The molar ratio of isomers was calculated based on the integration ratios of the above corresponding peaks (see Supporting Information). The intermediates (**C** and **D**, 0.01 mol) were next reacted with a 50% aqueous solution of triphenylsulfonium chloride (0.03 mol) in water, at room temperature overnight. The product was purified with dichloromethane and hexane. Triphenylsulfonium salt methacryloxy trifluoro benzenesulfonate (CF3 PAG; **E**/**F** = 4:1) was obtained in 62% yield as a colorless crystal. $^1$H NMR (25 °C, DMSO-$d_6$, ppm) $\delta$ 7.22−7.93 (m, 18H), 5.99 (s, 1H), 5.62 (s, 1H), 1.83 (s, 3H) for **E** and 7.22−7.93 (m, 18H); 6.28 (s, 1H); 5.80 (s, 1H); 2.00 (s, 3H) for **F**. $^{13}$C NMR (25 °C, DMSO-$d_6$, ppm) $\delta$ 166.2, 164.8, 153.6, 147.5, 146.0, 143.9, 136.1, 135.2, 134.9, 134.3, 132.1, 131.3, 131.1, 130.2, 129.5, 128.7, 128.3, 127.5, 125.4, 124.5, 122.0, 121.3, 115.1, 113.3, and 18.0. $^{19}$F NMR (25 °C, DMSO-$d_6$, ppm, ext. $CF_3COOH$) $\delta$ −60.26, −60.75. Anal. Calcd for $C_{29}H_{23}F_3O_5S_2$: C, 60.83; H, 4.05; F, 9.95. Found: C, 60.39; H, 4.34; F, 10.06.

**1.2. Triphenylsulfonium Salt 4-(Methacryloxy) 3-Nitro-benzenesulfonate (NO2 PAG).** Triphenylsulfonium salt 4-(methacryloxy) 3-nitro-benzenesulfonate (NO2 PAG) was prepared as outlined in Scheme 2. Sodium 2-nitrophenol-4-sulfonate was readily prepared in 82% yield.[20] It was then reacted with methacrylic acid in TFA and TFAA as a media to obtain sodium 4-(methacryloxy) 2-nitrobenzenesulfonate in 72% yield, characterized by $^1$H NMR (25 °C, DMSO-$d_6$, ppm) $\delta$ 8.24 (d, $J$ = 1.8 Hz, 1H); 7.99 (dd, $J$ = 8.0 and 1.8 Hz, 1H); 7.50 (d, $J$ = 8.0 Hz, 1H); 6.34 (s, 1H); 6.00 (s, 1H); 2.01 (s, 3H). The latter (0.01 mol) was then reacted with a 50% aqueous solution of triphenylsulfonium chloride (0.03 mol) in water, at room temperature overnight. The product was purified with dichloromethane and hexane. The triphenylsulfonium salt 4-methacryloxy-2-nitro benzenesulfonate (NO2 PAG) was obtained in 85% yield as a colorless crystal. $^1$H NMR (25 °C, DMSO-$d_6$, ppm) $\delta$ 8.23 (d, $J$ = 2.7 Hz, 1H), 7.09−7.93 (m, 17H), 6.33 (s, 1H), 6.00 (s, 1H), 2.00 (s, 3H). $^{13}$C NMR (25 °C, DMSO-$d_6$, ppm)

**Scheme 1. Synthetic Scheme of CF3 PAGs**



**Scheme 2. Synthetic Scheme of NO2 PAG**



δ 164.5, 147.3, 143.2, 140.5, 136.2, 134.4, 132.4, 131.3, 131.0, 130.3, 129.3, 125.3, 122.5, and 17.8. Anal. Calcd for $C_{28}H_{23}NO_7S_2$: C, 61.19; H, 4.22; N, 2.55. Found: C, 60.86; H, 4.34; N, 2.81.

**1.3. Triphenylsulfonium Salt of 1,1,2-Trifluorobutanesulfonate Methacrylate (MTFB PAG).** Triphenylsulfonium salt of 1,1,2-trifluorobutanesulfonate methacrylate (MTFB PAG) was prepared in Scheme 3.

