Polysiloxane Formation at the Irradiated Polymer Surface by the Chemical Vapor Deposition Method

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Polysiloxane formation by a chemical vapor deposition (CVD) method at the surface of UV-irradiated films of polymers containing imino sulfonates was studied. Since imino sulfonates can form sulfonic acids on UV irradiation, the irradiated surface of the polymers becomes hydrophilic. The water sorption from the atmosphere occurred at the irradiated surface of the polymers. The water sorption was studied using quartz crystal microbalance. When the irradiated surface of the polymer films was exposed to the vapor of tetraalkyl orthosilicates and their homologues at ambient temperature, polysiloxane networks were formed at the surface of the irradiated areas of the polymers. No polysiloxane networks were formed at unirradiated areas. The polysiloxane formation rate was affected by the structures of the polymers, imino sulfonates, and silicon compound. The polymer films obtained after irradiation and subsequent CVD treatment with the vapor of tetraalkyl orthosilicates or their homologues showed a good etch resistance to oxygen plasma. The polysiloxane formation at the irradiated surface of the polymers containing imino sulfonates as additives was compared with that of the polymers bearing imino sulfonate units as pendant groups.

Introduction

A gas-phase functionalization of irradiated or unirradiated areas of polymer films by volatile inorganic or organometallic compounds is important for photolithography, which needs high resoltuion. In 1984 Taylor and co-workers[1,2] reported a process in which a bisazide/isoprene cross-linkable polymer system was irradiated with UV light and, in a subsequent step, treated with the vapor of inorganic halide such as $SnCl_4$, $SiCl_4$, or $(CH_3)_2SiCl_2$. The inorganic compounds diffused more rapidly into the un-cross-linked areas of the film. This system gave a positive tone image, when the films were developed in an oxygen plasma. In 1985 MacDonald and co-workers[3] reported a process in which silicon is selectively introduced into the exposed regions of the film by allowing the reaction of silylating agents delivered in the gas phase with the phenolic hydroxyl groups that were generated by the photochemically formed acid-catalyzed thermolysis of poly(4-*tert*-butoxycarbonyloxystyrene). This system yielded a negative-tone image by oxygen reactive ion etching (O_2 RIE). Follet and co-workers[4] have reported plasma-developable electron-beam resists. The essential feature involved selective diffusion of dichlorodimethylsilane into the irradiated areas of poly(methyl methacrylate). This system was followed by hydrolysis of the chlorosilane upon exposure to water vapor, resulting in polymerization that formed an interpenetrating network of polysiloxane. O_2 RIE yielded an image with high resolution. Hydrophobic polymers such as chlorine-containing polystyrenes underwent oxidation to form hydroxyl and carbonyl groups when exposed in air with 248.4- or 193-nm light.[5-8] Since the exposed regions sorbed water from the atmosphere, the treatment of the exposed films with gaseous $TiCl_4$ formed a TiO_2 layer at the irradiated film surface. The TiO_2 layer worked as a barrier for O_2 RIE. This system also gave a negative-tone image by O_2 RIE.

It has been reported that imino sulfonate compounds undergo a photochemical decomposition to form sulfonic acid along with azines and ketones.[9] In recent papers[10,11] we have reported the photoinduced acid-catalyzed SiO_2 network formation at the irradiated polymer surface using the vapor of alkoxysilanes by a chemical vapor deposition (CVD) method. Polymethacrylates bearing 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-styrenesulfonate (NISS) units as photoacid generating groups were used. Upon photolysis NISS units were converted to styrenesulfonic acid units (Scheme I). Water sorption from the atmosphere occurred at the near surface of the exposed polymer films because the exposed areas of the polymer films became hydrophilic due to the acid formation. The water sorbed to the irradiated polymer surface could react with gaseous tetraalkyl orthosilicates to form SiO_2 networks. It has been known that some tetraalkyl orthosilicates can

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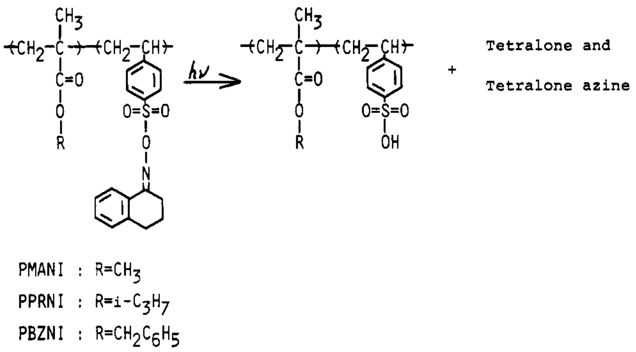
Scheme I

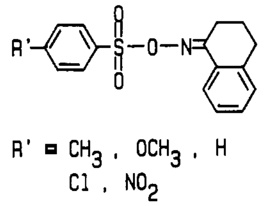


be rapidly hydrolyzed by water in the presence of acid or base as a catalyst.[12,13] The hydrated tetrahedral silanol undergoes a polycondensation reaction, resulting in SiO_2 networks:

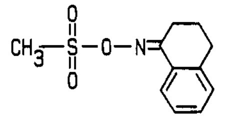
$$n\mathrm{Si(OR)_4} + 2n\mathrm{H_2O} \xrightarrow{\mathrm{H^+}} n\mathrm{SiO_2} + 4n\mathrm{ROH}$$

The photochemically formed sulfonic acid units are essentially important for the SiO_2 network formation.

