Polymerization of *N*-(*tert*-Butyldimethylsilyloxy)maleimide and Applications of the Polymers as Resist Materials

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ABSTRACT: A new silicon-containing maleimide monomer, *N*-(*tert*-butyldimethylsilyloxy)-maleimide (SiOMI) has been synthesized. SiOMI was radically copolymerized with styrene derivatives (XSt) to obtain alternating copolymers, P(SiOMI/XSt), in high conversions. The copolymers have high glass transition temperatures above 190°C, and the *tert*-butyldimethylsilyloxy groups are thermally stable up to 300°C. The SiOMI units in the copolymers were converted into *N*-hydroxymaleimide (HOMI) units by acidolytic deprotection of the *tert*-butyldimethylsilyloxy protecting groups. The facile deprotection of the side-chain *tert*-butyldimethylsilyloxy groups from the protected copolymers provided a significant change in solubility of the polymers due to the large polarity change. Submicron positive-tone images were obtained from the copolymers containing an onium salt as a photoacid generator by irradiation with electron beam and development with alkaline solutions. The polymer films also showed very high oxygen plasma etch resistance compared with novolac resins. The silicon-containing maleimide polymers were found to have required properties, such as good alkaline solubility after deprotection, superior adhesion, low optical density, high thermal stability with high T_g, and high plasma etch resistance for applications as deep ultraviolet and electron beam resist materials. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2507–2516, 1997

Key words: *N*-(*tert*-butyldimethylsilyloxy)maleimide; silicon-containing maleimide polymers; acidolytic deprotection; resist materials

INTRODUCTION

N-Substituted maleimide monomers (RMI) have great advantages to design speciality polymers for providing desired functionalities. Functional maleimides have been studied as versatile vinyl monomers with merits of facilitating functional polymer synthesis with various functionalities and excellent thermal stability.[1] Previously, we have reported the radical polymerizations of various *N*-substituted functional polymaleimides and some characteristic properties of the resultingpolymers.[2–6] A series of the styrenic copolymers of *N*-protected maleimides, such as *N*-(*tert*-butyloxycarbonyl)maleimide (*t*-BOCMI), *t*-BOC protected *N*-(*p*-hydroxyphenyl)-maleimide, and *N*-(*tert*-butoxy)maleimide (*t*-BuOMI), have been investigated as thermally stable resist materials in a deep ultraviolet (DUV) region based on the chemical amplification concept. Those polymaleimides investigated had acid-labile side chains that brought a remarkable change in polarity by acidolytic deprotection. Accordingly, the poly-

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mers after acidolytic deprotection became soluble in aqueous base solutions. The deprotection of *t*-BOCMI and *t*-BuOMI units in the polymers resulted in their conversion into unsubstituted maleimide (MI) and *N*-hydroxymaleimide (HOMI) units, respectively. The deprotection brings about a large change in solubilities of the RMI polymers so that they become soluble in aqueous base solutions.

Trialkylsilyl moieties have widely been used as protecting groups in organic synthesis because of the facile protection and acidolytic deprotection.[7,8] Maleimide monomers (RSiMI) having trialkylsilyl groups, *N*-(trimethylsilyl)maleimide (MSiMI), *N*-(*tert*-butyldimethylsilyl)maleimide (BSiMI) have been prepared by Matsumto et al.[9] and polymerized to give thermally stable RSiMI polymers. The trialkylsilyl groups of the polymer side chains are readily removed by acidolysis. We have studied styrenic copolymers of MSiMI as potential resist materials, and the polymers were hydrolyzed in the presence of an acid to give unsubstituted polymaleimides that have different solubilities from the original polymers.[10] In addition, various silicon-containing polymers were extensively investigated as promising resist materials for enhancing reactive-ion etching (RIE) resistance in advanced microlithographic processes.[11] Silicon-containing polystyrenes were applied as a negative-type electron beam resist.[12]

In this regard, functional polymaleimides having acid-labile silicon protecting groups are worthwhile to be considered as chemically amplified positive type resists. The resist materials based on the silicon-containing polymaleimides could delineate high-resolution positive-tone images with high sensitivity, thermal stability, and RIE resistance. In this article, synthesis and radical polymerizations of *N*-(*tert*-butyldimethylsilyloxy)maleimide (SiOMI) are reported, along with characterization of its styrenic copolymers. Their applications as resist materials are also described.

EXPERIMENTAL

Materials and Instruments

Furan, maleic anhydride, phenyl chloroformate, *tert*-butyldimethylsilyl chloride, *tert*-butylcatechol, *N*-hydroxysuccinimide (HOSI), styrene (St), *p*-methylstyrene (MeSt), *p*-chlorostyrene (ClSt), *p*-acetoxystyrene (AcOSt), and *p*-(*tert*-butyloxycarbonyloxy)-styrene (*t*-BOCSt) were purchased from Aldrich Chemical Co. The styrenic monomers (XSt) were purified by distillation, and *t*-BOCSt was used as received. Other chemicals were purified by conventional methods. Triphenyl-sulfonium hexafluoroantimonate (TPSHFA) was prepared as an ouium salt (OS) photoacid generator according to the known procedure.[13,14]

