

Novel Photoresists Incorporating [(Trimethylsilyl)oxy]styrene

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We have synthesized and characterized polymers of [(trimethylsilyl)oxy]styrene, [(*tert*-butoxycarbonyl)oxy]styrene, and/or -sulfone. These polymers have been shown to be effective matrix resins for deep-UV photoresists when formulated with photoacid generators (PAGs). The incorporation of silicon into the polymers gives increased thermal stability and reduced weight loss after postexposure bake as compared to resists formulated with poly([(*tert*-butoxycarbonyl)oxy]styrene sulfone) (PTBSS). The weight loss upon postexposure bake has been reduced from 35% for PTBSS to values as low as 17% for the silicon-containing polymers. Preliminary lithographic testing indicates that these polymers exhibit good sensitivity and contrast.

Introduction

The [(*tert*-butoxycarbonyl)oxy]styrene (TBS) unit has been extensively studied for its application in chemically amplified resist materials. Ito et al.¹⁻⁴ were the first to report on the use of this monomer in the design of a poly([(*tert*-butoxycarbonyl)oxy]styrene)/onium salt based resist that exhibited a deep-UV sensitivity less than 10 mJ/cm². Subsequently it was shown that SO₂ could be readily incorporated into a TBS matrix free-radical, solution copolymerization^{5,6} to afford both an effective, high-resolution deep-UV resist operating at 248 nm when formulated with a photoacid generator (PAG)⁷ or a single-component, chemically amplified X-ray resist.⁸ However, the fully protected TBS-based photoresist materials adhere poorly to silicon substrates, and a significant loss of film thickness (~35%) is observed during processing.⁷ Specifically, this weight loss is associated with *tert*-butoxycarbonyl (BOC) group cleavage upon exposure and postexposure bake (PEB) in the presence of photogenerated acid.

The *tert*-butoxycarbonyl-protected resin systems additionally require a strong acid to effect cleavage of the protective group. Under present processing conditions, the strong acids generated from typical PAG materials appear to be neutralized by ubiquitous base causing T-shaped resist profiles and aqueous base insoluble residues.⁹

The question of weight loss may be addressed by diluting the concentration of the monomer containing the BOC group. By copolymerizing TBS with another styrene monomer containing an alternative protective group, the amount of BOC groups could be decreased. This approach was effectively used in the design of poly(acetoxystyrene-co-[(*tert*-butoxycarbonyl)oxy]styrene-co-sulfone) (PASTBSS) as a matrix resin for chemically amplified resist formulations.¹⁰ PASTBSS undergoes efficient acidolysis of the BOC appendage followed by aqueous base-induced hydrolysis of the acetoxy moiety. The approach presented here utilizes two distinctly different acid-sensitive protective groups; the first being the traditionally used BOC moiety, while the second is an acid-sensitive group chosen to effect enhanced performance of the TBS-based materials. This alternative group must meet several criteria. It must (i) be thermally stable and yet acid labile, (ii) generate nonvolatile acidolysis and/or hydrolysis byproducts so as to help minimize film thickness loss upon exposure and PEB, (iii) ensure low optical density of the polymer, and (iv) promote adhesion to the substrate. One group that meets these criteria is the trimethylsilyl (TMS) group.

Silylation of alcohols and phenols has been frequently employed in recent years as a protective method in organic synthesis. Reasons for this include the stability of the corresponding TMS ethers toward highly reactive basic reagents, while they do undergo selective cleavage under mildly acidic conditions.¹¹ As TMS ethers are more labile than BOC groups, weaker acids are necessary to generate the parent phenol. The utilization of a weaker acid may in turn, alleviate the problems associated with acid neutralization that have been noted with TBS-based resist systems.⁹

The use of [(trimethylsilyl)oxy]styrene (TMSS) as a component of resist materials has been described. For instance, Cunningham and Park¹² and Yamaoka et al.^{13,14}

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were among the first to describe the use of silylated poly-(hydroxystyrene) as a matrix resin for deep-UV chemically amplified resist formulations, while MacDonald¹⁵ has reported a plasma-developed resist based upon gas-phase silylation of poly(hydroxystyrene). It is only recently that the silylated monomer (TMSS) has been investigated as a means to prepare poly([(trimethylsilyl)oxy]styrene) (PTMSS).¹⁶

Here, we have evaluated the utility of TMSS as a component of short-wavelength sensitive chemically amplified resists employing acid catalysis as the imaging mechanism. Homo-, co-, and terpolymers of TMSS, TBS, and/or sulfone have been synthesized and characterized. Preliminary lithographic results are also presented.

Experimental Section

Reagents. 4-Vinylphenyl acetate was obtained from Hoechst-Celanes. 4-[(*tert*-Butoxycarbonyl)oxy]styrene was obtained from Kodak and used as received. Anhydrous sulfur dioxide (SO₂) was obtained from Matheson Gas Products. Azobisisobutyronitrile (AIBN) was obtained from Alfa.

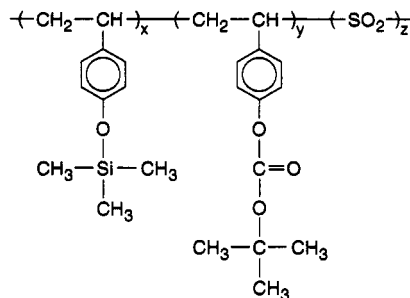
General Directions. All manipulations involved with the synthesis of polymers were performed on a vacuum line (0.05 mmHg). The polymerizations were carried out in a heavy-walled Kjeldahl flask modified with a vacuum/pressure stopcock allowing for the addition of monomer under vacuum, transfer, and distillation of SO₂ on the vacuum line.

Characterization. ¹H and ¹³C NMR spectra were recorded on solutions in CDCl₃ on a Brüker AM360 or a JEOL GX-500 spectrometer using the solvent proton signal as reference. Fourier transform infrared spectrometry (FTIR) was performed on a Mattson Instruments Galaxy Series 8020 FTIR spectrometer in dual-beam mode using double-polished silicon wafers or KBr disks. Ultraviolet spectroscopy was performed on a Hewlett-Packard 8452A diode array spectrophotometer on thin films of the polymers spun onto quartz disks from ethyl-3-ethoxypropionate (EEP, 15 wt %) solution. The film thickness of the UV samples was measured by a Sloan Dektak 3030 surface measuring system.

