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Fluorine-contained photoacid generators (PAGs) and corresponding polymer resists

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ABSTRACT

A new series of fluorinated anionic photoacid generators (PAGs) (F4-MBS-TPS, F4VBzBS-TPS, F4-IBBS-TPS, CF3 MBS-TPS, MTFBS-TPS and VBzTFBS-TPS), and corresponding PAG bound polymeric resists (HS-EA-PAG) based on hydroxystyrene (HOST) and 2-ethyl-2-adamantyl methacrylate (EA), (GB-EA-PAG) based on γ-butyrolactone methacrylate (GBLMA) and 2-ethyl-2-adamantyl methacrylate (EA) were prepared and characterized. The acid generating efficiency of PAG bound polymers (HS-EA-PAG) series 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-MBS-TPS bound polymer photoresists, these new PAG bound polymers should be effective resists for 193 nm or EUV lithography.

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1. Introduction

The chemically amplified resist (CAR) system has been brought into the technology of microelectronic devices since it was proposed by IBM in 1980. The main advantanges of chemically amplified resists are its high sensitivity and resolution. Generally, it is composed of protected polymer matrix and a small molecule photoacid generator (PAG). PAG is one of the critical components in CAR system, it generates acid and catalyzes important chemical transformations within the film, such as deprotection, polymerization initiation, chain scission, or cross-linking process [1]. The traditional PAG blended CAR system has inherent incompatibility that can lead to PAG phase separation, PAG aggregation, non-uniform initial PAG and photoacid distribution, as well as acid migration during the post-exposure baking (PEB) processes. At the critical patterning challenge down to 32 nm or below, these problems ultimately create a tradeoff between achieving the desired characteristics of high resolution, high sensitivity, and low line edge roughness through formulation changes [2]. To overcome these problems, some new perfluoroalkanesulfonate (PFAS) blend PAGs that provide strong acid, good lithographic performance, and process compatibility were developed [1,3]. However, it has been reported that the PFAS compounds with more than four consecutive CF_2 units are an environmental hazard [4,5]. On the other hand, several systems with ionic or non-ionic PAG grafting into the main-chain of polymer have been reported [6–12]. 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, improved resolution, lower outgassing, and lower line edge roughness (LER) than corresponding cationic PAG bound polymer or PAG blend polymer resists [9–13]. Fluorinated compounds show special properties and application of optical-electronic, thermochemistry, biomedical and nanotechnology, because of their highest electronegativity and smaller atomic radius [14,15]. Herein we report a series of fluorinated anionic vinyl monomer PAGs and corresponding photoresists incorporating them in the main chain of the polymer (Figs. 1 and 2). Fig. 2 also outlines the anticipated advantages of polymer microstructures incorporating PAGs in the resist backbone.

2. Experimental Section

2.1. Materials

m-Trifluoromethylphenol, 2,3,5,6-tetrafluoro-phenol, 2,2′-azobisisobutyronitrile (AIBN), 4-bromo-1,1,2-trifluoro-1-butene, methacryloyl chloride, *N*,*N*-dimethylformide (DMF), *p*-chloromethylstyrene were purchased from Aldrich. Trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA), and acetoxystyrene

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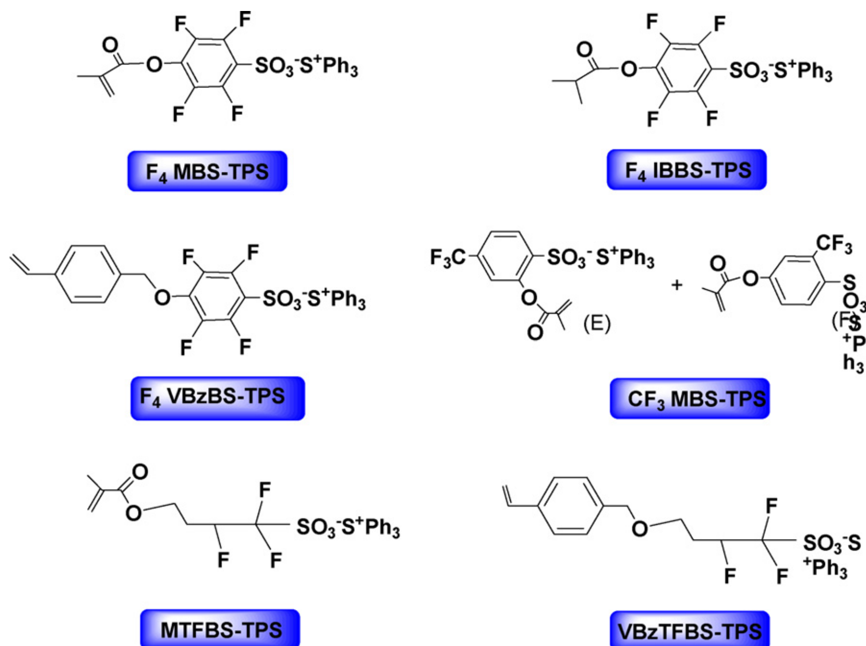