In this paper we report the formation of polysiloxane networks using the vapor of alkoxysilanes at the irradiated polymer surface bearing imino sulfonate compounds as additives (**1a–e**, **2**). The polysiloxane formation at the surface of the polymer films containing photoacid generator as an additive was compared with that of the copolymer systems in which the photoacid generating units were anchored to the polymer chain. The oxygen plasma etching properties of the polymer films which were irradiated and, in a subsequent step, exposed to the vapor of alkoxysilanes were studied. This system is interesting in relation to the surface imaging photoresists which can be developed with oxygen plasma.



1a-e



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Experimental Section

Materials. 1,2,3,4-Tetrahydro-1-naphthylideneamino *p*-toluenesulfonate (**1a**): To a solution of 1-tetralone oxime (5 g, 31 mmol) in pyridine (20 mL) below 10 °C was added *p*-toluenesulfonyl chloride (6.5 g, 34 mmol) portionwise over 10–20 min. The reaction mixture was stirred below 20 °C for 3 h and was poured with stirring into an ice-cold aqueous solution (195 mL) of 5% HCl. The reaction mixture was extracted with chloroform and the chloroform layer was dried over K_2CO_3. After evaporation of the chloroform under reduced pressure, the crude product was obtained. The crude product was recrystallized from *n*-heptane: yield 90%, mp 98 °C. Anal. Calcd for $C_{17}H_{17}NO_3S$ (315.39): C, 64.47; H, 5.43; N, 4.44. Found: C, 64.70; H, 5.40; N, 4.42.

Similarly, the following compounds were obtained from 1-tetralone oxime and corresponding sulfonyl chlorides. The yields, melting points, solvents for recrystallization, and elemental analysis data are listed below.

1,2,3,4-Tetrahydro-1-naphthylideneamino 4-methoxybenzenesulfonate (**1b**): yield 90%, mp 82 °C; *n*-heptane–benzene (4:1, v/v) mixture. Anal. Calcd for $C_{17}H_{17}NO_4S$ (331.39): C, 61.62; H, 5.17; N, 4.23. Found: C, 61.55; H, 5.12; N, 4.49.

1,2,3,4-Tetrahydro-1-naphthylideneamino benzenesulfonate (**1c**): yield 95%, mp 136–138 °C; *n*-heptane. Anal. Calcd for $C_{16}H_{15}NO_3S$ (301.37): C, 63.77; H, 5.02; N, 4.64. Found: C, 63.77; H, 4.93; N, 4.56.

1,2,3,4-Tetrahydro-1-naphthylideneamino 4-chlorobenzenesulfonate (**1d**): yield 89%, mp 126–127 °C; *n*-heptane–benzene (24:1, v/v) mixture. Anal. Calcd for $C_{16}H_{14}NO_3SCl$ (335.81): C, 57.23; H, 4.20; N, 4.17. Found: C, 57.29; H, 4.15; N, 4.40.

1,2,3,4-Tetrahydro-1-naphthylideneamino 4-nitrobenzenesulfonate (**1e**): yield 89%, mp 139 °C; *n*-heptane–benzene (4:1, v/v) mixture. Anal. Calcd for $C_{16}H_{14}N_2O_5S$ (346.36): C, 55.32; H, 4.35; N, 8.06. Found: C, 55.52; H, 4.08; N, 8.07.

1,2,3,4-Tetrahydro-1-naphthylideneamino methanesulfonate (**2**): yield 98%; mp 116–117 °C; *n*-heptane–benzene (28:1, v/v) mixture. Anal. Calcd for $C_{11}H_{13}NO_3S$ (239.30): C, 55.21; H, 5.48; N, 5.85. Found: C, 55.21; H, 5.46; N, 5.87.

Synthesis of copolymers of 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-styrenesulfonate (NISS) with either methyl methacrylate, isopropyl methacrylate, or benzyl methacrylate was reported elsewhere.[11] Poly(methyl methacrylate) (PMMA, $M_n = 1.5 \times 10^5$), poly(isopropyl methacrylate) (PPRMA, $M_n = 1.9 \times 10^5$), and poly(benzyl methacrylate) (PBZMA, $M_n = 2.9 \times 10^5$) were prepared by the radical polymerization of corresponding monomers using azobis(isobutyronitrile) (AIBN) as an initiator. Tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), tetra-*n*-propyl orthosilicate (TPOS), methyltrimethoxysilane (MTMOS), and methyltriethoxysilane (MTEOS) were reagent grade and used without further purification.