Analytical thin-layer chromatography (TLC) was performed on commercial Merck plates coated with silica gel GF254 (0.25 mm thick). Size-exclusion chromatography (SEC) was performed with a Waters Model 510 pump in conjunction with a Waters Model 410 differential refractometer detector and a Viscotek Model 100 differential viscometer detector. A set of Polymer Laboratories DL-gel, 5- μ m particle size MIXC pore-type columns were used with tetrahydrofuran as the eluting solvent. Data acquisition and analysis were performed by an AT&T 6312 microcomputer equipped with an ASYST Unical software system. The molecular weight data are reported relative to a universal calibration curve generated from narrow molecular weight, linear polystyrene standards (Polymer Laboratories).

Thermal analysis data were obtained using a Perkin-Elmer TGA-7 thermogravimetric analyzer interfaced with a TAC 7 thermal analysis controller and a PE-7700 data station. TGA samples were heated at a rate of 20 °C/min with a purified N₂ gas flow of 20 cm³/min. DSC samples were heated at a rate of 20 °C/min.

Elemental analyses (C, H, S, and Si) were determined by Robertson Microlit Laboratories Inc., Madison, NJ.



POLYMER	x	y	z
3	1	0	0
4	3	1	0
5	1	1	0
6	1	3	0
7	3	0	1
8	2.25	0.75	1
9	1.5	1.5	1
10	0.75	2.25	1

Figure 1. Chemical compositions of polymers 3–10. The subscripts *x*, *y*, and *z* represent mole ratios.

Rutherford backscattering spectrometry (RBS) spectra were recorded using a 2.120-MeV He²⁺ ion beam at a backscattering angle of 160°. The spectra were accumulated for a total ion dose of 40 μ C using a 10-nA beam current.

4-Vinylphenol, 1. 4-Vinylphenyl acetate (333 g, 2.06 mol) was added dropwise to an ice-chilled solution of 30% NH₄OH (240 mL) and the reaction temperature was not allowed to rise above 15 °C. After the reaction solution cleared, carbon dioxide was bubbled through the solution until the pH was neutral. As the product precipitated, water (~150 mL) was added to facilitate dispersion of the carbon dioxide. The product was filtered, washed with water, and dried to obtain 241 g of 1 as white crystals (97% yield). ¹H NMR δ 5.00 (dd, 1H, CH₂=), 5.47 (d, 1H, CH₂=), 6.50 (d, 1H, CH=), 6.74 (d, 2H, ArH), 7.14 (d, 2H, ArH), 7.43 (s, 1H, OH).

4-[(Trimethylsilyl)oxy]styrene, 2. 4-Vinylphenol (1, 90.1 g, 0.748 mol) was treated with hexamethyldisilazane (HMDS, 160 mL, 0.975 mol) for 30 min at room temperature. The product was purified by fractional distillation at 45 °C (0.05 mmHg) to give 135 g of 2 as a clear oil (94% yield). ¹H NMR δ 0.30 (s, 9H, SiCH₃), 5.15 (dd, 1H, CH₂=), 5.63 (dd, 1H, CH₂=), 6.68 (dd, 1H, CH=), 6.84 (dd, 2H, ArH), 7.32 (dd, 2H, ArH). ¹³C NMR δ 0.18 (CH₃), 111.71 (CH₂=), 120.07 (Ph CH), 127.36 (Ph CH), 131.13 (CH=), 136.27 (Ar C), 155.02 (Ar C).

General Procedure for the Synthesis of Copolymers of 4-[(*tert*-butoxycarbonyl)oxy]styrene (TBS) and 4-[(Trimethylsilyloxy)styrene (Polymers 3–6, Figure 1, Table 1. A mixture of AIBN and toluene were placed in a modified Kjeldahl reactor flask which was then placed in a -75 °C bath and the flask was evacuated. The degassed styrene monomers were transferred under vacuum into the reactor flask. The initiator to styrene mole ratio was 1:50 and the volume of toluene was equal to the styrene monomer volume. The reactor flask was sealed off and placed in a 65 °C bath. After 4–8 h, the flask was cooled to room temperature and acetone was added. The polymer was isolated by precipitation into 2-propanol and further purified by redissolution into acetone followed by precipitation into 2-propanol. The purified polymer was placed in a vacuum oven overnight at room temperature. All polymers were recovered as white solids. Polymers were typically prepared in 30–40% yield, with the recovered amounts being in the range 7–15 g.

General Procedure for the Synthesis of Copolymers of 4-[(*tert*-Butoxycarbonyl)oxy]styrene, 4-[(Trimethylsilyl)oxy]styrene and Sulfone (Polymers 7–10, Figure 1, Table 1). A mixture of AIBN and toluene in a modified Kjeldahl reactor flask was placed in a -75 °C bath and the flask evacuated. The AIBN to styrene monomer mole ratio was 1:50, and the total volume of toluene was equal to the volume of SO₂ (vide infra). The degassed styrene monomers were transferred under vacuum into the reactor flask. SO₂ was distilled into a graduated flask

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Table 1. Polymer Molecular Characteristics

no.	polymer ^a TMSS:TBS:SO ₂ composition	M _w	M _w /M _n	% yield	UV (abs/μm, at 248 nm)	T _(BOC deprotection) (°C)	T _(decomposition) (°C)	T _g (°C)
3	TMSS	55 200	1.2	26	0.19		419	78
4	TMSS ₃ :TBS ₁	68 300	1.3	25	0.24	229	429	85
5	TMSS ₁ :TBS ₁	64 500	1.3	22	0.20	213	396	106
6	TMSS ₁ :TBS ₃	75 500	1.6	54	0.14	206	399	117
7	TMSS ₃ :SO ₂	40 500	1.6	4			254	
8	TMSS _{2.25} :TBS _{0.75} :SO ₂	36 700	1.7	13	0.42	186	246	164 ^b
9	TMSS _{1.5} :TBS _{1.5} :SO ₂	58 100	3.3	33	0.38	180	240	178 ^b
10	TMSS _{0.75} :TBS _{2.25} :SO ₂	38 600	2.0	30	1.4	164	233	184 ^b