Fig. 1. Photoacid generator (PAG) structures.

were purchased from Tokyo Kasei Kogyo Co., Ltd., Japan. Methacrylic acid and isobutyric acid were purchased from ACROS ORGANICS. Triphenylsulfonium chloride 50% aqueous solution was purchased from City Chemical LLC, USA. 2-Ethyl-2-adamantylmethacrylate (EAMA) and γ-butyrolactone methacrylate (GBLMA) were supplied by AZ Electronic Materials Ltd. 2-Thienylmethyl methacrylate (TMM) was prepared according to the reported method [16]. 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.

2.2. 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 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).

2.3. Synthesis of photoacid generators

2.3.1. F4-MBS-TPS, F4-IBBS-TPS and F4-VBzBS-TPS

Triphenylsulfonium salt 4-(*methacryloxy*)-2,3,5,6-*tetrafluoro benzenesulfonate* (*F4-MBS-TPS,* Scheme 1) [7,8]: First, 4-hydroxy-2,3,5,6-tetrafluoro benzenesulfonate was prepared as per literature method [17]. This was then reacted with methacrylic acid in trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) as media, under a nitrogen atmosphere overnight, to get sodium 4-(methacryloxy)-2,3,5,6-tetrafluorobenzenesulfonate(F4-MBS-Na) in 97% yield, characterized by ^{1}H NMR (25 °C, ppm) δ6.45 (s, 1H); 6.13 (s, 1H); 2.06 (s, 3H), ^{19}F NMR (25 °C, ppm, ext. CF_3COOH): δ −152.35 (m, 2F); −137.68 (m, 2F). Then it was reacted with triphenylsulfonium chloride 50% aqueous solution in water, at room temperature overnight. The product was refined with dichloromethane and hexane, F4-MBS-TPS was obtained in 90% yield as a colorless crystal, mp: 57–59 °C. ^{1}H NMR (500 MHz, DMSO-d_6, δ) 7.42–7.92 (m, 15H); 6.45 (s, 1H); 6.12 (s, 1H); 2.03 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, δ) 162.8, 141.0, 136.3, 134.5,