^{1}H-NMR spectra were taken on a Varian Gemini 2000 (200 MHz) spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. ^{13}C-NMR spectra were also obtained with the same Gemini spectrometer in deuteriochloroform. Infrared (IR) spectra were recorded on a Polaris Fourier transform infrared (FTIR) spectrophotometer (Mattson Instrument Co.), and elemental analysis was done with a Perkin–Elmer Model 240C elemental analyzer. Thermal analysis was carried out on a Du Pont Model 910 DSC and Model 951 TGA at a heating rate of 10°C/min under nitrogen atmosphere. Ultraviolet (UV) absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer. Solution viscosities of polymers were measured with a Cannon–Fenske viscosity tube (No. 50) or an Ubbelohde viscometer tube mounted on an automatic measuring apparatus (Schott–Gerate GmbH) at 25°C in dioxane. Molecular weights of the polymers were determined in chloroform–tetrahydrofuran (1 : 1 by vol) at 40°C using a Waters 510 HPLC pump and Waters 410 Differential Refractometer Detector consisting of four μ-styragel columns without calibration. The molecular weights were estimated relative to polystyrene standards. Film thickness was measured by a Model P-10 Surface Profiler of Tencor Instruments. Exposure of the polymer films was made on a Hybralign Series 400 Exposure System of Optical Associates Inc. equipped with a 500 W short-arc Hg–Xe lamp and optics tuned to 260 nm DUV light in conjunction with an Oriel narrow band pass filter for 250 nm or a UV illuminator of Ushio Inc. equipped with a 500 W high-pressure mercury lamp. Oxygen reactive-ion etching (RIE) was done using a Plasma Technology RIE 80 system. Electron beam exposures were performed on a Cambridge Instrument EBMF 10.5 at 30 keV in the Inter-University Semiconductor Research Center of Seoul National University.

Synthesis of *N*-(*tert*-Butyldimethylsilyloxy)-maleimide (SiOMI)

N-Hydroxymaleimide (HOMI) was prepared by methanolysis of *N*-(phenyloxycarbonyloxy)maleimide according to a known procedure in a yield of 45%[3,4,15] (126–127°C mp; 124–126°C in Akiyama et al.[15]). HOMI (8.00 g, 0.07 mol) was reacted with *tert*-butyldimethylsilyl chloride (10.60 g, 0.07 mol) in the presence of triethylamine (7.20 g, 0.07 mol) in THF (80 mL) at 5°C for 2 h. After the reaction, volatiles were evaporated. SiOMI was obtained from the crude product by column chromatography on alumina with THF as an eluent, followed by distillation under a reduced pressure.

ANAL. Yield 13.10 g (70%); bp 78°C (3.5 mmHg). IR (neat): ν (cm^{-1}) 3100 (olefinic C—H); 2900 (*t*-Bu); 1730 (imide C=O); 1257 (Si—O); 840 (olefinic C—H). ^{1}H-NMR (CDCl$_3$, 200 MHz): δ (ppm) 6.65 (s, 2H, CH=); 1.03 [s, 9H, C(CH$_3$)$_3$]; 0.22 (s, 6H, Si(CH$_3$)$_2$). ^{13}C-NMR (CDCl$_3$, 200 MHz): δ (ppm) 165.9 (C=O); 131.6 (C=C); 25.1 [$C(\underline{C}H_3)_3$]; 18.0 [$\underline{C}(CH_3)_3$]; −5.6 [Si(CH$_3$)$_2$]. Calcd for $C_{10}H_{17}NO_3Si$: C, 52.8%; H, 7.54%; N, 6.16%. Found: C, 52.6%; H, 7.58%; N, 6.14%.

Synthesis and Hydrolysis of Model Compound *N*-(*tert*-Butyldimethylsilyloxy)succinimide (SiOSI)

N-Hydroxysuccinimide (HOSI) (1.00 g, 0.026 mol) was reacted with *tert*-butyldimethylsilyl chloride (1.31 g, 0.026 mol) in the presence of triethylamine (0.87 g, 0.026 mol) in THF (20 mL) at 5°C for 2 h. SiOSI was purified by column chromatography on alumina with THF as an eluent, followed by distillation under reduced pressure.

ANAL. Yield 1.60 g (70%); mp 53–57°C. IR (neat): ν (cm^{-1}) 2934 (C—H); 2860 (*t*-Bu); 1781 and 1714 (imide C=O); 1252 (Si—O). ^{1}H-NMR (CDCl$_3$, 200 MHz): δ (ppm) 2.65 (s, 4H, —CH$_2$—CH$_2$—); 1.0 [s, 9H, C(CH$_3$)$_3$]; 0.20 [s, 6H, Si(CH$_3$)$_2$].

Hydrolysis of SiOSI (1.30 g, 0.005 mol) was carried out using catalytic amounts of sulfuric acid in THF (10 mL) at 60°C for 2 h, and then THF was removed under reduced pressure. Dichloromethane (20 mL) was added, and the resulting mixture was extracted with ethanol and dried over anhydrous magnesium sulfate. The solvent was stripped off, and the solid product was obtained as white solid. Recrystallization from ethyl acetate afforded 0.46 g (69% yield) of HOSI.

ANAL. mp 94–97°C (95–98°C in the literature[16]). IR (KBr): ν (cm^{-1}) 3408 (—OH); 2920 (—CH$_2$—CH$_2$—); 1783 and 1715 (imide C=O). ^{1}H-NMR (DMSO-d$_6$, 200 MHz): δ (ppm) 2.58 (s, 4H, —CH$_2$—CH$_2$—). ^{13}C-NMR (DMSO-d$_6$, 200 MHz): δ (ppm) 172.3 (C=O); 24.9 (—CH$_2$—CH$_2$—).