^a The abbreviation TMSS denotes [(trimethylsilyl)oxy]styrene and TBS denotes [(tert-butoxycarbonyl)oxy]styrene. The subscripts refer to the monomer ratios found in the respective polymers. ^b T_g of polymer after thermal removal of BOC.

at -75 °C, degassed by a freeze/thaw method, and then distilled into the reactor. The molar feed ratio of styrene to SO₂ was 1:25. The reactor flask was sealed off and placed into a 65 °C bath. After 4–8 h, the flask was cooled to room temperature, and the excess SO₂ removed under vacuum. Acetone was added, and the polymer was isolated by precipitation into petroleum ether. The polymer was purified by redissolution into acetone followed by precipitation into petroleum ether. The purified polymer was placed in a vacuum oven overnight at room temperature. All polymers were recovered as white solids. Polymers were typically prepared in 20–30% yield with the recovered amounts ranging from 5 to 15 g.

Polymer Characterization. All polymer structures were verified by ¹H NMR spectroscopy in CDCl₃ and had the following spectral characteristics: δ 0.27 (SiCH₃), 1.56 (C-CH₃), 2.0–3.5 (CH and CH₂), 6.0–7.3 (ArH). The IR spectra displayed the following characteristics: 1759 (C=O), 1250 (C-O), 914 cm⁻¹ (Si-O).

The ¹³C NMR spectra were recorded at 50 °C on a JEOL GX-500 spectrometer at a resonance frequency of 125 MHz. Quantitative spectra were obtained with gated decoupling without the nuclear Overhauser effect (NOE) and a pulse decay of 15 s. The samples were prepared in chloroform-*d* (CDCl₃) as 10–20 wt % solutions. The spectra were referenced to CDCl₃ (77.0 ppm at 50 °C). ²⁹Si NMR spectra (99.25 MHz) were recorded with the same samples at 50 °C without the NOE, with a pulse delay of 25 s and were referenced relative to hexamethyldisiloxane (7.30 ppm from TMS).

Polymer 3. Anal. Calcd: C, 68.7; H, 8.38; Si, 14.6. Found: C, 68.4; H, 8.27; Si, 14.4. GPC: M_w = 55 200; M_n = 45 200; D = 1.2; IV = 0.19.

Polymer 4. Anal. Calcd: C, 69.3; H, 8.09; Si, 10.6. Found: C, 69.3; H, 8.33; Si, 10.6. GPC: M_w = 68 300; M_n = 53 500; D = 1.3; IV = 0.23.

Polymer 5. Anal. Calcd: C, 69.9; H, 7.82; Si, 6.81. Found: C, 69.9; H, 8.00; Si, 6.74. GPC: M_w = 64 500; M_n = 49 000; D = 1.3; IV = 0.21.

Polymer 6. Anal. Calcd: C, 70.4; H, 7.56; Si, 3.29. Found: C, 70.3; H, 7.77; Si, 3.11. GPC: M_w = 75 500; M_n = 46 000; D = 1.6; IV = 0.21.

Polymer 7. Anal. Calcd: C, 58.9; H, 7.19; Si, 12.5; S, 7.15. Found: C, 60.1; H, 6.52; Si, 12.3; S, 7.50. GPC: M_w = 40 500; M_n = 26 000; D = 1.6; IV = 0.11.

Polymer 8. Anal. Calcd: C, 59.7; H, 6.97; Si, 9.11; S, 6.93. Found: C, 60.6; H, 7.24; Si, 10.4; S, 5.98. GPC: M_w = 36 700; M_n = 21 900; D = 1.7; IV = 0.06.

Polymer 9. Anal. Calcd: C, 60.5; H, 6.77; Si, 6.72; S, 5.89. Found: C, 62.0; H, 6.87; Si, 6.34; S, 5.58. GPC: M_w = 58 100; M_n = 17 700; D = 3.4; IV = 0.18.

Polymer 10. Anal. Calcd: C, 61.2; H, 6.57; Si, 2.86; S, 6.56. Found: C, 63.9; H, 6.88; Si, 2.84; S, 4.68. GPC: M_w = 38 600; M_n = 19 500; D = 2.0; IV = 0.12.

PAG Synthesis. PAGs 11–13 were obtained from F. M. Houlihan, and their synthesis was performed as described elsewhere.^{17,18}

Resist Formulation. Solutions were prepared by dissolving the PAG (15 wt % relative to the weight of the polymer) in a solution of the matrix polymer (15 wt/vol %) in ethyl ethoxypropionate (EEP). The solutions were spin-coated onto 4-in. HMDS (hexamethyldisilazane) primed silicon substrates. The resist-coated substrates were baked at 120 °C for 30 s. The substrates were then exposed on a Süss Model MA56A contact aligner equipped with a Lambda Physik excimer laser or a GCA LaserStep prototype deep-UV exposure tool operating at 248 nm. After exposure, the substrates were baked at 120 °C for 1 min. The developing solution was comprised of tetramethylammonium hydroxide (TMAH, 25% in water) diluted further in water. The ratio of TMAH solution to water varied from 1:10 to 1:9, and 2-propanol was occasionally added to the developing solution (5 vol %) as needed. The exposed and baked films were developed in the aqueous base solution for 15–120 s. Film thickness was measured on a Nanospec film thickness gauge (Nanometrics, Inc.). Resolution and image quality were determined by examining developed patterns with a JEOL Model 35CFS scanning electron microscope or with a WILD M 650 stereomicroscope.