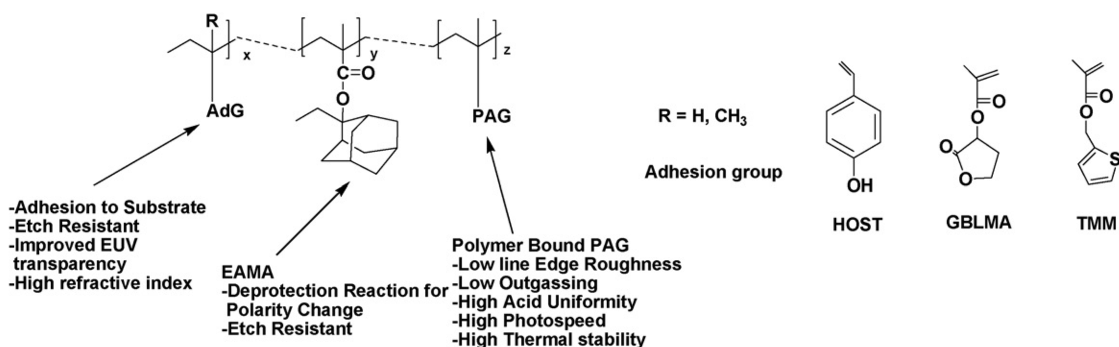
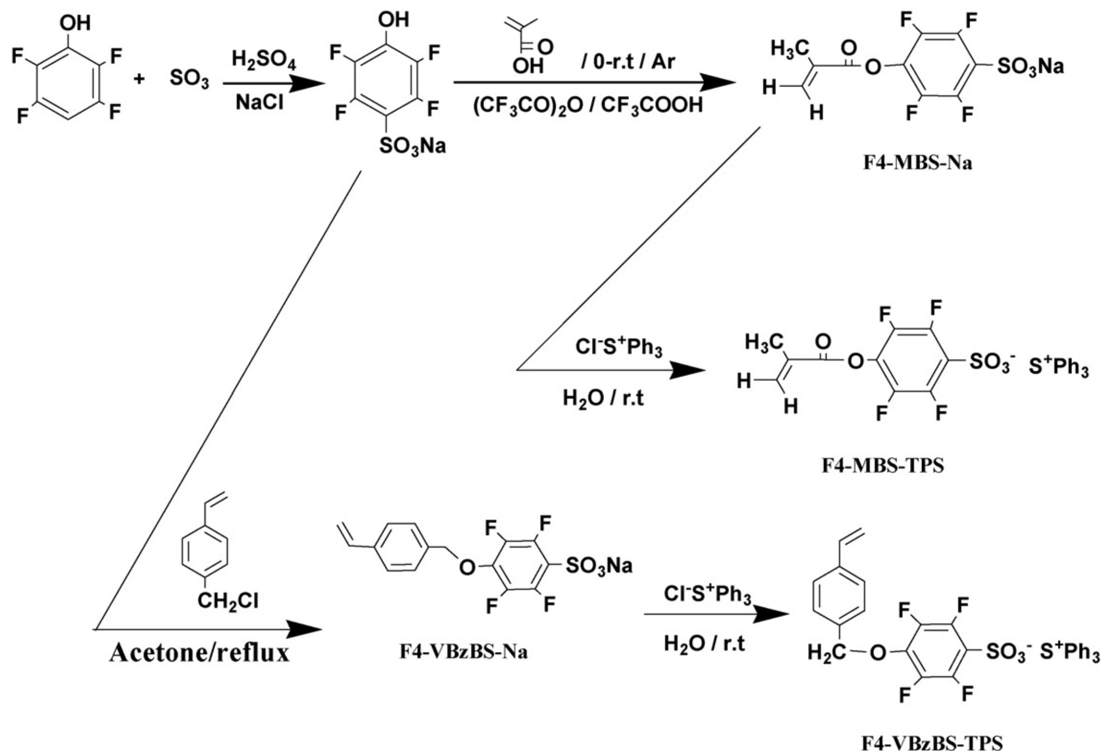


Fig. 2. Design of polymer microstructures for EUV lithography.



Scheme 1. Synthetic scheme of F4-MBS-TPS, F4-IBBS-TPS and F4-VBzBS-TPS.