Polymerization

Polymerizations were carried out using 2,2′-azobisisobutyronitrile (AIBN) as a radical initiator in 1,4-dioxane at 55°C in sealed glass ampoules. The SiOMI monomer 2 and the comonomers were charged in 1 : 1 molar ratio. Radical polymerizations were conducted under the conditions described in Table I. The polymerization mixture was poured into a large amount of methanol to isolate the resulting polymer. The polymer was filtered, washed with methanol, and then dried under vacuum. The structure of obtained polymers was fully characterized by IR and nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. Copolymerization of SiOMI and styrene was carried out according to the following procedure to obtain P(SiOMI/St).

To a 25 mL reaction vessel with a nitrogen inlet and an outlet placed were SiOMI (2.00 g, 8.8 mmol), styrene (0.92 g, 8.8 mmol), and AIBN (0.057 g, 0.35 mmol) in 12.5 mL dioxane. The copolymerization was carried out for 3 h at 55°C. The product was diluted with dioxane and precipitated by slowly adding to 500 mL of methanol. The white powdery copolymer P(SiOMI/St) (4a) was obtained in a yield of 90% (2.60 g) after drying *in vacuo* at 40°C. The inherent viscosity of the polymer was measured to be 0.81 dL g^{-1} in dioxane at 25°C. The results of elementary analyses support the alternating chain structure of the copolymers in good agreement with the calculated values.

ANAL. Calcd for P(SiOMI/St) (4a): C, 65.2; H, 7.61; N, 4.23. Found: C, 64.2; H, 7.67; N, 4.25.

ANAL. Calcd for P(SiOMI/MeSt) (4b): C, 66.1; H, 7.88; N, 4.05. Found: C, 65.8; H, 7.85; N, 4.03.

ANAL. Calcd for P(SiOMI/ClSt) (4c): C, 59.1; H, 6.61; N, 3.83. Found: C, 58.5; H, 6.54; N, 3.77.

ANAL. Calcd for P(SiOMI/AcOSt) (4d): C, 61.7; H, 6.98; N, 3.59. Found: C, 61.3; H, 6.81; N, 3.65.

ANAL. Calcd for P(SiOMI/*t*-BOCSt) (4e): C, 61.7; H, 7.43; N, 3.13. Found: C, 61.0; H, 7.33; N, 3.08.

Image-Making of Resists

A 15 wt % solution of P(SiOMI/*t*-BOCSt) containing TPSHFA (3.0 wt % with respect to the polymer) in cyclohexanone was prepared and filtered with a membrane filter of 0.2 μm pore size. In a developing step, a commercial developer, 2.38 wt % aqueous tetramethylammonium hydroxide (TMAH), was diluted with four times of water. The solution was applied onto silicon wafers at

Table I Radical Copolymerizations of SiOMI with Styrene Derivatives

Polymer[a]	AIBN[b] (mol %)	M/S[c] (g mL)	Time (h)	Yield (%)	Inherent Viscosity[d]	$\bar{M}_w$[e] × 10^{-3}
P(SiOMI)	2	0.5	24	30	0.12	—
P(SiOMI/St) 4a	2	0.25	3	90	0.61	145
P(SiOMI/St) 4a	2	0.45	2	91	0.60	—
P(SiOMI/MeSt) 4b	2	0.25	3	92	0.53	93
P(SiOMI/ClSt) 4c	2	0.25	4	89	0.49	71
P(SiOMI/AcOSt) 4d	2	0.25	4	92	0.49	71
P(SiOMI/*t*-BOCSt) 4e	2	0.25	4	97	0.51	71
P(SiOMI/*t*-BOCSt) 4e	1	0.40	5	97	0.57	—

[a] The copolymers have an alternating structure when copolymerized in 1 : 1 molar feed ratio at 55°C.

[b] Mole percent of the initiator to the combined monomers.

[c] The ratio of the weights of combined monomers to the volume of dioxane in polymerization.

[d] Measured at a concentration of 0.20 g/dL in dioxane at 25°C.

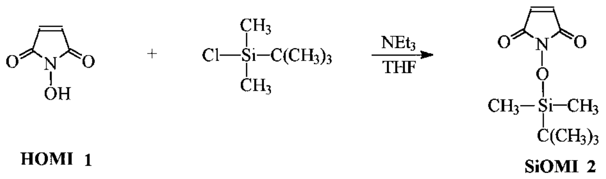
[e] The molecular weights were measured by GPC in a mixture of chloroform and THF (1 : 1 by vol) and estimated relative to the polystyrene standards.

2500–3000 rpm for 30 s using a spin-coater from Headway Research. The resist films were prebaked at 80°C for 90 s, and the film thickness was measured to be about 0.7 μm. The films were irradiated with 30 KeV electron beam and underwent post-exposure bake (PEB) at temperatures varying from 70 to 100°C on a hot plate to effect deprotection of *t*-BOC and silyl groups. Immersion development was carried out using the diluted TMAH solution at room temperature. Positive-tone images were obtained by developing for 20 s and subsequent rinse with pure water. Negative-tone images were also obtained by development with anisole for 60 s. A scanning electron microscope (SEM) at 15 kV was used to take photomicrographs of the resist image patterns.