Measurements. *Water Sorption.* A laboratory-constructed piezoelectric apparatus was used to measure water sorption in the polymer films. The frequency output from the oscillator was measured by a Yokogawa FC-864 frequency meter. The AT-cut quartz crystal with gold electrodes (Webster Electronics, WW1476) had a resonance frequency of 10.000 MHz. The frequency change is linearly related to the mass sorbed on the quartz plate.[14,15] In our case a frequency shift of 1 Hz corresponded to a mass change of 0.84 ng.

Polymers were deposited onto the quartz crystal (1.2 cm diameter) by casting from chloroform solution. The area coated with the polymer film was usually 0.19 cm². The quartz crystal was placed in the middle of the sealed glass vessel which had a quartz window for UV irradiation. An aqueous solution of inorganic salts (2 M - KNO_3, saturated NaBr, or saturated $CaCl_2$) was placed at the bottom of the vessel to control its humidity at a constant temperature. Irradiation of the polymer films on the quartz crystal through the quartz window of the vessel was carried out with a 5-W low-pressure Hg lamp (Toshiba LP-11B). The intensity of the incident light, determined with a chemical actinometer (potassium ferrioxalate)[16] was 0.1 mJ/(cm² s) at 254 nm.

Water sorption into the unirradiated polymer films was measured as follows. The quartz crystal coated with the polymer (area = 0.19 cm²) was placed in a 500-mL four-necked flask. After flowing dry N_2 gas for 1 h (80 mL/min), 100 mL of 2 M - KNO_3 aqueous solution was placed at the bottom. The vessel was sealed and equilibrated for 2 h at 30 °C. The frequencies of the quartz crystal under dry N_2 atmosphere and humid atmosphere were recorded, and water sorption was calculated.

Deposition of Polysiloxane. The polymer films (8.8 × 22 mm) were prepared on glass plates (8.8 × 50 mm) by casting from chloroform solution and drying under vacuum at room temperature. The polymer weight on the glass plate was usually 2×10^{-4} g (thickness ≈ 1 μm). After exposure with 254-nm light, the glass plate coated with polymer film was placed at the center of a 500-mL glass vessel which had gas-inlet and -outlet valves.

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Table I. Characteristics of Imino Sulfonate Compounds

imino sulfonate	R′[a]	T_m[b] (°C)	T_d[c] (°C)	abs peak (nm)	$10^{-4}\,\epsilon$[d] (L/mol cm)	Φ[e]
1a	CH_3	98	151	256	1.51	0.046
1b	OCH_3	82	152	243	1.97	0.039
1c	H	138	144	256	1.41	0.062
1d	Cl	127	137	255	1.42	0.060
1e	NO_2	139	139	253	2.35	0.023
2		117	159	255	1.34	0.080

[a] See Scheme II. [b] Melting point. [c] Decomposition temperature from DSC. [d] Molar extinction coefficient at 254 nm in dichloromethane. [e] Quantum yield for the photochemical formation of sulfonic acid in PMMA film in air.

Water (50 mL) was placed at the bottom of the vessel and equilibrated for 10 min prior to introduction of $Si(OR)_4$ or $CH_3Si(OR)_3$ gas. The relative humidity in the vessel was 100%. During the polysiloxane network formation, nitrogen gas (50 mL/min) flowed through a bubbler which contained liquid $Si(OR)_4$ or $CH_3Si(OR)_3$. The bubbler and reaction vessel were placed in a thermostatic oven at 30 °C. The amounts of polysiloxane formed at the near surface of the polymer film were determined from the difference between the weight of the sample plate before and after exposure to the vapor of the silicon compounds. The amounts of polysiloxane formation increased with film thickness and became constant at the film thickness above the absorbance of ca. 2 at 254 nm.

Quantum Yield. The quantum yields (Φ) for the formation of sulfonic acid were obtained as follows: Sample films were prepared by casting from 10 mL of THF solution of PMMA (1.5 wt %) containing 20 mg of imino sulfonate compounds in a Petri dish (diameter 7 cm) and drying under vacuum at 50 °C for 1 h. The thicknesses of the films were about 30 μm. The absorbance of the film at 254 nm was above 2.0. A film was irradiated at room temperature in air with a low-pressure Hg lamp (0.7 mJ/(cm^2 s)). The intensity of the incident light was determined with a chemical actinometer.[16] After irradiation, a known amount of film was dissolved in 5 mL of dichloromethane. A portion of the sample solution was subjected to the determination of sulfonic acid using a colorimetric method with a merocyanine dye,[17] 1-hexadecyl-4-[(4-oxocyclohexadienylidene)ethylidene]-1,4-dihydropyridine. The Φ values for the sulfonic acid formation were determined as the number of moles of formed sulfonic acids per einstein of 254-nm light absorbed by the imino sulfonate compounds. The photolysis degree of the imino sulfonate compounds was 40–70% which was determined by HPLC.

Oxygen Plasma Etching. Oxygen plasma etching was carried out at room temperature using a laboratory-constructed apparatus where the oxygen plasma was generated using two parallel electrodes and rf power supplies. The typical etching conditions were 20 W (13.56 MHz), power density of 1.0 W/cm^2, 30–125 mTorr, and oxygen flow of 1 sccm.