Results and Discussion

Synthesis. Silylated poly(vinylphenol) has been reported to be an effective matrix resin for chemically amplified resist formulations utilizing several classes of PAG materials.^{12–14,19,20} Typically, silicon was incorporated into the polymers by silylation of poly(vinylphenol). Complete functionalization is, however, difficult to attain by this method. It has been postulated that as portions of the polymers become more hydrophobic due to silylation, phase separation from the phenolic (or hydrophilic) regions prevents complete functionalization.¹⁴ Recent work has shown that the problem of incomplete derivatization can be circumvented by polymerizing a silicon-containing monomer in the presence of a radical initiator to give the silicon-bearing homopolymer.¹⁶ We used this technique as a means to incorporate silicon into the PTBSS-based resist. Our goal was to obtain a photoresist with a lower percent of weight loss after PEB with better resolution and process robustness.

Large quantities of pure 4-vinylphenol, 1, could be readily synthesized by a method similar to that developed by Gupta.²¹ The [(trimethylsilyl)oxy]styrene monomer (TMSS, 2) is then easily prepared by treating 4-vinylphenol, 1, with hexamethyldisilazane (HMDS). The various silicon-containing polymers were synthesized by radical polymerization of TMSS with or without TBS and/

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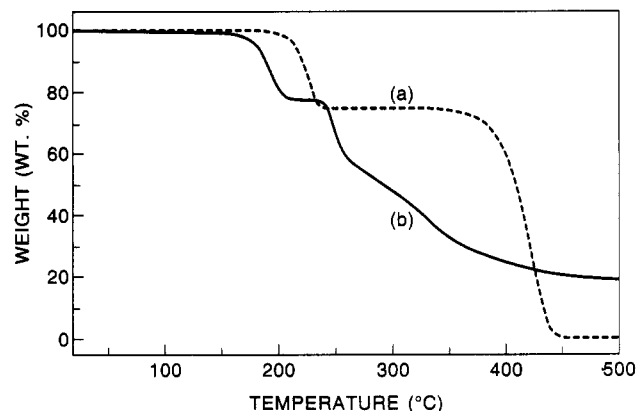


Figure 2. Thermal gravimetric analysis curves for (a) polymer 5 without sulfone and (b) polymer 9 with sulfone.

or sulfur dioxide (Figure 1). All the silicon-containing polymers could be readily synthesized by this method except for polymer 3, where the Si-O bonds appeared to cleave during either polymerization or workup such that this material was difficult to isolate. The loss of the trimethylsilyl (TMS) group can be readily detected by both elemental analysis and proton NMR spectroscopy. The yields were generally high and increased with increasing TBS content.

All polymers shown in Figure 1 were thoroughly characterized by various spectroscopic and chromatographic techniques and a partial summary of their properties is shown in Table 1. As seen in Table 1, the molecular weights did not vary significantly with the polymer composition. The polydispersity was lower than expected and increased slightly as more TBS was incorporated into the polymer. The observation of polydispersities lower than two is consistent with the results reported by Bonfils.¹⁶ The low values for the polydispersity may be a reflection of interactions between the polymers and column packing materials used during GPC analysis and thus may not truly reflect the molecular weight distribution of these systems.

The optical densities of polymers 3-6 are very similar in that the TMSS unit has as low an absorbance as the TBS counterpart (Table 1). Incorporation of sulfone into the polymer backbone leads to an increase in the absorbance of the polymers (7-10).

The composition of the polymers was determined by proton NMR spectroscopy and thermal gravimetric and elemental analyses. Specifically, these methods were used to determine the ratio of the TMSS monomer to TBS. By all methods, the styrene monomer ratio was equal to the monomer feed ratio. Integration of the silyl methyl protons at 0.85 ppm relative to either the butoxy protons at 1.55 ppm or to the aromatic protons (6-7.3 ppm) gives an approximate value for the ratio of the styrene monomers in the polymers. Elemental analysis also indicated that the ratio of TMSS to TBS in the polymers was approximately equal to the monomer feed ratio. From the elemental analyses, the ratio of styrene monomers to sulfone was found to range from 2.4:1 to 3:1. Similar ratios of styrene monomer to sulfone are seen in the PTBSS resist.⁶

Thermogravimetric analysis (TGA) provided a method to clearly distinguish between the loss of the BOC group and the thermal decomposition of the polymer (Table 1). This is illustrated by Figure 2 in which the polymers 5 and

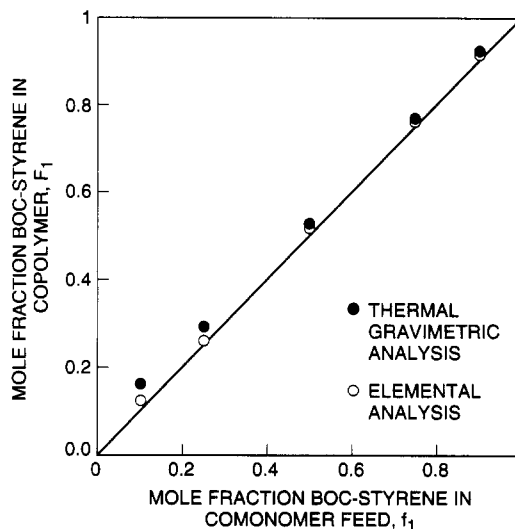


Figure 3. Instantaneous composition diagram in which the TBS content of the monomer feed mixture (f_1) is plotted against the instantaneous composition of the TBS (F_1) in the copolymer.

9 (both materials having a 1:1 TMSS:TBS ratio, with 9 additionally containing sulfone) are compared. In general, removal of the BOC group occurs at 164-229 °C, depending on the polymer structure. From the percent of weight loss after thermal deprotection of the BOC group, the styrene monomer ratio in the polymers was again calculated to be equal to the monomer feed ratio.

The radical reactivity ratios of the two styrene monomers with respect to each other can be determined by analysis of the instantaneous copolymer compositions (taken at 5-10% conversion), which were evaluated by both TGA and elemental analysis. The TBS composition of the copolymer (F_1) was plotted against the percentage of TBS in the monomer feed ratio (f_1) and is shown in Figure 3. The actual curve coincides within experimental error with the diagonal line indicating that the radical reactivity ratios of both monomers are essentially equal to one.