RESULTS AND DISCUSSION

Synthesis of Monomer

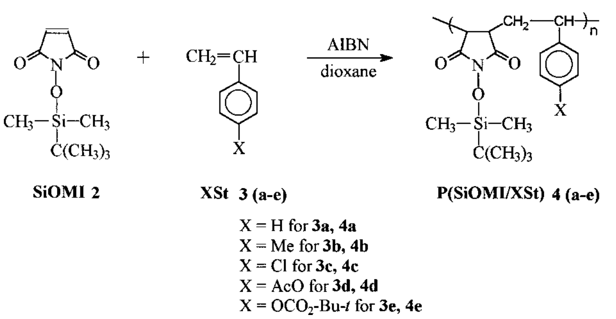
N-(*tert*-Butyldimethylsilyloxy)maleimide (SiOMI) was prepared by reacting HOMI with *tert*-butyldimethylsilyl chloride in a yield of 70%, as shown in Scheme 1. The chemical structure of SiOMI was fully confirmed by IR, ^{1}H-NMR, ^{13}C-NMR, and elemental analysis. In a proton NMR spectrum, SiOMI shows three singlet peaks at 6.6, 1.0, and 0.2 ppm for the protons of olefin, *t*-butyl, and dimethylsilyl groups, respectively. Although some *N*-(alkylsilyl)maleimides were already prepared by Matsumto et al.,[9] an attempt to synthesize the simplest silyloxymaleimide, *N*-(trimethylsilyloxy)-maleimide, was unsuccessful owing to the lack of stability of the compound. The difference in the stability between *N*-(trimethylsilyl)maleimide and *N*-(trimethylsilyloxy)maleimide is deducible from the *pKa* values as 6 to 7 for N—O—H of *N*-hydroxysuccinimide derivatives and about 10 for N—H of succinimide derivatives.[17] That is the reason why the 4-(trimethylsilyloxy)styrene (TMSS) monomer was successfully prepared and copolymerized to apply as resist materials.[18]



Scheme 1

Radical Copolymerizations

SiOMI was readily copolymerized with styrene derivatives (XSt), such as St, MeSt, ClSt, AcOSt, and *t*-BOCSt in high yields (>90%) within 3–4 h, as depicted in Scheme 2. The copolymerizations of SiOMI with XSt were carried out with 1 : 1 molar feed ratio in the presence of a radical initiator AIBN at 55°C in dioxane, and the results are summarized in Table I. Under these conditions, the homopolymerization of SiOMI was sluggish and gave rather low-molecular-weight products. The polymers have inherent viscosities in the range of 0.5–0.6 dL/g in dioxane with molecular weights of 7–14 × 10^4 by gel permeation chroma-



Scheme 2

tography (GPC) measurements. The molecular weights of the polymers were controllable by adjusting the concentrations of the radical initiator and the monomers in copolymerizations. To obtain large amounts of copolymers having suitable molecular weights for resist applications, some of the copolymerizations were conducted using large quantities of the AIBN initiator. The poly(SiOMI-co-XSt), i.e., P(SiOMI/XSt) (4a–4e), were confirmed to have alternating structures based on the proton NMR spectra and elemental analyses. In our previous reports, it was also demonstrated that an electron-rich monomer (styrenes) and an electron-poor monomer (maleimides) lead to an alternating copolymer structure in radical copolymerizations.[1–6,19]

Thermal Properties and Acidolytic Deprotection of Polymers

The copolymers P(SiOMI/XSt) (4) show thermal decomposition (T_d) beginning at about 300°C and high T_gs at about 200°C in thermal analysis, as listed in Table II. The side-chain *tert*-butyldimethylsilyloxy groups in the polymers are thermally stable up to 300°C. A *tert*-butyloxycarbonyl (*t*-BOC) protected copolymer, P(SiOMI/*t*-BOCSt) (4e), revealed an endothermic event corresponding to the deprotection of *t*-BOC groups at 192°C in the first run of differential scanning calorimetry (DSC). Deprotection of *t*-BOC group in the protected polymer P(SiOMI/*t*-BOCSt) leads to the deprotected polymer P(SiOMI/HOSt) since *t*-BOCSt units are converted into *p*-hydroxystyrene (HOSt) units. The first DSC run was stopped at 210°C; and the same sample, which is the deprotected polymer P(SiOMI/HOSt), was subjected to the second run after cooling down to room temperature. As a result, the deprotected copolymer P(SiOMI/HOSt) showed T_g at 205°C in the second DSC run. Around this deprotection temperature, the mass loss of 4e detected by thermogravimetric analysis (TGA) was estimated to be 22%, which is the same amount as the theoretically calculated mass loss of 22.5% due to the evolution of carbon dioxide and isobutylene from the copolymer, as shown in Figure 1 (curve a).

Table II Thermal Properties of P(SiOMI/XSt)[a]

P(SiOMI/XSt) 4	T_g (°C)[b]	T_d (°C)[d]
P(SiOMI/St) 4a	196	300
P(SiOMI/MeSt) 4b	191	300
P(SiOMI/ClSt) 4c	202	305
P(SiOMI/AcOSt) 4d	206	305
P(SiOMI/*t*-BOCSt) 4e	205[c]	320

[a] Thermal analysis done at a heating rate of 10°C min^{-1} under nitrogen.
[b] T_g = glass transition temperature measured by DSC.
[c] T_g was measured in the second DSC run for P(SiOMI/HOSt).
[d] T_d = onset decomposition temperature of main chains measured by TGA. (Figs. 1 and 2)