Results and Discussion

Photolysis of Imino Sulfonates. Characteristics of the imino sulfonate compounds (**1a–e** and **2**) are shown in Table I. They showed absorption maximum at around 250 nm and a weak shoulder peak at around 300 nm. The molar extinction coefficient (ε) at 254 nm were 1.34×10^4–2.35×10^4 L/(mol cm). The ε values at 313 nm were 24–35 L/(mol cm) except for **1e**, which was 840 L/(mol cm). The thermal decomposition temperatures of **1a–e** and **2** from DSC measurements were 137–159 °C. It has been reported that upon irradiation with UV light the cleavage of —O—N═ bonds in imino sulfonates and the subsequent abstraction of hydrogen atoms from residual solvent in the polymer film or from polymer molecules leads to the formation of sulfonic acids, azines and ketones.[9] The quantum yields (Φ) for the photochemical formation of sulfonic acid of **1a–e** and **2** were 0.023–0.08 and decreased in the order **2** > **1c** ≈ **1d** > **1a** > **1b** > **1e**. This order did not parallel the order of the electron-withdrawing or -donating inductive effects of the substituents on the phenyl ring of sulfonic acid moiety. The Φ values for **1a–e** and **2** were smaller than those for the photoacid generators such as 2,6-dinitrobenzyl esters of 4-substituted benzenesulfonic acid (Φ = 0.1–0.16)[18] and triphenylsulfonium hexafluoroantimonate (Φ = 0.26–0.4),[19] although the Φ values for the nitrobenzyl esters and onium salts were obtained at low photolysis degrees (<20%) using thin films (~1 μm) of PMMA or poly(4-*tert*-butoxycarbonyloxystyrene).

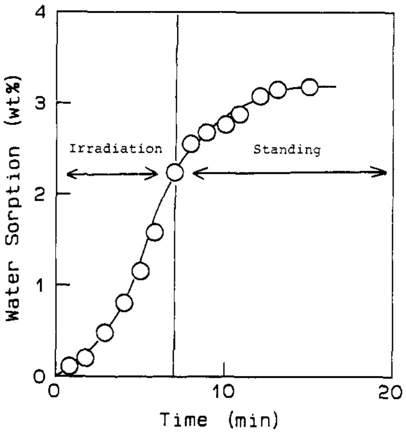

Figure 1. Water sorption to the irradiated PMMA containing 7.5 mol % of **1a** at 30 °C. Relative humidity: 95%. Intensity of irradiation light: 0.11 mJ/(cm^2 s).

Water Sorption. Figure 1 shows the relationship between irradiation time and water sorbed into the irradiated film of PMMA containing 7.5 mol % of **1a** at 30 °C. The weight of the polymer film cast on the quartz crystal was 1300 ng, and the area of film was 0.19 cm^2. If the polymer is assumed to have a density of 1 g/cm^3, the film thickness is 68 nm and the absorbance of the film at 254 nm is <0.1. Water sorption began the moment that the polymer film was irradiated with 254-nm light. It increased with irradiation time and more gradually increased after irradiation until the sorption equilibrium was established. The sorbed water could be removed, when the sample film was placed under a dry nitrogen atmosphere, and sorption and desorption were completely reversible. Table II shows the water sorption properties of irradiated and unirradiated polymer films containing **1a–e** or **2**. The water sorption was measured for 1000 ng of polymer films with area of 0.19 cm^2. For unirradiated films of polymers containing **1a–e**, the water sorption was 0.2–1.5 wt %. Although water sorption increased with the fraction of imino sulfonate compounds, the hydrophobic nature of the methacrylate ester groups decreased the water sorption ability. For irradiated films of polymers containing **1a–e** or **2**, the water sorption was 0.3–6.0 wt %. For the PMMA–**1a** system, the water sorption increased with increasing sulfonic acids formed photochemically. The hydrophobic nature of the methacrylate ester groups

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Table II. Water Sorption to the Polymer Films Containing Imino Sulfonate Compounds

imino sulfonate	imino sulfonate content (mol %)	polym matrix	water sorption (wt %)[a] unirradiated	irradiated[b]	H_2O/acid[c]
1a	3.0	PMMA	*d*	1.2	28
1a	7.5	PMMA	1.1	2.8	28
1a	15.0	PMMA	1.5	6.0	34
1a	7.5	PPRMA	0.5	0.9	11
1a	7.5	PBZMA	0.2	0.3	5
1b	7.5	PMMA	0.7	4.3	52
1c	7.5	PMMA	*d*	3.5	26
1d	7.5	PMMA	1.2	4.7	37
1e	7.5	PMMA	*d*	1.0	21
2	7.5	PMMA	*d*	2.6	14

[a] Relative humidity 95% at 30 °C. [b] Exposed dose with 254-nm light was 46 mJ/cm^2. Photolysis degrees of **1a–e** and **2** were 11–30%. [c] Molar ratio of sorbed water to photochemically formed sulfonic acid. [d] Not measured.

decreased the water sorption. If compared among PMMA films containing 7.5 mol % of different kinds of imino sulfonates, the water sorption decreased in the order **1d** > **1b** > **1c** > **1a** > **2** > **1e**. This order was not consistent with the decrease of Φ values. The number of water molecules sorbed by one molecule of sulfonic acids formed photochemically was 14–52, being dependent on the structure of sulfonic acids. The ratio of sorbed H_2O to acid decreased in the order **1b** > **1d** > **1a** ≈ **1c** > **1e** > **2**. The water sorption ability can not be determined by the strength of the sulfonic acids formed photochemically.