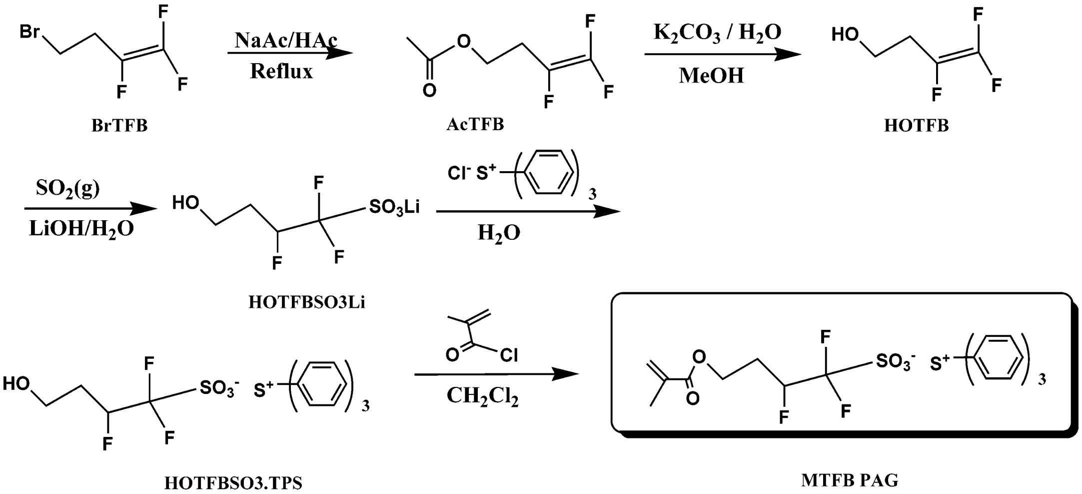
The lithium salt of 1,1,2-trifluoro-4-hydroxy-1-butanesulfonate ($HOTFHBSO_3Li$) was prepared according to the literature.[21] This (5.0 mmol) was then dissolved in 50 mL of deionized water. A 50% aqueous solution of triphenylsulfonium chloride (10.0 mmol) was added with stirring at room temperature. The reaction mixture was stirred overnight and extracted with dichloromethane. The organic layer was dried over $MgSO_4$. The solvent was removed, and the product was dried under vacuum to get $HOTFHBSO_3$·TPS as a white solid (yield 42%). FT-IR(film), $\upsilon$/cm$^{-1}$ 3448 (OH, stretch); 3060 (phenyl ring C−H, stretch); 1568, 1475, 1446 (phenyl ring); 1243 (CF, S=O); 1088 (S=O); 1065 (S=O). $^1$H NMR (25 °C, $CDCl_3$, ppm) δ 7.3−7.8 (m, 15H); 5.0−5.2 (m, 1H); 3.7−3.9 (m, 2H); 2.0−2.4 (m, 2H).

$HOTFHBSO_3$·TPS (5.0 mmol) was dissolved in 10 mL of dried dichloromethane. Methacryloyl chloride (6.0 mmol in 3 mL of dichloromethane) was added dropwise at 0 °C under nitrogen flow, then warmed to room temperature, and kept for 2 days. Next the solution was washed with water, and the organic layer was dried over $MgSO_4$. On removal of the solvent, the product was obtained and dried under vacuum to get a white glassy solid in yield of 75%. FT-IR (film), $\upsilon$/cm$^{-1}$ 2981, 2890 ($CH_3$, stretch); 1715 (C=O); 1568, 1475, 1446 (phenyl ring); 1242 (CF, S=O); 1088 (S=O); 1066 (S=O). $^1$H NMR (25 °C, $CDCl_3$, ppm) δ 7.25−7.74 (m, 15H), 6.06 (s, 1H), 5.51 (s, 1H), 5.22 (m, 1H), 4.34 (d, m, 2H), 2.24−2.63 (m, 2H), 1.89 (s, 3H). $^{13}$C NMR (25 °C, $CDCl_3$, ppm) δ 168.0, 149.6, 134.9, 132.3, 132.0, 131.6, 130.9, 129.0, 125.9, 120.3, 89.9, 60.8, 29.2, 18.8. $^{19}$F NMR (25 °C, ppm, $CDCl_3$, ext. $CF_3COOH$) δ −113.8 to −119.6 (d, d, 2F), −203.1 (m, 1F). Anal. Calcd for $C_{26}H_{25}F_3O_5S_2$: C, 57.98; H, 4.68; F, 10.58. Found: C, 57.68; H, 4.53; F, 10.33.