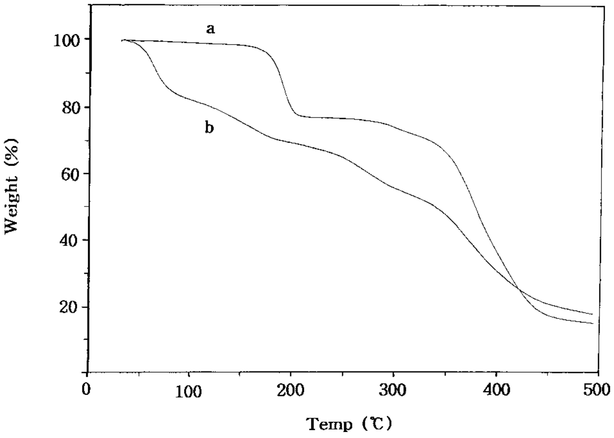


Figure 1 TGA thermograms of (a) P(SiOMI/*t*-BOCSt) and (b) the same polymer containing 5 wt % onium salt after exposure to DUV with 60 mJ/cm^2 for photoacid generation in the film state.

To investigate the deprotection behavior induced by photochemically generated acids, an onium salt (photoacid generator) TPSHFA was combined with P(SiOMI/XSt), and spin-cast films of the mixture were prepared. The acidolytic deprotection of the *t*-BOC groups was found to begin at about 50°C and was completed before 100°C, when P(SiOMI/*t*-BOCSt) containing 5 wt % onium salt was subjected to DUV exposure with 60 mJ/cm^2 as shown, in Figure 1 (curve b). By comparison of curves (a) and (b) in Figure 1, the thermal deprotection of *t*-BOC groups resulted in the same mass loss of 22% with or without UV exposure. Similarly, the acidolytic deprotection of *tert*-butyldimethylsilyloxy groups was elucidated by the TGA thermograms of P(SiOMI/St) (4a) with or without TPSHFA. In Figure 2, the large mass loss from P(SiOMI/St) was observed before 200°C when the polymer was exposed to DUV. The acidolytic deprotection from P(SiOMI/*t*-BOCSt) (4e) to P(HOMI/HOSt) (5) described in Scheme 3 was easily followed by IR spectral change using a film of P(SiOMI/*t*-BOCSt) containing 5 wt % onium salt on a sodium chloride plate, as shown in Figure 3. The starting protected polymer has strong absorption bands at 2940 cm^{-1} for *t*-butyl; at 1780 and 1710 cm^{-1} for carbonyls of imide and carbonate groups; and at 1256 cm^{-1} for Si—C, and at 1152 cm^{-1} for Si—O of the *tert*-butyldimethylsilyloxy groups. Upon DUV exposure with 60 mJ cm^2 and heating at 100°C for 2 min, a strong absorption band at 3450 cm^{-1} for hydroxyl groups of phenol and N—OH appeared, and the strong absorption at 1152 cm^{-1} completely disappeared due to the deprotection of *tert*-butyldimethylsilyloxy groups. The absorption at 1780 cm^{-1} decreased substantially due to the deprotection of *t*-BOC groups, and the strong absorption of Si—C bond at 1256 cm^{-1} decreased, as shown in Figure 3. The IR spectrum of the deprotected polymer was found to be identical to that of the authentic P(HOMI/HOSt) obtained by radical polymerization of the corresponding monomers HOMI and HOSt.

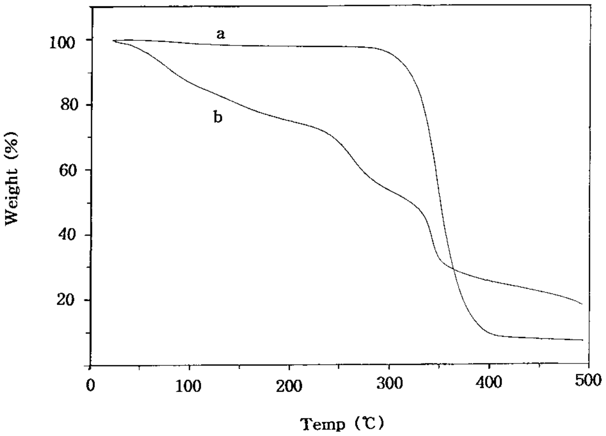
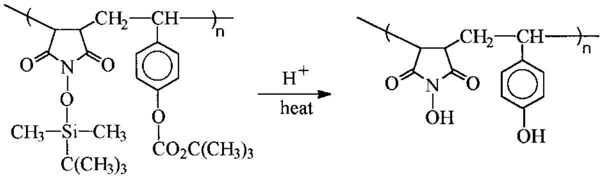


Figure 2 TGA thermograms of (a) P(SiOMI/St) and (b) the same polymer containing 5 wt % onium salt after exposure to DUV with 60 mJ/cm^2 for photoacid generation in the film state.



P(SiOMI/*t*-BOCSt) 4e **P(HOMI/HOSt) 5**

Scheme 3

Other protected polymaleimides, P(*t*-BuOMI/XSt) and P(iPOCMI/XSt), which were obtained from the polymerizations of functional maleimide monomers *t*-BuOMI and *N*-(isopropyloxycarbonyloxy)maleimide (iPOCMI) with XSt, were deprotected to P(HOMI/XSt) thermally at about 280 and 235°C, respectively.[4,6] Both the protected polymers were also acidolytically deprotected to P(HOMI/XSt) below 150°C much lower than their thermal deprotection temperatures. This is the different point, that P(SiOMI/XSt) is thermally stable until chain decomposition but is capable of deprotection below 100°C.