As reported for gas sorption in polymer films,[20,21] water sorption seems to occur by two processes: (1) dissolution of water molecules into the polymer matrix according to Henry's law; (2) the Langmuir type adsorption of water molecules at microvoids in the polymer matrix. The water may be present as a dissolved "water cluster", since a number of water molecules was sorbed by one molecule of the photochemically formed sulfonic acid.

The water sorption to the irradiated polymer films increased with increasing film thickness and reached a constant value above the thickness of ca. 70 nm. Thus the water sorption occurs at the very surface of the polymer films. This is not due to the inability of light to penetrate below that thickness, since the absorbance of the polymer film was <0.1 at 254 nm. As has been discussed before,[11] this may be due to the formation of a "hydrophobic barrier" by the aggregation of 1-tetralone and/or 1-tetralone azine as byproducts of the photolysis of imino sulfonates. The barrier prevents further diffusion of water molecules.

Polysiloxane Formation. In the presence of water and strong acid, the hydrolysis and subsequent polycondensation reactions of $Si(OR)_4$ lead to the formation of silicon oxide networks, which is well-known as the sol–gel process for silica glass formation.[12,13] When the irradiated polymer films containing **1a–e** or **2** were exposed to the vapor of $Si(OR)_4$ or $CH_3Si(OR)_3$ at 30 °C, polysiloxane networks were formed in the near surface region of the films. Figure 2 shows FT-IR spectra of the irradiated PMMA film containing 20 mol % of **1a** before and after exposure to the vapor of MTEOS. The spectra were measured by a ATR method using Ge prism. The film which was irradiated at 254 nm (530 mJ/cm^2) and subsequently exposed to MTEOS vapor for 20 min at 30 °C and at 100% RH showed new peaks at 1272 ($Si–CH_3$) and 1200–1000 cm^{-1} (Si–O–Si). When the unirradiated polymer films containing 20 mol % of **1a** were exposed to MTEOS vapor at the same conditions described for the irradiated polymer films, no formation of polysiloxane was observed by an ATR FT-IR examination. Thus the sulfonic acids formed photochemically were essential for the formation of polysiloxanes by the hydrolysis of $Si(OR)_4$ and its homologues.

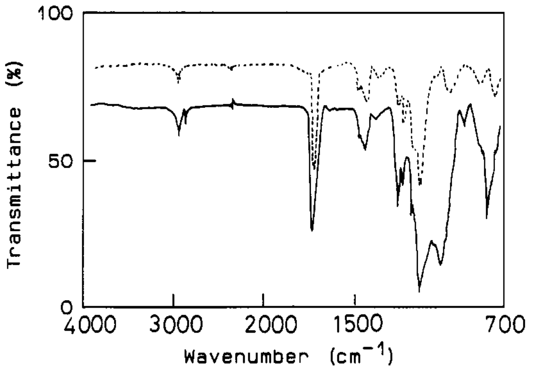

Figure 2. FT-IR spectra of the irradiated PMMA film containing 20 mol % of **1a** before (- - -) and after (—) exposure to the vapor of MTEOS at 30 °C.

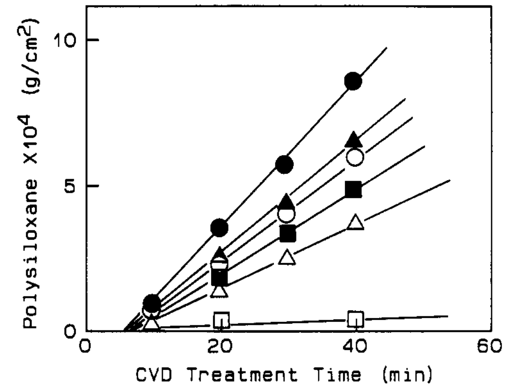

Figure 3. Effect of imino sulfonate structure on the polysiloxane formation at the irradiated surface of PMMA films containing 7.5 mol % of **1a–e** or **2** using MTEOS vapor at 30 °C. Imino sulfonate: (△) **1a**, (▲) **1b**, (■) **1c**, (●) **1d**, (□) **1e**, and (○) **2**. Exposure dose: 126 mJ/cm^2.