Fineman-Ross plots²² were generated from the instantaneous polymer compositions determined by both methods of analysis. The reactivity ratio for the TBS (r_a) was calculated to be 1.3 using the TGA data and 1.1 using data derived from elemental analysis. The reactivity ratio for TMSS (r_b) was calculated to be 1.1 or 1.0, with TGA or elemental analysis data, respectively. As $r_a \approx r_b \approx 1$, fluctuations in the copolymer composition are not expected to occur under the reaction conditions employed here, and the monomer units are expected to be placed randomly along the polymer chain. The present system may closely approximate an ideal copolymerization, in which the product of r_a with r_b equals 1. In this situation, the propagating polymer species shows the same preference toward reaction with either monomer.²²

Characterization. As evidenced by the TGA data, incorporation of the silyl ether unit into the polymers examined here greatly enhances their thermal stability. As shown in Table 1, the onset temperature of polymer decomposition decreases with a decrease in the percent composition of TMSS. Concurrently, the onset temperature of thermal deprotection of the BOC group is lowest in the polymers with the lowest percentage of silyloxy groups.

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Table 2. NMR Compositional Analysis of Polymer Samples 5, 8, and 9

no.	polymer	styrene monomer type (%)			$R(\text{sty}/\text{SO}_2)$	
		-OH	TBS	TMSS	NMR ^a	EA
9	TMSS _{1.5} :TBS _{1.5} :SO ₂	13	43	44	2.55	2.4; 2.5 ^b
8	TMSS _{2.25} :TBS _{0.75} :SO ₂					
	A	10	28	62	2.30	2.5
	B	9	28	63	2.19	2.4
5	TMSS ₁ :TBS ₁		54	46		

^a $R = P(M)/[1 - P(M)]$ and was calculated as in ref 6. ^b Analysis was performed 6 months apart on the same sample.

Similar to that observed with the PTBSS resist system,⁶ the incorporation of sulfone into the polymers decreases their thermal stability (Table 1). The onset temperature for polymer decomposition is approximately 160–180 °C lower in polymers containing sulfone (7–10) than for the corresponding materials without sulfone (3–6). Similarly, the onset temperature of BOC group deprotection is lowered by about 30–40 °C in the sulfone containing polymers (7–10). An example of these phenomena are shown in Figure 2 which compares TGA curves for polymers 5 and 9, both of which have the same styrene ratio (1:1 TMSS:TBS), while 9 contains sulfone and 5 does not.

The glass transition temperatures (T_g) for these polymers also varied with composition (Table 1). For polymers 3–6, the T_g increases from 78 to 117 °C as the percent of TBS in the polymer increases. Trimethylsilyloxy groups tend to lower glass transition temperatures due to their increased flexibility.²³ The T_g 's for polymers 7–10 were higher than the onset temperatures for the thermal deprotection of the BOC groups. Therefore, the T_g could only be observed in the silyloxy-hydroxy polymers obtained after thermal removal of the BOC groups. There is a general increase in the T_g of the sulfone-containing polymers (7–10) with an increasing percentage of hydroxystyrene which correlates to an increase in the amount of BOC-styrene in the polymers. These results are consistent with previous work which has shown that inclusion of sulfone into a polymer raises the T_g by 30–40 °C.¹⁰

A series of samples with varying amounts of each monomer were analyzed by ¹³C NMR (Table 2) and the ¹³C NMR spectrum of polymer 8A is shown in Figure 4. As previously reported for the BOC substituted polymer, the α - and β -carbon backbone resonances (30.1–68.0 ppm) are not affected by substitution of the silyl ether group on the styrene ring and the assignments are the same as those made previously.⁶ The silyl ether methyl groups resonate between 0.275 and 1.86 ppm. The C1 (123.39, 132.21–138.63 ppm), C2 and C6 (128.57–130.73 ppm), and C3 and C5 (120.21–121.42 ppm) ring carbons overlap with those of the BOC-substituted rings. The TMSS C4 ring carbons resonate between 154.6 and 156.2 ppm, downfield from the TBS C4 ring carbons at 149.0–152.0 ppm and show sensitivity to the sequence distribution as was observed in the deprotected polymer, poly(4-hydroxystyrene sulfone).⁶ The resonances of the C4 carbons of the silylated segments show some overlap with the C4 carbon resonance of the deprotected polymer. The poly(4-hydroxystyrene sulfone) C3 and C5 ring carbons at 116.17 ppm⁶ are

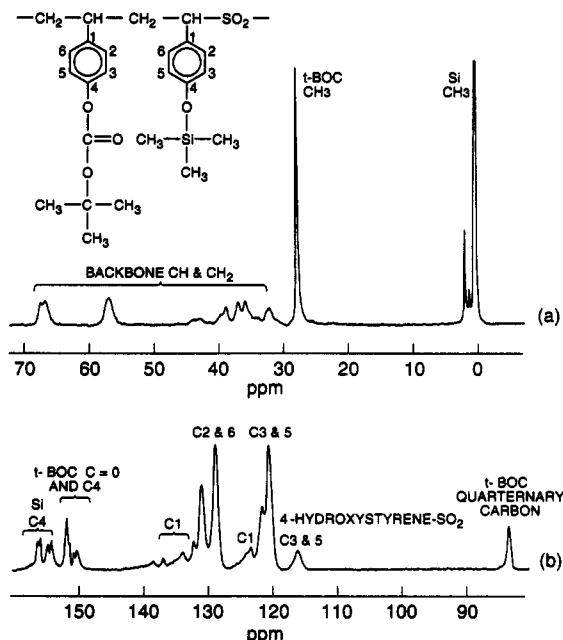


Figure 4. ¹³C NMR spectrum of polymer 8A. The following abbreviations are used in the figure: Si C4 refers to C4 of the TMSS unit, t-BOC C = O and C4 refer to the carbonyl and C4 of the TBS unit and 4-hydroxystyrene-SO₂ C3 and 5 refers to the C3 and C5 peaks emanating from the partially hydrolyzed sulfone polymer.

integrated to obtain the amount of deprotection in the samples. The methyl carbon resonances from both the BOC (27.75 ppm) and the silyl ether groups are integrated to determine the amounts of each of these groups in the polymer.