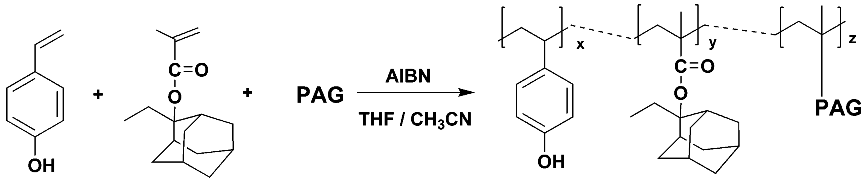
**2. Synthesis of Polymers.** Terpolymers were prepared by free radical polymerization in sealed pressure vessels (Scheme 4). Hydroxystrene (HOST), 2-ethyl-2-adamantyl-methacrylate (EAMA), anionic PAGs, and 2, 2′-azobisisobutyronitrile (AIBN) as a free radical initiator (5 mol % to the monomers) were dissolved in freshly distilled anhydrous tetrahydrofuran (THF) and acetonitrile (v/v = 1:1). Polymerization was performed at 65 °C for 24 h. The polymer solutions were precipitated into a large amount of diethyl ether or petroleum ether and dried in vacuum. The products were then redissolved in THF and precipitated with petroleum ether twice and then dried in vacuum for 24 h. The polymer composition was calculated by $^1$H NMR. The results are given in Table 1.

**3. Acid Generation Efficiency.** In order to investigate the potential photoresist performance of PAG bound polymers, the following protocol was conducted: resist films were spin-cast onto 4 in. Si wafers, whose weights were predetermined on an analytical balance, from 7.0 wt % resist solutions in cyclohexanone. After casting, the films were baked at 130 °C for 5 min to remove the solvent and were weighed again. The amount of resists on the film was calculated. The resist films were exposed to a 254 nm UV lamp equipped with a radiometer. Dose was calculated by exposure times multiplied by lamp intensity. Each film to be analyzed was stripped from the silicon wafer with DMSO and added to 1 mL of a stock solution of 0.3 mM tetrabromophenol blue (TBPB) in DMSO. The total volume was then raised to 10 mL by addition of DMSO. The resulting solution was characterized on a UV spec-

**Scheme 3. Synthetic Scheme of MTFB PAG**



**Scheme 4. Synthetic Scheme of Terpolymers**



trometer. The amount of acid generated in the film by UV radiation was determined by monitoring the absorbance change of the TBPB indicator at 602 nm,[22] against the calibration curves predetermined by using known amounts of triflic acid. Calibration curves showed a linear relationship between the amount of acid added to the indicator solution and the resulting absorbance intensity change at 602 nm. For comparison, the acid generation efficiency of each resist is expressed as mole of acid/mol of PAG units in the resist. The number of moles of PAG units in each resist was determined by $^1$H NMR and resist weight.

## Results and Discussion

The anionic bound PAGs were prepared in moderate to good yield and characterized by $^1$H, $^{19}$F, and $^{13}$C NMR, as well as elemental analyses. The terpolymers were obtained in yields from 31.3 to 42.3%, with PAG contents 8.3, 7.6, and 5.3% (mole ratio) for HS-EA-CF3 PAG, HS-EA-NO2 PAG, and HS-EA-MTFB PAG, respectively. The molar composition of each unit in the terpolymers was determined by $^1$H NMR. The characteristic peaks: around 9.1 ppm is assigned to the proton of the hydroxyl group of HOST, 7.6−7.8 ppm is assigned to the protons from PAG's cation TPS, 6.6−7.1 ppm from HOST and PAG's anionic part, 0.7−2.6 ppm from the EAMA and main-chain of the polymer. The molar composition was calculated based on the integration ratios of the above corresponding peaks (see Supporting Information). The molecular weights were determined by GPC with THF as a mobile phase. The results showed the polymer HS-EA-CF3 PAG, HS-EA-NO2 PAG had $M_w$ of 3700 with PDI 2.0 and 3900 with PDI 2.1 compared to HS-EA-F4 PAG of $M_w$ of 3600 with PDI 1.6. The polymer HS-EA-MTFB PAG had a lower $M_w$ 2600 with PDI 1.6, which showed that the MTFB PAG is not as active as CF3, NO2, and F4 PAG aromatic structures. The thermal stability of the polymers was identified by estimating the percentage of the weight loss of the polymer on thermal decomposition using TGA. The polymer HS-EA-MTFB PAG ($T_d$ 170 °C) is superior to HS-EA-CF3 PAG, HS-EA-NO2 PAG, and HS-EA-F4 PAG ($T_d$: 159, 162, and 145 °C, respectively). The glass transition temperature of polymer HS-EA-MTFB PAG was 117 °C; the other polymers showed no obvious $T_g$, suggesting that polymer HS-EA-MTFB PAG has softening behavior due to the alkyl plasticization chain structure of the PAG. The other polymers are probably quite rigid, resulting from the restrictive motion of the aromatic structures of the PAG. As reported previously for analogous rigid polymers,[23] no transitions were observed below the decomposition temperature for these polymers in this study also.