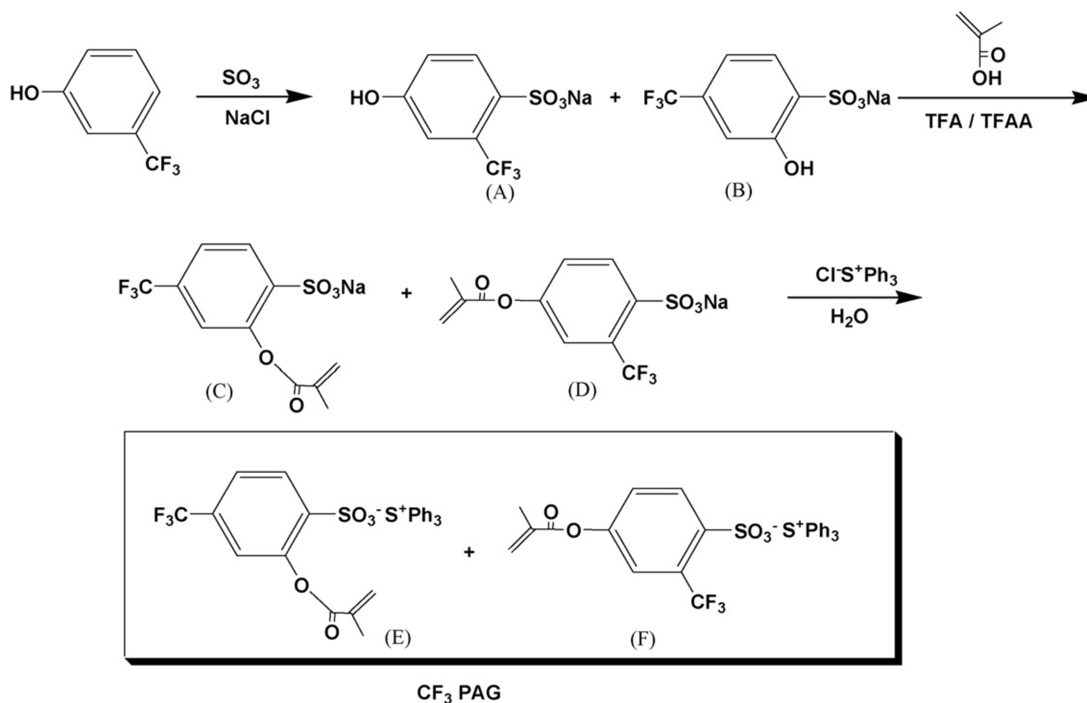
133.1, 132.5, 131.3, 130.4, 128.7, 125.4, 124.2 and 17.9. ^{19}F NMR (470 MHz, DMSO-d_6, δ, ext. CF_3COOH): −152.55 (m, 2F); −137.62 (m, 2F). Anal. Calcd for $C_{28}H_{20}F_4O_5S_2$: C, 58.33; H, 3.50; F, 13.18; O, 13.87; S, 11.12. Found: C, 58.39; H, 3.34; F, 12.85; O, 13.83; S, 11.06.

Triphenylsulfonium salt 4-(*isobutyloxy*)-2,3,5,6-*tetrafluorobenzenesulfonate* (*F4-IBBS-TPS*) was prepared by a method similar to F4-MBS-TPS using isobutyric acid instead of methacrylic acid in 78.0% yield as a colorless crystal, mp: 62–64 °C. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.42–7.95 (m, 15H); 3.02 (heptet, *J* = 7.2 Hz, 1H) and 1.26 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 172.9, 140.9, 136.2, 134.3, 132.4, 131.3, 131.0, 128.6, 125.1, 124.1, 33.1 and 18.4. ^{19}F NMR (470 MHz, DMSO-d_6, δ, ext. CF_3COOH): −153.82 (m, 2F); −138.73 (m, 2F). Anal. Calcd for $C_{28}H_{22}F_4O_5S_2$: C, 58.12; H, 3.83; F, 13.13; O, 13.83; S, 11.08. Found: C, 58.34; H, 3.56; F, 12.79; O, 13.54; S, 10.83.

Triphenylsulfonium salt 4-(*vinyl benzyloxy*)-2,3,5,6-*tetrafluoro benzenesulfonate* (*F4-VBzBS-TPS,* scheme 1) [18]: *P*-Chloromethylstyrene (20 mmol, 3.04 g) in 10 ml acetone was added dropwise to the aqueous solution of sodium 4-hydroxy-2,3,5,6-tetrafluoro benzenesulfonate (22 mmol, 5.90 g) under nitrogen at reflux over 24 h. After cooling to room temperature, the solid was filtered and washed with acetone, and dried under high vacuum overnight to give pure product sodium salt, 4-(vinyl benzyloxy)-2,3,5,6-tetrafluoro benzenesulfonate (F4-VBzBS-Na) as white solid in 72% yield characterized by ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.49 (d, *J* = 8.1 Hz, 2H); 7.45 (d, *J* = 8.1 Hz, 2H); 6.72 (dd, *J* = 11.2 and 17.8 Hz, 1H); 5.85 (d, *J* = 17.8 Hz, 1H); 5.26 (d, s *J* = 11.2 Hz, 3H). ^{19}F NMR (470 MHz, DMSO-d_6, δ, ext. CF_3COOH): −156.35 (m, 2F); −139.68 (m, 2F). Then (F4-VBzBS-Na) was reacted with triphenylsulfonium chloride 50% aqueous solution in water, at room temperature overnight. The product was refined with dichloromethane and hexane, triphenylsulfonium salt 4-(vinyl benzyloxy)-2,3,5,6-tetrafluoro benzenesulfonate (F4-VBzBS-TPS) was obtained in 76% yield as a colorless crystal. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.42–7.92 (m, 19H); 6.73 (dd, *J* = 11.2 and 17.8 Hz, 1H); 5.86 (d, *J* = 17.8 Hz, 1H); 5.27 (d,s *J* = 11.2.0 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 146.1, 144.1, 142.2, 141.7, 141.0, 139.2, 137.6, 136.2, 135.2, 134.4, 132.5, 131.4, 130.4, 128.9, 126.3, 125.2, 124.2, 121.3, 115.1, and 75.8. ^{19}F NMR (470 MHz, DMSO-d_6, δ, ext. CF_3COOH): −156.55 (m, 2F); −139.82 (m, 2F).