Some degree of deprotection is observed for the sulfone polymers (Figure 4 and Table 2). With the 1:1 TMSS:TBS/sulfone polymer (9), the deprotection appears to originate equally from the BOC and the silyl ether groups. According to the monomer feed ratio used to synthesize this material, the polymer should contain 50% of each styrene monomer but only 43–44% of each is observed. Samples were analyzed by elemental analysis immediately after synthesis and then again 6 months later. The results did not change within experimental error during this time period. Two samples with a 3:1 TMSS:TBS composition, 8, were also examined by NMR (Table 2). Sample 8A was analyzed less than a week after synthesis and sample 8B after more than a month. Both showed 9–10% deprotection, which appeared to originate from the silyl ether groups. The fact that both samples showed the same amount of deprotection indicates that the deprotection occurs during the synthetic workup or shortly afterward. This phenomenon may preclude the use of TMS-derived poly(aryl sulfones) for lithographic applications unless the extent of deprotection can be precisely controlled. Long-term stability has not been monitored by NMR. The R values (styrene-type monomers:SO₂) calculated by NMR (Table 2) were consistent with those obtained from elemental analysis with errors not more than the amount of deprotection in the polymer. No deprotected sites were observed in polymer 5 (Table 2) which is similar to 9 but does not contain SO₂. It appears that sulfur dioxide may play a role in the partial deprotection of the polymers.

The ²⁹Si NMR spectra of the substituted styrene copolymers were recorded with the hopes of correlating

(23) Jurek, M. J.; Tarascon, R. G.; Reichmanis, E. *Chem. Mater.* 1989, 1, 319.

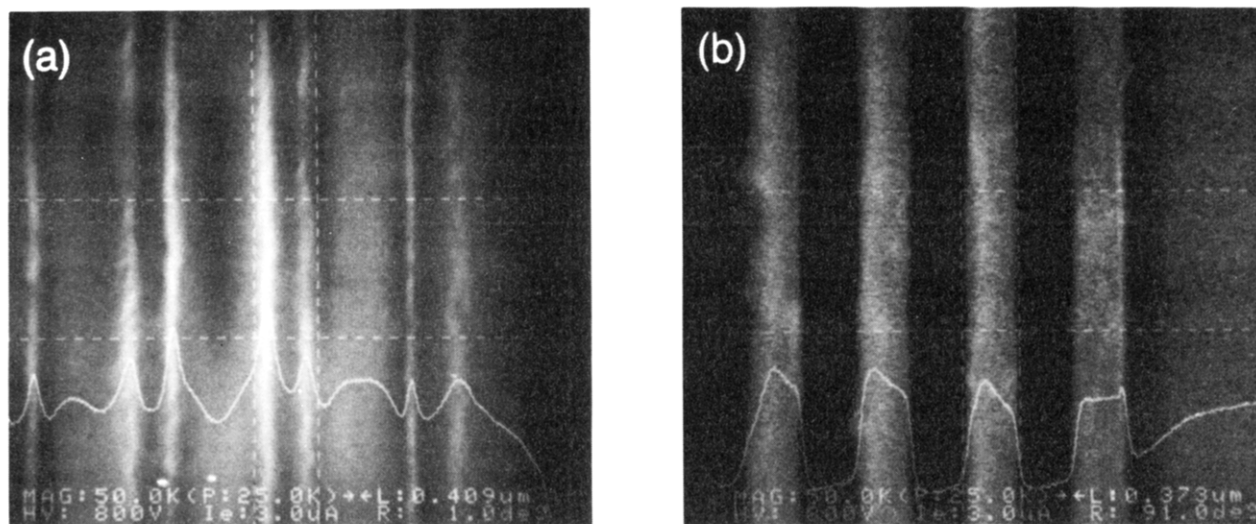


Figure 5. SEM photos of line/space patterns of (a) polymer 6 with 0.40- μm resolution and (b) polymer 10 with 0.35- μm resolution.

the silyl ether methyl or the C4 carbon resonances to the sequences responsible for these resonances to help determine the positioning (sequence distribution) of the silyl ether styrene units relative to the TBS units. However, the ^{29}Si NMR spectrum for copolymer 5 shows a broad envelope of resonance and the correlation required to determine sequence distribution could not be made. ^{29}Si NMR could, however, be used to monitor the purity of the polymer samples, since the spectra do clearly differentiate the silicon-bearing moieties. For example, the silyl ether methyl in the TMSS-TBS copolymer 5 shows one resonance at 18.46 ppm, while the silyl ether methyl of the TMSS monomer (2) resonates at 17.9 ppm and hexamethyldisiloxane (the product from hydrolysis of the silyl ether) resonates at 7.30 ppm.

Lithography. In the first lithographic study, all available polymers were formulated with 2,6-dinitrobenzyl tosylate (11) as the PAG. Subsequent studies with polymers 3–5, and 6 involved the use of several different photoacid generators. Contrast was determined for resists formulated with all polymers except for 3 and 7. Images obtained with resist samples prepared from polymer 3 could not be cleared from the silicon substrate, despite changing a variety of processing parameters. This result will be examined further in a later section of this paper. As stated previously, 7 contains a small amount of hydroxystyrene which would affect the lithographic behavior of this material. The lithographic results for resist solutions of polymers 4–6 and 8–10 containing the sulfonate PAG 11 are shown in Table 3. As postulated, dilution of the TBS monomer with TMSS decreased the amount of weight lost during PEB, as did incorporation of sulfone into the polymers. Additionally, as shown in Table 3, the sensitivity of the photoresists generally increased with an increasing amount of Si-styrene. Under the present processing conditions, the contrast for all the materials is high.