Figure 3 shows the effect of imino sulfonate structure on the polysiloxane formation at the irradiated surface of PMMA film containing 7.5 mol % of **1a–e** or **2**. The polysiloxane formation rate decreased in the order **1d** > **1b** > **2** > **1c** > **1a** ≫ **1e**. This suggests that the rate can be determined by the combination of several factors such as water sorption ability of the irradiated polymer films, strength of the photochemically formed acids, and Φ values. An induction period (ca. 5 min) for the polysiloxane formation was observed. This period was needed to fill the reaction chamber with the vapor of alkoxysilanes.

Figure 4 shows the effect of methacrylate ester structure on the polysiloxane formation at the irradiated polymer surface containing 15 mol % of **1a**. The polysiloxane formation decreased in the order PMMA > PPRMA > PBZMA, the same trend observed in water sorption experiments (see Table II). The hydrophobic nature inhibited the polysiloxane formation.

In Figure 5 the rate of polysiloxane formation (R_p) at the irradiated polymer surface was plotted as a function of **1a** fraction in the polymer films. The R_p values were

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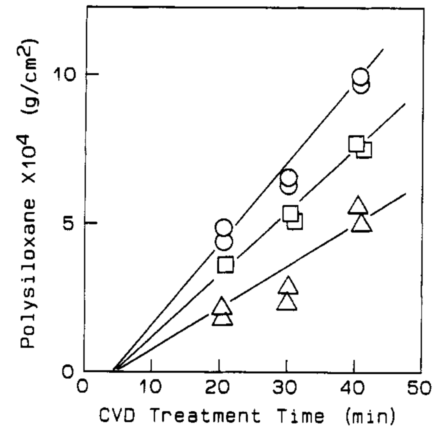

Figure 4. Effect of the polymer structure on the polysiloxane formation at the irradiated surface of polymer films containing 15 mol % of **1a** using MTEOS vapor. Polymer: (○) PMMA, (□) PPRMA, and (△) PBZMA. Exposure dose: 105 mJ/cm^2.

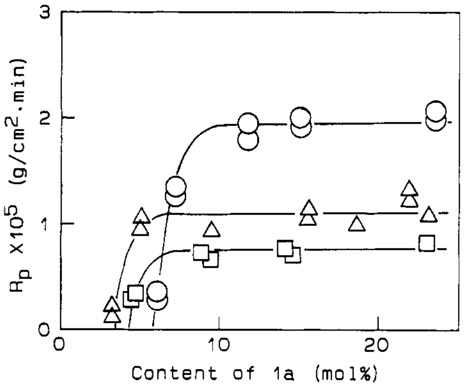

Figure 5. Effect of **1a** content in polymer films on the polysiloxane formation rate (R_p) at the irradiated surface of polymer films using MTEOS vapor at 30 °C. Polymer: (○) PMMA, (△) PPRMA, and (□) PBZMA. Exposure dose: 183 mJ/cm^2. CVD treatment time: 30 min.

obtained from the slope of the linear plots of the amounts of polysiloxane formed versus CVD treatment time. The polysiloxane formation rate increased with increasing **1a** content and showed a saturation at **1a** content above ca. 5–7 mol %. The irradiation conditions were kept constant for all systems. The saturation phenomenon is not due to the poor compatibility of the polymers with **1a** because the polymer films were clear and any evidence suggesting the phase separation were not obtained from DSC measurement of the films containing **1a**. It has been reported that the photochemically formed acids can diffuse in polymer matrix.[22] The photochemically formed sulfonic acids may be concentrated at the surface of the films because the acids at the surface of the film can be hydrated by the sorbed water and the hydrated acids cannot diffuse into the hydrophobic bulk phase. As the result the acid can be concentrated at the surface. Since above 10 mol % of **1a** the irradiation light was completely absorbed at the film surface, the total amounts of the photochemically formed acids at the near surface were independent of **1a** content.

Figure 6 shows the effect of silicon compound structure on the polysiloxane formation at the irradiated PMMA films containing 7.5 mol % of **1a**. The polysiloxane formation rate decreased in the order MTMOS > TMOS > MTEOS > TEOS > TPOS. It has been reported[11] that the pseudo-first-order rate constant (k_{obs}) for the hydrolysis of the silicon compounds using *p*-toluenesulfonic acid as a catalyst decreases in the order MTEOS ≈ MTMOS > TMOS > TEOS ≈ TPOS and that the concentration (V_c) of the silicon compounds in the vapor phase decreases in the order MTMOS > TMOS > MTEOS > TEOS > TPOS, which is consistent with their boiling points. Thus it was confirmed that the polysiloxane formation rates at the irradiated polymer surface containing **1a** were determined by both k_{obs} and V_c values.

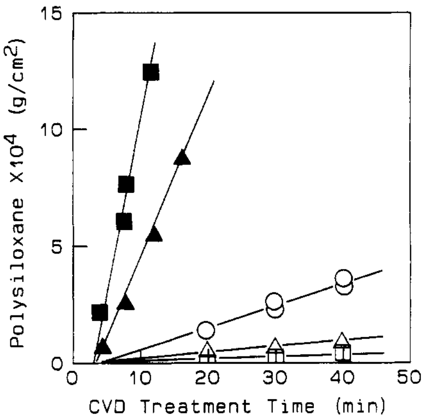

Figure 6. Effect of silicon compound structure on the polysiloxane formation at the irradiated surface of PMMA films containing 7.5 mol % of **1a**. Silicon compound: (■) MTMOS, (▲) TMOS, (○) MTEOS, (△) TEOS, and (□) TPOS. Exposure dose: 126 mJ/cm^2.