Model Reaction of Acidolytic Deprotection

In order to confirm the acidolytic desilylation of the SiOMI polymers, a reaction was carried out using a model compound, *N*-(*tert*-butyldimethylsilyloxy)succinimide (SiOSI), as shown in Scheme 4. SiOSI was prepared by a reaction of *N*-hydroxysuccimide (HOSI) and *tert*-butyldimethylsilyl chloride. Silyl ethers and esters are known to be easily hydrolyzed in the presence of strong acids to form silanol.[20] In our approach, the photochemically generated acid from an onium salt TPSHFA catalyzes the hydrolysis of silyl ether groups in the SiOMI polymer films.

The model compound SiOSI was easily hydrolyzed in the presence of catalytic amounts of sulfuric acid at 60°C for 2 h. In FTIR spectra, SiOSI has strong absorption bands at 2934 cm^{-1} for *t*-butyl, 1780 and 1714 cm^{-1} for imide carbonyls, and 1252 cm^{-1} for Si—C of *tert*-butyldimethylsilyloxy groups. The hydrolyzed product HOSI exhibits a strong absorption band at 3300 cm^{-1} for hydroxyl groups, but it shows no absorption for Si—C bonds. The hydrolysis of SiOSI to HOSI was also confirmed by a proton NMR spectrum. The spectra of the hydrolyzed product are consistent with those of the authentic HOSI, and the melting point (94–97°C) of hydrolyzed product is

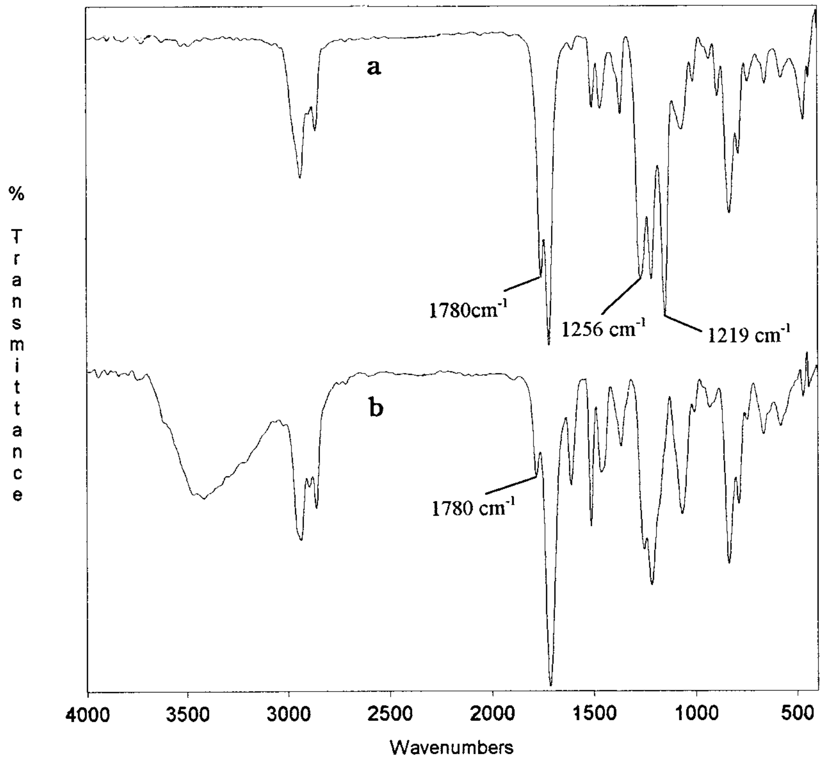
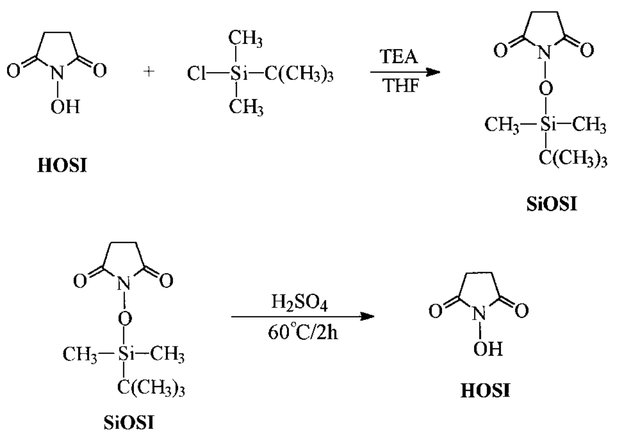


Figure 3 IR spectral change of P(SiOMI/*t*-BOCSt) film containing 5 wt % of onium salt (a) before deprotection and (b) after exposure to DUV with 60 mJ/cm^2 and heating at 100°C for 2 min.

identical with that of authentic HOSI.[16] The result of the hydrolysis implies that the SiOMI units in the copolymers P(SiOMI/XSt) are converted into HOMI units to give P(HOMI/XSt) by acidolytic deprotection.

Solubility of Polymers

All of the SiOMI copolymers are white powders having a good film-forming property. The copolymers of P(SiOMI/St) and P(SiOMI/*t*-BOCSt) show considerable change in solubility after deprotection due to the large polarity change, as listed in Table III. The deprotected polymers in the table were obtained by exposure to DUV and heating or post-exposure bake (PEB) at 110°C in the film state.