In Figure 5 are shown line/space patterns obtained from resists formulated with polymers 6 and 10. Both polymers contain the same ratio of TMSS to TBS, though polymer 10 also contains sulfone. In Figure 5a, the line/space pattern of polymer 6 is not resolved. However, the line/space pattern in polymer 10 can be resolved to 0.35 μm (Figure 5b). The addition of the highly polar sulfone unit into the polymer matrix may influence the molecular interactions between the PAG or the photogenerated acid

Table 3. Materials Lithographic Characteristics Utilizing 2,6-Dinitrobenzyl Tosylate (11)

polymer composition	no.	% wt loss ^a	D_p (mJ/cm ²)	γ
TMSS ₁	3	20		
TMSS ₃ :TBS ₁	4	17	100	7
TMSS ₁ :TBS ₁	5	31	152	>10
TMSS ₁ :TBS ₃	6	34	95	>10
TMSS _{2.25} :TBS _{0.75} :SO ₂	8	19	84	8
TMSS _{1.5} :TBS _{1.5} :SO ₂	9	24	110	>10
TMSS _{0.75} :TBS _{2.25} :SO ₂	10	28	32	>10

^a During PEB.

and the polymer matrix affording improved lithographic imaging characteristics.

Profiles of 0.5- μm features obtained in resist films utilizing polymers 6 and 10 are shown in Figure 6. In the sulfone-free polymer (Figure 6a), the residual material may indicate that the matrix is not being fully deprotected. It is plausible that either the PAG or the photogenerated acid has migrated away from the silicon substrate/polymer interface, disallowing chemistry to occur in this region. The diffusion of the PAG or acid may be hindered if coordination or complexation occurs with the polar sulfone group. This is seen in Figure 6b, as essentially no residual material is present at the resist/substrate interface. The T-shaped profiles indicate that the photogenerated acid at the polymer/air interface has been neutralized by atmospheric base, a phenomenon that can be corrected by the use of an overcoat.²⁴

As mentioned previously, all polymers afforded resists that gave reasonable lithographic results except for the homopolymer 3. Several experiments were performed to investigate the failure of this material to be cleared from the silicon substrate. Under typical processing conditions of a PEB at 120 °C for 1 min followed by aqueous base development, approximately 200 Å of material was consistently left in the exposed regions.

Rutherford backscattering spectrometry (RBS) experiments were performed to determine the carbon, oxygen, nitrogen, and sulfur concentrations in the residue that remained after exposure and development of resists formulated with polymer 3 and the sulfonate PAG 11. The RBS data indicate that there is a 29:1 ratio of C:S,

(24) Nalamasu, O.; Reichmanis, E.; Cheng, M.; Pol, V.; Kometani, J. M.; Houlihan, F. M.; Neenan, T. X.; Bohrer, M. P.; Mixon, D. A.; Thompson, L. F. *Proc. SPIE* 1991, 1466, 13.

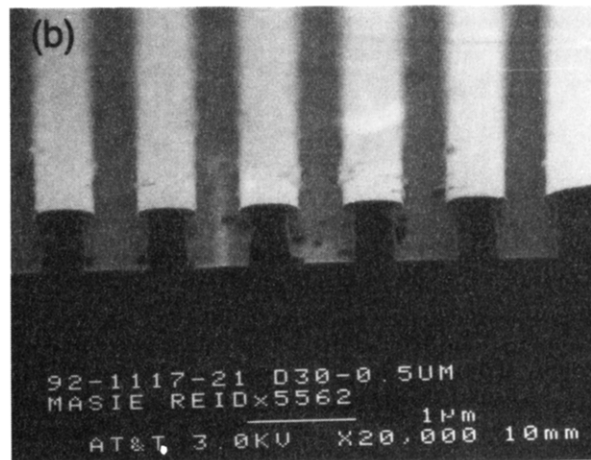
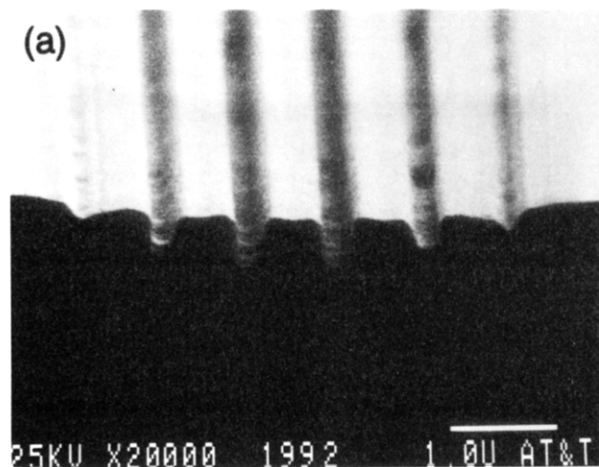


Figure 6. SEM photos of profiles of (a) polymer 6 and (b) polymer 10.

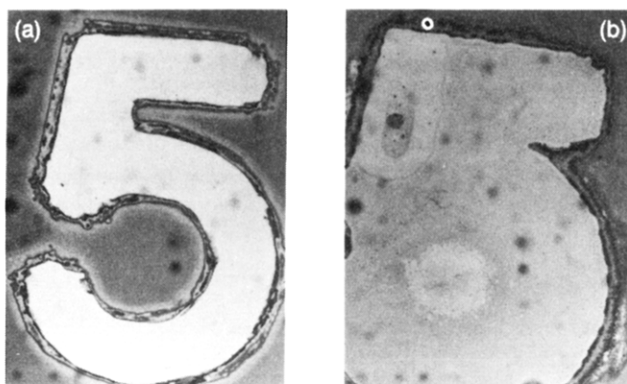


Figure 7. Effect of PEB on diffusion of acid generated from a sulfonate PAG in a matrix of polymer 3: (a) 120 °C for 1 min; (b) room temperature for 2 days.

a value that is significantly higher in sulfur than would be expected for a polymer film with uniformly distributed PAG. As sulfur is present only in the PAG, it appears that the PAG or the photogenerated acid is a significant component of the residue.