*2.3.2. Triphenylsulfonium salt 2-(methacryloxy)4-trifluoromethyl benzenesulfonate (**E**) and triphenylsulfonium salt 4-(methacryloxy)2-trifluoromethyl benzenesulfonate (**F**) (CF3-MBS-TPS)*

Triphenylsulfonium salt 2-(methacryloxy)4-trifluoromethyl benzenesulfonate (**E**) and triphenylsulfonium salt 4-(methacryloxy)2-trifluoromethyl benzenesulfonate (**F**) (CF3-MBS-TPS) were prepared as shown in Scheme 2 [19,20]. 2-Hydroxy-4-trifluoromethylbenzenesulfonic acid (**A**) and 4-hydroxy-2-trifluoromethylbenzenesulfonic acid (**B**) were prepared as per literature method, yield 63% (**A**:**B** = 7:3), characterized by ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.56 (d, *J* = 8.3 Hz, 1H); 7.36 (d, *J* = 8.3 Hz, 1H); 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 and trifluoroacetic anhydride 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) δ 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 ration 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 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



Scheme 2. Synthetic scheme of CF3 MBS-TPS.

methacryloxy trifluoro benzenesulfonate (CF3 MBS-TPS; **E**:**F** = 4:1) was obtained in 62% yield as a colorless crystal. ^{1}H NMR (500 MHz, DMSO-d_6, δ): 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 (125 MHz, DMSO-d_6, δ): 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 (470 MHz, DMSO-d_6, δ, ext. CF_3COOH): −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.

2.3.3. Triphenylsulfonium salt of 1,1,2-trifluorobutanesulfonate methacrylate (MTFBS-TPS) and triphenylsulfonium salt of 4-(vinyl benzyloxy)1,1,2-trifluorobutanesulfonate (VBzTFBS-TPS)

Triphenylsulfonium salt of 1,1,2-trifluorobutanesulfonate methacrylate (MTFBS-TPS) and triphenylsulfonium salt of 4-(vinyl benzyloxy)1,1,2-trifluorobutanesulfonate (VBzTFBS-TPS) was prepared in Scheme 3. It was prepared as per reported Ref. [19].