Scheme 4

The SiOMI polymers, P(SiOMI/XSt), are very soluble in common organic solvents, such as chloroform, toluene, chlorobenzene, and dimethylformamide (DMF), but insoluble in aqueous base solutions, hexane, and methanol. The deprotected polymers, P(HOMI/XSt), are soluble in aqueous base solutions, dioxane, and DMF but insoluble in common organic solvents, such as chloroform, toluene, and chlorobenzene. The good solubilities of the deprotected polymers obtained by UV exposure in aqueous base solutions are of utmost importance for practical applications as resist materials. The acidolytic deprotection of *tert*-butyldimethylsilyloxy groups in P(SiOMI/XSt) that occurs at 100°C or lower temperatures indicates the applicability of the polymers as a chemically amplified resist in a DUV region.

Table III Solubility Comparison of P(SiOMI/St) and P(SiOMI/*t*-BOCSt) Before and After Deprotection by Exposure

Solvent	P(SiOMI/St) and P(SiOMI/*t*-BOCSt)	Deprotected Polymers[b]
Acetone	++	−
Chloroform	++	−
Chlorobenzene	++	−
Anisole	+	−
Cyclohexanone	++	−
2-Ethoxyethyl acetate	+	−
N,*N*-Dimethylformamide	++	+
Tetrahydrofuran	++	−
Dioxane	++	+
1.0*N* NaOH (aq)	−	++
2.38 wt % TMAH (aq)[a]	−	++

Symbols are as follows: ++, very soluble; +, soluble; −, insoluble.

[a] A commercial aqueous tetramethylammonium hydroxide solution (0.262*N*).

[b] The deprotected polymer films were obtained from P(SiOMI/St) and P(SiOMI/*t*-BOCSt) containing 3 wt % onium salt by exposure to DUV with 60mJ/cm^2 and heating at 110°C for 2 min.

Lithographic Evaluation

The spin-coated films of P(SiOMI/XSt) are transparent and have relatively low optical densities (OD) below 0.15 μm^{-1} at 250 nm. The polymer films containing 5 wt % of TPSHFA as an onium salt (OS) exhibit increased OD values about 0.30 μm^{-1} and further increased after exposure and PEB. In Table IV, the UV absorption of the polymers and resist films are listed. The OD values do not change much, even after deprotection by exposure. In the case of the resist film of P(SiOMI/*t*-BOCSt) (4e) containing 5 wt % TPSHFA, it results in the substantial increase in UV absorbance due to phenolic functionalities, as shown in Figure 4, because the polymer is deprotected to P(HOMI/HOSt) (5). The major contributor to the increase in UV absorption of the resist films at 250 nm is the onium salt photoacid generator (Fig. 4, curve b). The HOMI units in the deprotected polymers P(HOMI/XSt) do not contribute to UV absorption the same as the former functional polymaleimides in that all of the units of *t*-BuOMI, iPOCMI, and *N*-(*t*-BOC-oxy)maleimide were deprotected to HOMI units.[3,4,6]

The resist films consisting of P(SiOMI/XSt) and 5 wt % of TPSHFA are insoluble in aqueous base solutions, and the unexposed areas of the films showed no change in thickness in 2.38 wt % TMAH solution. On the contrary, the exposed areas are very soluble in aqueous base solutions. Figure 5 shows a typical sensitivity curve of a 0.8 μm thick resist based on P(SiOMI/*t*-BOCSt) containing 5 wt % OS. After exposure to 250 nm DUV and PEB at 70°C for 2 min, the sensitivity of the resist is about 8 mJ/cm^2, with a high contrast

Table IV UV Absorption of P(SiOMI/XSt) and Resist Films at 250 nm

P(SiOMI/XSt) 4	Absorbance[a] (μm^{-1}) Polymer	Polymer/OS	Exposed	PEB
P(SiOMI/St) 4a	0.14	0.29	0.34	0.37
P(SiOMI/MeSt) 4b	0.14	0.29	0.32	0.37
P(SiOMI/ClSt) 4c	0.13	0.30	0.33	0.35
P(SiOMI/AcOSt) 4d	0.14	0.30	0.32	0.38
P(SiOMI/*t*-BOCSt) 4e	0.15	0.30	0.35	0.46

[a] Absorbance measured in 1.0 μm thick films; 5 wt % onium salt (OS) to polymer; exposure to 250 nm with 60mJ/cm^2; PEB at 90°C for 2 min.

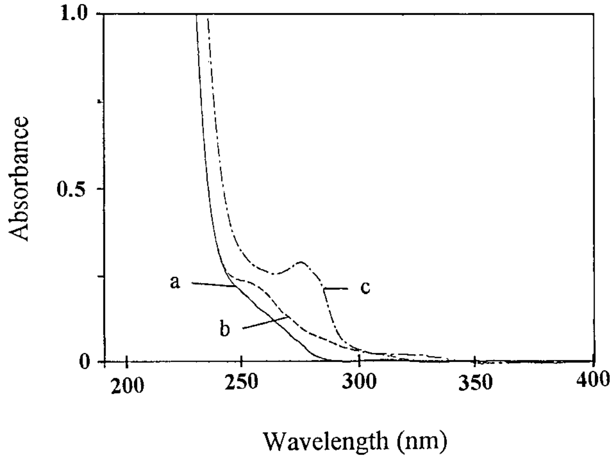


Figure 4 UV absorption spectra of P(SiOMI/*t*-BOCSt) containing 5 wt % of onium salt cast on a quartz plate: (a) prebaking at 80°C for 1 min, (b) exposure to DUV for 60 mJ/cm^2, and (c) PEB at 100°C for 2 min.