The results of acid generating (see Figure 3) show that the acid generation efficiency for HS-EA-MTFB PAG, HS-EA-NO2 PAG, HS-EA-F4 PAG, and HS-EA-CF3 PAG are 81, 74, 68, and 54% at the dose of 150 mJ/cm$^2$, respectively. This demonstrates that the acid generation of PAGs is in the following order, MTFB PAG > NO2 PAG > F4 PAG > CF3 PAG. The stronger the electron withdrawing group substituted on the aromatic ring, the higher the acidity of the PAG, leading to higher acid generation. The MTFB PAG has strong electron

**Table 1. Polymerization Results**

| | mole feed ratio | | | polymer composition | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| polymer (resist) | HOST | EAMA | PAG | HOST | EAMA | PAG | yield/% | $M_w$ (PDI) | $T_d$[b]/°C | $T_g$/°C |
| HS-EA-CF3 PAG | 35 | 60 | 5.0 | 40.3 | 51.4 | 8.3 | 31.3 | 3700 (2.0) | 159 | *c* |
| HS-EA-NO2 PAG | 35 | 60 | 5.0 | 37.8 | 54.6 | 7.6 | 36.2 | 3900 (2.1) | 162 | *c* |
| HS-EA-MTFB PAG | 30 | 65 | 5.0 | 38.5 | 56.2 | 5.3 | 42.3 | 2600 (1.6) | 170 | 117 |
| HS-EA-F4 PAG[a] | 25 | 72.5 | 2.5 | 35.0 | 57.9 | 7.1 | 37.3 | 3600 (1.6) | 145 | *c* |

[a] See references 13 and 17. [b] The decomposition temperature was determined according to weight loss below 5.0%. [c] Could not be determined by DSC.

withdrawing fluorines next to the sulfonium group, and this promotes higher acid generation on exposure.

As for the DUV absorption, the results are in the following order: HS-EA-CF3 PAG (2.02 $\mu m^{-1}$) > HS-EA-NO2 PAG (1.29 $\mu m^{-1}$) > HS-EA-MTFB PAG (0.71 $\mu m^{-1}$) > HS-EA-F4 PAG (0.53 $\mu m^{-1}$). Since they have a similar HOST ratio and the EAMA does not contribute to significant absorption at the DUV wavelength, the total absorption difference among them may be due to the differences of PAG absorption and its loading.[24] Strong absorption results in poor resist profiles, whereas low absorption leads to poor resist sensitivity. These results indicate that the MTFB PAG and NO2 PAG should be promising anionic PAGs for EUV lithography.

## Conclusion

A new series of functionalized anionic PAGs [methacrylate substituted benzene sulfonic PAGs (such as, NO2 PAG, CF3 PAG, and F4 FAG as reference) and perfuoroalkanesulfonic PAG (MTFB PAG), as well as corresponding PAG bound polymeric resists, were prepared and characterized. The acid generation efficiency of PAG bound polymers was in the range of 54−81%, which is consistent with the electron withdrawing power of the substituents. The acid generation of the referenced F4 PAG bound polymer was 68%. On the basis of their acid generation efficiency and DUV absorption as well as the previously reported EUVL results of F4 PAG bound polymer photoresists,[17] these new PAGs and corresponding PAG bound polymers should be effective resists for EUV lithography. Further investigations on high-resolution EBL and EUVL imaging, outgassing, and acid diffusion studies will be reported subsequently.