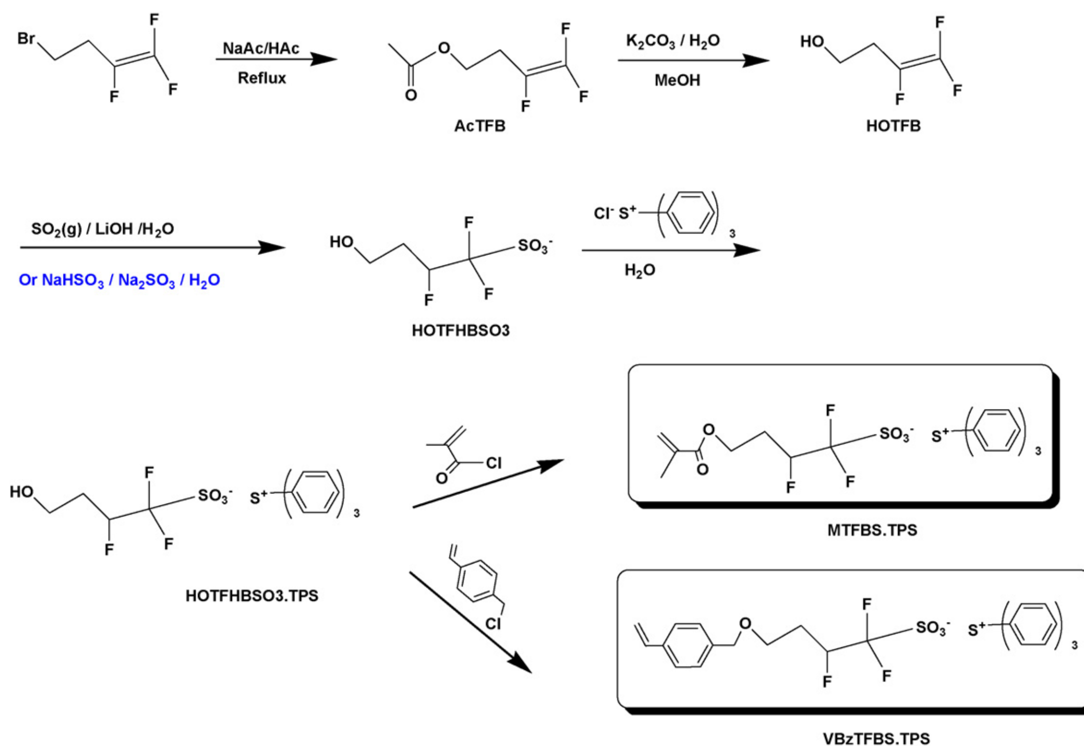
Triphenylsulfonium salt of 1,1,2-*trifluorobutanesulfonate methacrylate* (*MTFBS-TPS*): The lithium salt of 1,1,2-trifluoro-4-hydroxy-1-butanesulfonate ($HOTFHBSO_3Li$) was prepared according to the literature [21]. This (5.0 mmol) was then dissolved in 50 ml deionized water. A 50% aqueous solution of 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 white solid (yield 42%). FT-IR(film), ν cm^{-1}: 3448 (OH, str.); 3060 (phenyl ring C–H, str.); 1568, 1475,1446 (phenyl ring); 1243 (CF, S=O); 1088 (S=O); 1065 (S=O). ^{1}H NMR (500 MHz, DMSO-d_6, 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 dried dichloromethane. Methacryloyl chloride (6.0 mmol in 3 ml dichloromethane) was added dropwise at 0 °C under nitrogen flow, then warmed to room temperature, kept it 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), ν cm^{-1}: 2981, 2890(CH_3, str.); 1715 (C=O); 1568, 1475, 1446 (phenyl ring); 1242 (CF, S=O); 1088 (S=O); 1066 (S=O). ^{1}H NMR (500 MHz, DMSO-d_6, 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 (125 MHz, DMSO-d_6, 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 (470 MHz, DMSO-d_6, δ, ext. CF_3COOH): −113.8 −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.