(γ) of 5.6. Combination with 3 wt % TPSHFA gave a resist with high transmittance and high sensitivity. High-resolution image patterns were obtained by irradiation with 30 KeV electron beam (EB) and PEB treatment at temperatures lower than 100°C. A commercial 2.38 wt % TMAH solution was diluted with four times water, and the diluted base solution was used as a developer. A SEM photograph showing a resolution of 0.7 μm line and space patterns formed in a 0.65 μm-thick film was obtained in Figure 6. Negative-tone images were also obtained when developed with anisole.

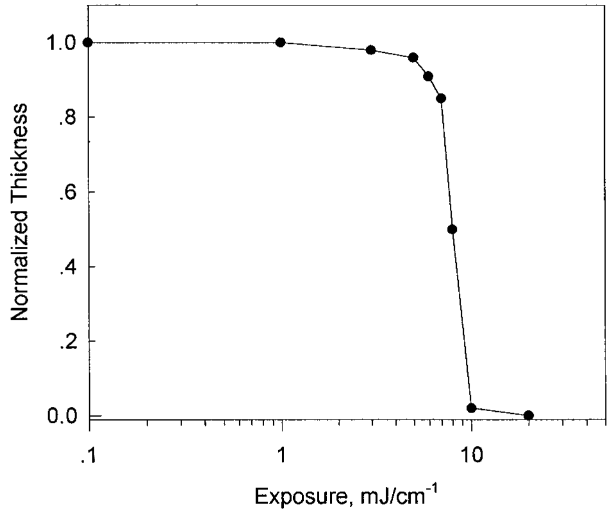


Figure 5 Plots of normalized thickness of P(SiOMI/*t*-BOCSt) resist film versus DUV exposure dose at 250 nm with PEB at 70°C for 2 min.

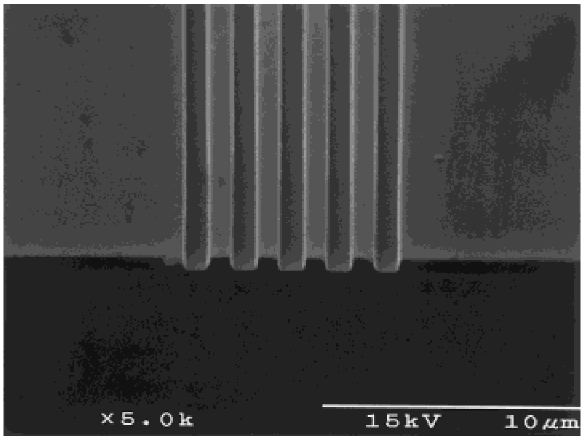


Figure 6 A SEM photograph of 0.8 μm coded line and space patterns formed in 0.65-μm-thick P(SiOMI/*t*-BOCSt) resist film with EB dose of 6 μC/cm^2 and PEB at 70°C for 60 sec.

Oxygen Plasma Stability

It is well known that silicon-containing polymers bestow superb resistance to oxygen reactive-ion etching (RIE) and are applicable to multilevel resist processes.[11] Etch rates of the SiOMI polymers are listed in Table V. All of the P(SiOMI/XSt) have high O_2 RIE resistance comparable to the novolac resin of molecular weights of 6000. The higher contents of silicon in the polymers the higher RIE resistance is achieved. This high resistance to O_2 RIE is ascribable to SiOMI units and essential for advanced lithographic processes, such as bilevel and multilevel resist processes.

CONCLUSIONS

A new silicon-containing maleimide monomer, *N*-(*tert*-butyldimethylsilyloxy)maleimide (SiOMI), was synthesized and radically copolymerized with styrenes (XSt) to give *tert*-butyldimethylsilyloxy-protected, acid-labile polymers P(SiOMI/XSt). P(SiOMI/XSt) were converted into the *N*-hydroxymaleimide copolymers P(HOMI/XSt) by acidolytic deprotection of the *tert*-butyldimethylsilyloxy groups. The polymers have promising properties for applications as chemical amplification resists, as follows: high sensitivity, solubility in

Table V Etch Rates of P(SiOMI/XSt) and Novolac Resin in O_2 RIE

P(SiOMI/XSt) 4	Silicon Contents (%)	Etch Rate (Å/min)	Etch Ratio* (Novolac to Polymer)
Novolac (M_w = 6,000)	0	2500	1.0
P(SiOMI/St) 4a	8.5	500	5.0
P(SiOMI/MeSt) 4b	8.1	550	4.5
P(SiOMI/ClSt) 4c	7.7	700	3.5
P(SiOMI/AcOSt) 4d	7.2	700	3.5
P(SiOMI/*t*-BOCSt) 4e	6.3	1100	2.3

Etch conditions were as follows: oxygen pressure, 100 mTorr; flow rate, 100 sccm; RF power, 110 W.

* Etch ratio compared to the novolac resin.

alkaline solutions after facile deprotection, thermal stability with high T_g, adhesion, etc. Submicron positive-tone images were obtained by irradiation with EB using the resist films made from P(SiOMI/*t*-BOCSt) containing 3 wt % TPSHFA as a photoacid generator. The high resistance of the polymers to oxygen RIE is a essential property for applications to bilevel or multilevel resist processes.

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