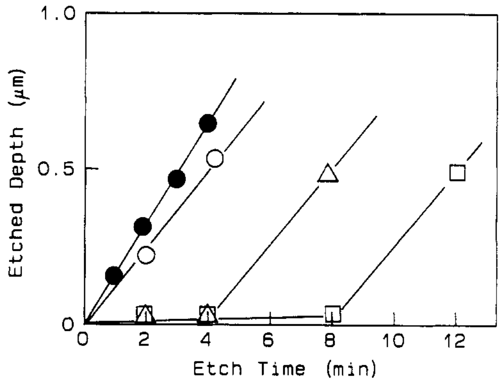

Figure 7. Plots of thickness loss versus etch time for the irradiated PMMA films containing different amounts of **1a**. CVD treatment using MTEOS vapor was carried out for 30 min at 30 °C. Content of **1a**: (●) 0, (○) 5, (△) 10, and (□) 15 mol %. Exposure dose: 52 mJ/cm^2. Relative humidity: 95%.

Oxygen Plasma Etching. Figure 7 shows the thickness loss of polymer films as a function of etch time using oxygen plasma. The irradiated PMMA films containing different amount of **1a** were exposed to the vapor of MTEOS. An exposure dose was 52 mJ/cm^2 for all polymer films. The etch speed for PMMA film was 0.14 μm/min for our apparatus. The films of PMMA containing 10 and 15 mol % of **1a** showed a good etch resistance to oxygen plasma for 4 and 8 min, respectively. The etch speed of the irradiated PMMA films containing 10 and 15 mol % of **1a** after CVD treatment was 100 times slower than that of PMMA film. The etch-resistance holding period increased with **1a** content. The PMMA film with 5 mol % of **1a** did not show significant etch resistance to oxygen plasma. The content of polysiloxane formed at the irradiated surface of the PMMA film containing 15 mol % of **1a** was 1.7 wt % which was determined by a ATR FT-IR method with

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(22) Nakamura, J.; Ban, H.; Deguchi, K.; Tanaka, A. *Jpn. J. Appl. Phys.* **1991**, *30*, 2619.

Table III. Polysiloxane Formation Rate (R_p) at the Irradiated Surface of Copolymer and Blended Polymer Films[a]

	R_p (μg/cm^2 min)	
R	copolym system[b]	blended system[c]
CH_3	13.1	18.8
i-C_3H_7	3.4	14.2
$CH_2C_6H_5$	0.2	8.5

[a] Film thickness: 1 μm, photolysis degrees of both NISS units and 1a: 70%. $CH_3Si(OC_2H_5)_3$ vapor was used. [b] Copolymers of alkyl methacrylates and 1,2,3,4-tetrahythylideneamino p-styrenesulfonate (NISS). NISS unit fractions were 16–18 mol %. [c] Blended systems of poly(alkyl methacrylates) and 1a. 1a contents were 16–18 mol %.

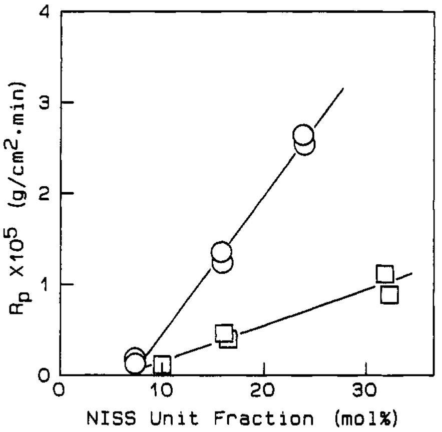

Figure 8. Effect of NISS unit fraction in the polymers on the polysiloxane formation rate (R_p) at the irradiated surface of the films using MTEOS vapor at 30 °C. Polymer: (□) copolymer of NISS and isopropyl methacrylate and (○) copolymer of NISS and methyl methacrylate. Exposure dose 183 mJ/cm^2. CVD treatment time: 30 min.

Ge prism using octamethylcyclotetrasiloxae as a standard. The polysiloxane content obtained was the average value in the surface (thickness ≈ 0.4 μm) of the film. The polysiloxane content at the very top surface may be much higher than the obtained value.