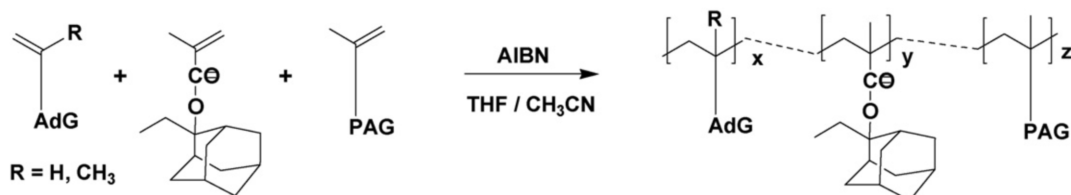
Triphenylsulfonium salt of 4-(*vinyl benzyloxy*)1,1,2-*trifluorobutanesulfonate* (*VBzTFBS-TPS*) was prepared by a method similar to MTFBS-TPS using *P*-chloromethylstyrene instead of methacrylic acid under the condition of DMF and TEA at room temperature, 36 h. The product was obtained as a white glassy solid in yield of 75%. FT-IR(film), ν cm^{-1}: 3030, 2981, 2890(phenyl ring, CH_3, str.); 1568, 1475, 1446 (phenyl ring); 1242 (CF, S=O); 1088 (S=O); 1066 (S=O). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.33–7.92 (m, 19H), 6.74 (dd, J = 11.2 and 17.8 Hz, 1H); 5.83 (d, J = 17.8 Hz, 1H); 5.25 (d, J = 11.2.0 Hz, 1H); 4.96–5.14(m, 1H); 4.76(s, 2H); 3.45–3.56(m, 2H); 2.12–2.32(m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, δ): 146.4, 136.1, 134.9, 134.2, 132.2, 131.3, 131.1, 130.3, 129.8, 129.2, 128.7, 126.3, 125.2, 121.3, 114.9, 88.6, 87.1, 55.8, 46.5, 32.3. ^{19}F NMR (470 MHz, DMSO-d_6, δ, ext. CF_3COOH): δ −112.8 −120.4 (d, d, 2F), −202.9 (m, 1F). Anal. Calcd for $C_{31}H_{29}F_3O_4S_2$: C, 63.46; H, 4.98; F, 9.71. Found: C, 63.73; H, 5.23; F, 10.16.

2.4. Synthesis of polymers

Terpolymers were prepared by free radical polymerization in sealed pressure vessels (Scheme 4). Hydroxystrene/γ-butyrolactone methacrylate/2-thienylmethyl methacrylate, 2-ethyl-2-adamantyl-methacrylate, anionic PAGs, and 2, 2′-azobisisobutyronitrile (AIBN) as a free radical initiator (5 mol% to the monomers) were dissolved in freshly distilled anhydrous tetrahydrofuran and acetonitrile



Scheme 3. Synthetic scheme of MTFBS-TPS and VBzTFBS-TPS.



Scheme 4. Synthetic scheme of terpolymers.

(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. Results and discussion

The anionic bound PAGs were prepared in moderate to good yield, and characterized by ^{1}H NMR (see Fig. 3), ^{19}F NMR and ^{13}C NMR, as well as elemental analyses. The terpolymers were obtained in yields from 31.3 to 43.2%, with PAG contents in the

Table 1
Polymerization results

Polymer	Mole feed ratio			Polymer composition			Yield (%)	M_w[a] (PDI)	Stability[b] (°C)	T_g (°C)
	AdG	EAMA	PAG	AdG	EAMA	PAG				
GB-EA-F4-MBS-TPS	25	72.5	2.5	44.8	48.6	6.6	36.2	3100 (3.1)	178	151
GB-EA-CF3 PAG	25	72.5	2.5	42.4	51.2	6.4	31.4	2700 (2.1)	181	162
GB-EA-MTFB-TPS	30	67.5	2.5	42.6	51.7	5.7	43.0	3100 (3.1)	195	166
TMM-EA-F4-MBS-TPS	33.6	63.6	2.8	41.3	46.3	12.4	28.5	2970 (1.6)	187	147
TMM-EA-MTFB-TPS	32.7	64.5	2.8	42.7	46.0	11.3	35.7	3050 (2.1)	147	123
HS-EA-F4-MBS-TPS[a]	25	72.5	2.5	35.0	57.9	7.1	37.3	3600 (1.6)	145	[c]
HS-EA-F4-VBzBS-TPS	25	72.5	2.5	52.4	40.8	6.8	31.3	3200 (2.1)	149	[c]
HS-EA-CF3 MBS-TPS	35	60	5.0	40.3	51.4	8.3	31.3	3700 (2.0)	159	[c]
HS-EA-MTFBS-TPS	30	65	5.0	38.5	56.2	5.3	42.3	2600 (1.6)	170	117
HS-EA-VBzTFBS-TPS	30	65	5.0	33.4	57.9	6.7	43.2	2900 (1.8)	186	139

[a] The molecular weight was determined by GPC with THF as mobile phase and polystyrene as narrow standards.
[b] The decomposition temperature was determined according to weight loss around 3.0%.
[c] Could not be determined by DSC, probably due to rigidity of these polymers, resulting from the bulky adamantyl and triphenylsulfonium moiety of the PAG in the polymer.