**Acknowledgment.** The authors gratefully acknowledge Intel Corporation for financial support.

**Supporting Information Available:** $^1$H NMR spectra of intermediates **C** and **D** for CF3 PAG and polymer HS-EA-MTFBPAG in DMSO-$d_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) International Technology Roadmap for Semiconductors (ITRS). http://public.itrs.net/, Lithography.

(2) Sttlen, R. H.; Sweeney, D. W. *IEEE J. Quantum Electron.* **1999**, *35* (5), 694.

(3) Covert, K. L.; Russell, D. J. *J. Appl. Polym. Sci.* **1993**, *49*, 657.

(4) Ito, H. *Adv. Polym. Sci.* **2005**, *172*, 37.

(5) Suzuki, Y.; Johnson, D. W. *Proc. SPIE−Int. Soc. Opt. Eng.* **1998**, *3333*, 735.

(6) Kannan, K.; Koistinen, J.; Beckman, K.; Evans, T.; Gorzelany, J. F.; Hansen, K. J.; Jones, O. P. D.; Helle, E.; Nyman, M.; Giesy, J. P. *Environ. Sci. Technol.* **2001**, *35*, 1593.

(7) Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G. *Environ. Toxicol. Chem.* **2003**, *22*, 196.

(8) Ayothi, R.; Yi, Y.; Cao, H.; Yueh, W.; Putna, S.; Ober, C. K. *Chem. Mater.* **2007**, 19, 1434.

(9) Stewart, M. D.; Tran, H. V.; Schmid, G. M.; Stachowiak, T. B.; Becker, D. J.; Willson, C. G. *J. Vac. Sci. Technol.* B **2002**, *20*, 2946.

(10) He, D.; Solak, H.; Li, W.; Cerrina, F. *J. Vac. Sci. Technol., B* **1999**, *17*, 3379.

(11) Matsuzawa, N. N.; Oizumi, H.; Mori, S.; Irie, S.; Yano, E.; Okazaki, S.; Ishitani, A. *Microelectron. Eng.* **2000**, *53*, 671.

(12) Wang, M.; Jarnagin, N. D.; Yueh, W.; Roberts, J. M.; Gonsalves, K. E. *J. Mater. Chem.* **2006**, *16*, 3701.

(13) Wang, M.; Gonsalves, K. E; Yueh, W.; Roberts, J. M. *Macromol. Rapid Commun.* **2006**, *27*, 1590.

(14) Wu, H.; Gonsalves, K. E. *Adv. Mater.* **2001**, *13*, 195.

(15) Thiyagarajan, M.; Dean, K.; Gonsalves, K. E. *J. Photopolym. Sci. Technol.* **2005**, *18*, 737.

(16) Watanabe, T.; Fukushima, Y.; Shiotani, H.; Hayakawa, M.; Ogi, S. Endo, Y.; Yamanaka, T.; Yusa, S.; Kinoshita, H. *J. Photopolym. Sci. Technol.* **2006**, *19*, 521.

(17) Wang, M.; Gonsalves, K. E.; Rabinovich, M.; Yueh, W.; Roberts, J. M. *J. Mater. Chem.* **2007**, *17*, 1699.

(18) Lee, C.; Wang, M.; Jarnagin, N. D.; Gonsalves, K. E.; Roberts, J. M.; Yueh, W.; Henderson, C. L. *Proc. SPIE−Int. Soc. Opt. Eng.*, Vol. 6519, Part 1, Advances in Resist Technology and Processing XXIV, March 23, 2007; 65191E.

(19) Dannley, R. L.; Tornstrom, P. K. *J. Org. Chem.* **1975**, *40* (16), 2278.

(20) Ruth, K. *J. Chem. Soc., Trans.* **1921**, *119*, 2105.

(21) Cowie, J. M. G.; Spence, G. H. *Solid State Ionics* **1999**, *123*, 233.

(22) Thackeray, J. W.; Denison, M. D.; Fedynyshyn, T. H.; Kang, D.; Sinta, R. Following the Acid: Effect of Acid Surface Depletion on Phenolic Polymers. In *Microelectronics Technology*; ACS Symposium Series 614; American Chemical Society: Washington, DC, 1995; p 110.

(23) Pasini, D.; Klopp, J. M.; Frechet, J. M. J. *Chem. Mater.* **2001**, *13*, 4136.

(24) Private communication from Prof. C. L. Henderson and C. Lee at Georgia Institute of Technology.

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