Comparison of Copolymer and Blended Systems. The SiO_2 network formation at the surface of polymers (PMANI, PPRNI, and PBZNI) bearing imino sulfonate units bound to the polymer chain has been reported.[11] The structure of polymers and definitions for the acronyms PMANI, PPRNI and PBZNI are shown in Scheme I. We have found some important differences between the copolymer and the polymer–imino sulfonate blended systems for the formation of polysiloxane at the irradiated surface of the films. Table III shows the influence of the methacrylate structure on the polysiloxane formation rate at the irradiated surface of copolymer and polymer–imino sulfonate blended systems. The polysiloxane formation rate decreased in the order $CH_3 > i\text{-}C_3H_7 > CH_2C_6H_5$ for both copolymer and polymer–imino sulfonate blended systems. However, the degree of the decrease in the polysiloxane formation rate by the hydrophobic nature of the methacrylate ester groups was lower for the polymer–imino sulfonate blended systems than for the copolymer systems. The weak dependence of polysiloxane formation rate on the hydrophobic nature of the polymer–imino sulfonate blended systems may be due to that polysiloxane can be formed at very surface of the films because the photochemically formed acids can diffuse toward the irradiated surface of the films. Figure 8 shows the effect of NISS unit fraction in PMANI and PPRNI series copolymers on the polysiloxane formation rate (R_p). R_p linearly increased with NISS unit fraction for both copolymer films. A saturation phenomenon observed for the polymer–imino sulfonate blended systems (see Figure 5) was not observed for the copolymer systems. Figure 9 shows the oxygen plasma etching of PMANI (NISS unit: 25 mol %) film which was irradiated and subsequently exposed to the vapor of MTEOS at 30 °C. The etching speed of PMANI having 25 mol % of NISS units was 0.11 μm/min, which was slightly lower than that of PMMA. It has been reported that an introduction of aromatic units into polymers lowers the rate of the oxygen plasma etching.[23] The films of PMANI (NISS unit: 25 mol %) which were irradiated with 254-nm light (171 mJ/cm^2) and subsequently exposed to MTEOS vapor for 15 and 20 min showed a good etch resistance to oxygen plasma. The initial thickness loss (0.03 μm) which was not observed for the polymer–imino sulfonate blended systems (see Figure 7) was observed. The initial thickness loss is due to the loss of polymeric materials to form SiO_2 layer during the oxygen plasma etching. This suggests that the amounts of the polysiloxane network formed at the near surface of the copolymer films are lower than that of the polymer–imino sulfonate blended systems. If the amounts of the photochemically formed acids in the films are equal in the copolymer and polymer–imino sulfonate blended systems, the amount of the acids at the surface of the blended systems is higher than that of the copolymer systems because of the diffusion of the acids to the irradiated surface for the blended systems. The high concentration of acid at the film surface can give a surface densely packed with polysiloxane networks.

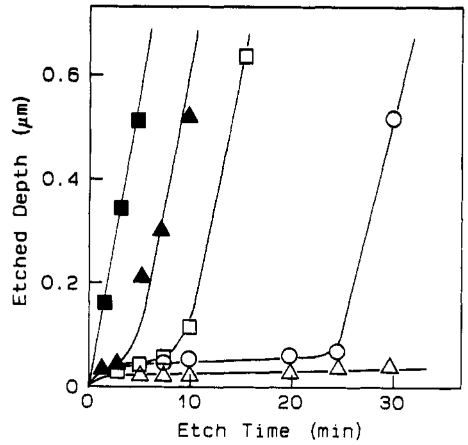

Figure 9. Plots of thickness loss versus etch time for the films of copolymers of NISS (25 mol %) and methyl methacrylate. The sample films were irradiated with exposure dose of 171 mJ/cm^2 and, in the subsequent step, exposed to the MTEOS vapor at 30 °C. Relative humidity: 58%. CVD treatment times: (■) 0, (▲) 10, (□) 13, (○) 15, and (△) 20 min.

The surface imaging systems using selective silylation with hexamethyldisilazane and its homologues into the exposed or unexposed areas of photoresists have been studied because they are very important in relation to the microlithography.[24,25] We are convinced that the preliminary results point out the potential for application of this system as a surface imaging system. This system can

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(23) Taylor, G. N.; Wolf, T. M. *Polym. Eng. Sci.* **1980**, *20*, 1087.
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(25) MacDonald, S. A.; Schlosser, H.; Ito, H.; Clecak, N. J.; Willson, C. G. *Chem. Mater.* **1991**, *3*, 435.

give a negative tone image by the development using oxygen plasma.

Conclusions

When the irradiated polymer films containing imino sulfonates as photoacid-generating compounds were exposed to the vapor of tetraalkyl orthosilicates and their homologues under humid conditions at 30 °C, polysiloxane networks were formed at the near surface of the films. No polysiloxane networks were formed at unirradiated polymer surface. The polysiloxane network formation was affected by the water sorption ability of the irradiated polymer films, the number of the photochemically formed acids, the hydrolytic reactivity of the silicon compounds, and the concentrations of the silicon compounds in the vapor phase. The polymer films obtained after UV irradiation and subsequent CVD treatment with the vapor of alkoxysilanes showed a good etch resistance to oxygen plasma. In regard to the polysiloxane network formation by the CVD method at the irradiated polymer surface and the profile of oxygen plasma etching of the irradiated polymers after CVD treatment, there were significant differences between the polymers containing imino sulfonates as additives and the polymers bearing pendant imino sulfonate units.