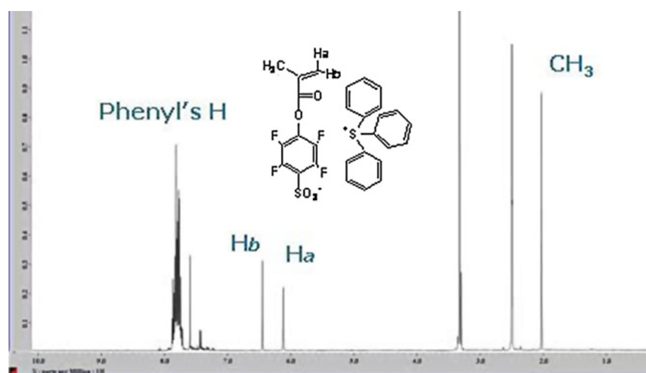


Fig. 3. ^{1}H NMR of F4-MBS-TPS in DMSO-d_6.

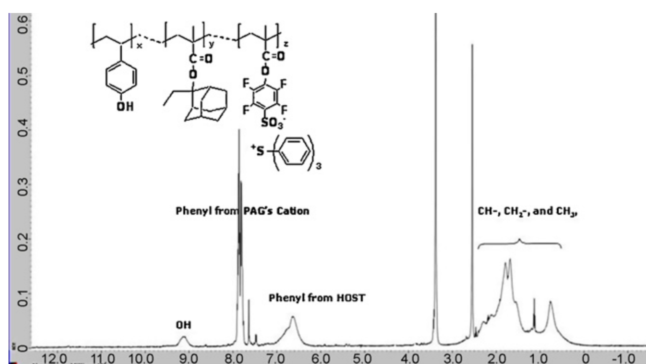


Fig. 4. ^{1}H NMR of HS-EA-F4-MBS-TPS in DMSO-d_6.

range of 5.3–8.3%, except for the TMM series with high PAG content of 11.3, 12.4% (mole ratio) for TMM-EA-MTFBS-TPS, TMM-EA-F4-TPS, respectively, which depends on the reactivity of the monomers. The molar composition of each unit in the terpolymers was determined by ^{1}H NMR (Fig. 4). The characteristic peaks: around 9.1 ppm is assigned to the proton of 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 polymer. The molar composition was calculated based on the integration ratios of the above corresponding peaks. The molecular weights were determined by GPC with THF as mobile phase. The results indicated the fluorinated PAG grafting polymers had a moderate molecular weight and molecular weight distribution (MWD), there is no big difference among different PAGs. 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 decomposition temperatures (T_d) were in the range of 147–195 °C. The glass transition temperature (T_g) of polymer GB or TMM systems was between 123 and 166 °C related to the thermostability. As for HOST system polymers, we just got the T_g of HS-EA-MTFBS PAG was 117 °C, the other polymers that bound CF3, F4 or VBzF4-PAG showed no obvious T_g, suggesting that polymer HS-EA-MTFBS 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 [12], no transitions were observed below the decomposition temperature for these polymers in this study also.

The acid generation efficiency for HS-EA-MTFBS-TPS, HS-EA-F4-MBS-TPS, HS-EA-CF3 MBSTPS are 81, 68, and 54% at the dose of 150 mJ/cm^2, respectively [19]. This demonstrates that the acid generation of PAGs is in the following order, MTFBS-TPS > F4-MBS-TPS > CF3 MBS-TPS. The stronger the electron-withdrawing group substituted on the aromatic ring, the higher the acidity of the PAG, leading to higher acid generation. The MTFBS-TPS and VBzTFBS-TPS has strong electron withdrawing fluorines next to the sulphonium group, this promotes higher acid generation on exposure.

4. Conclusion

A new series of functionalized anionic PAGs [methacrylate-substituted benzene sulfonic PAGs] (CF3 MBS-TPS, F4-MBS-TPS, F4-VBzBS-TPS) and perfuoroalkanesulfonic PAGs (MTFBS-TPS and VBzTFBS-TPS), 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 substitutes. Based on previously reported 193 nm and EUVL results of F4-MBS-TPS bound polymer photoresists [10,15], these fluorinated PAGs and corresponding PAG bound polymers should be effective resists for 193 nm or EUV lithography.

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