The thickness of the residual material was not affected by substrate priming conditions or by variation of the polymer film thickness on the silicon substrate. In addition, varying the PEB temperature did not influence the presence of the residue that remains after development of resists formulated from polymer 3. Increasing the PEB temperature to 150 °C, while keeping the time constant (1 min) did not effect clearing of the resist from the silicon substrate. With a PEB of 70 °C for 1 min, which is below the T_g of the polymer, there was a 4% weight loss in the exposed regions and no net change in film thickness in these regions after aqueous development. In another experiment, the exposed substrate was allowed to stand at ambient temperature (22 °C) for 2 days in place of the standard 120 °C for 1-min PEB. This caused the image to "spread out" or distort as shown in Figure 7, indicating that acid mobility at room temperature is significant. The image shown in Figure 7a was obtained upon 120 °C/1-min PEB, while Figure 7b depicts the results of the ambient temperature processing described above. At the ambient PEB temperature, there is still about 400 Å of material left in the fully exposed regions after aqueous development.

A comparison of the IR spectra of the polymeric film after prebake and exposure/PEB demonstrates that after exposure and PEB, the Si-O peak at 914 cm^{-1} disappears and an O-H stretch centered at 3300 cm^{-1} appears,

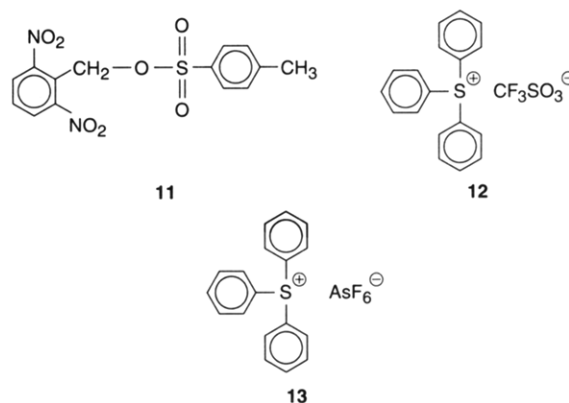


Figure 8. Chemical structures of PAGs 11-13.

suggesting that deprotection does occur. The residual film is only 100 Å thick after aqueous base development, so characterization of the residue by infrared spectroscopy was not possible.

To explore whether the appearance of residue is directly related to the PAG, other photoacid generators were utilized: triphenylsulfonium triflate (12) and triphenylsulfonium hexafluoroarsenate (13, Figure 8). With both onium salt PAG (12, 13) materials only a 4% weight loss upon exposure and PEB is observed for a resist utilizing the silylether homopolymer 3, and no development of images could be achieved. As a comparison, PAGs 12 and 13 were also used with the TMSS-TBS copolymers 5 and 6. When formulated with the triflate PAG (12), the 1:3 TMSS:TBS copolymer 6, exhibited lithographic behavior similar to that which was observed with PAG 11, namely, ~35% weight loss upon exposure and PEB, and a contrast >10. The clearing dose was found to be 26 mJ/cm^2 . There is a 10% weight loss after PEB for polymer 6 formulated with the arsenate PAG (13), but the photoresist film does not develop in either aqueous TMAH or aqueous TMAH containing 5% 2-propanol. Similarly, polymer 5 formulated with PAG 13 also does not form an image.

We believe that the above lithographic results indicate that either the PAG or the photogenerated acid may be volatilizing from or undergoing phase segregation in selected polymer matrices. In fact, Hult et al. have reported that migration of onium salts readily occurs in polystyrene systems as evidenced by ESCA.²⁵ They

(25) Hult, A.; MacDonald, S. A.; Willson, C. G. *Macromolecules* 1985, 18, 1804.

concluded that the air/polymer interface was depleted in the salt, with more polar salts suffering greater surface depletion than the less polar onium salts. Additionally, they found that spin-coating of the resist solution depletes the PAG at the resist/air interface, concentrating it at the substrate surface when the PAG has poor solubility in the polymer. In the examples presented here, it is postulated that the incorporation of the hydrophobic monomer, TMSS, affects the miscibility of PAG materials and their acidic photoproducts with the resist matrix resins, which in turn may lead to a degradation in lithographic performance.

The hydrolytic stability of the silicon-bearing resists was an additional concern. Thus, aging studies were carried out on solutions of the polymers in EEP. The solutions containing a sulfonate PAG were incubated at 40 °C for 2 weeks in a water bath. In polymers containing sulfone (7–10), the silyl ether groups were cleaved after 1–4 days. By comparison, polymers without sulfone (3–6) underwent hydrolysis at a much slower rate. The percent hydrolysis was determined by integration of the peak for the Si–C stretch at 914 cm^{-1} relative to the peak for the C–C stretch of the polymer backbone at 1510 cm^{-1} in the IR spectra. The propensity of the polymers containing sulfone (7–10) to undergo hydrolysis of the TMS group may arise from the difficulty to completely remove free SO_2 from the materials upon isolation. In the presence of atmospheric moisture, the presence of SO_2 would lead to acid formation which would then act as a catalyst to promote hydrolysis of the silyl ether units.

Conclusion

We have demonstrated that TMSS may be copolymer-

ized with TBS and sulfone to yield polymers that have excellent thermal properties and reduced weight loss in comparison to PTBS and PTBSS on PEB. The onset temperature of deprotection is as high as 229 °C as compared to 160 °C for PTBSS, while the weight loss can be reduced from 35% in PTBSS down to 17%. The reactivity ratios of TMSS and TBS are approximately 1. Preliminary lithographic results indicate that care must be taken in properly selecting the PAG chemistry such that it would be compatible with the silicon-containing matrix resins. The fully silylated material 3, could not be effectively imaged upon formulation with either an onium salt or nitrobenzyl ester PAG. Increased TBS content in the polymers appeared to decrease resist sensitivity to PAG and/or acid structure allowing high contrast and high resolution imaging. Incorporation of the more polar sulfone unit promoted enhanced lithographic performance. These experiments emphasize the importance of understanding the chemical structure–property relationships of polymer matrices and PAG materials used in chemically amplified resist formulations. Further studies related to understanding the inter- and intramolecular interactions that lead to precise lithographic characteristics are in progress.

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