Photochemically Induced Acid-Catalyzed Desilylation of Polymer Films

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Received July 26, 1994. Revised Manuscript Received January 31, 1995®

Removal of silicon-containing species from the UV-irradiated areas of polymer films was studied. Polymers which have silyl ester or silyl ether side groups were synthesized. The polymer films containing imino sulfonate compounds as the photoacid generator were irradiated with 254-nm light and in a subsequent step, the irradiated films were exposed to the vapor of organic solvents such as acetone, methanol, or *n*-hexane at room temperature to remove the volatile silicon species formed in the film by the photochemically induced acid-catalyzed hydrolysis of the silyl ester and silyl ether units. The acid-catalyzed hydrolysis rate of silyl esters and ethers was also enhanced by the vapor treatment with organic solvents. The rate of escape of the silicon species formed in the film was strongly dependent upon the polymer structure, the kind of organic solvent and structure of the silyl ester or silyl ether units. UV irradiation and subsequent exposure of the films to the vapor of organic solvents enhanced the rate of oxygen plasma etching of the film due to the loss of the silicon species.

Introduction

Functionalization of irradiated or unirradiated areas of polymer films by inorganic or organometallic compound has been studied by many researchers to obtain plasma-developable resists. When the polymers containing inorganic components such as silicon, tin, germanium, or titanium were placed in an oxygen plasma environment, the inorganic components can be converted to a nonvolatile oxide. Since the oxide retards the etching rate in an oxygen plasma, the regions containing the inorganic components remain after the etching. Taylor and co-workers[1,2] reported a process in which a bisarylazide/isoprene cross-linkable polymer system was irradiated with UV light and, in a subsequent step, treated with the vapor of inorganic halides such as $SnCl_4$, $SiCl_4$, or $(CH_3)_2SiCl_2$. In this system reaction products containing Si or Sn could be formed at the near surface of the polymer films. Pattern development for microlithography was achieved using oxygen reactive ion etching (O_2 RIE).

In an alternative scheme, the surface functionalization of polymer films bearing photochemically formed phenolic –OH groups using hexamethyldisilazane was studied by MacDonald and co-workers.[3,4] Coopmans and Roland[5] described the gas-phase silylation of a diazonaphthoquinone/phenolic matrix resin, yielding a negative tone image by O_2 RIE. The selective formation of polysiloxane or metal oxides at the irradiated areas of polymer films is an important method to obtain a negative tone plasma-developable resist system. Follett and co-workers[6] have reported the plasma-developable electron-beam resists. In this system dichlorodimethylsilane selectively diffused into the irradiated areas of a poly(methyl methacrylate) film, and this step was followed by hydrolysis of the chlorosilane upon exposure to water vapor, resulting in the formation of polysiloxane networks. In another approach hydrophobic polymers such as chlorine-containing polystyrene underwent oxidation to form hydroxyl and carbonyl groups when irradiated in air with 248.4- or 193-nm light. Since the irradiated regions sorbed water from the atmosphere, the treatment of the irradiated films with gaseous $TiCl_4$ led to the formation of a TiO_2 layer at the surface.[7–10] The selective formation of polysiloxane networks at the irradiated areas of the films was performed using the photoacid generating polymers and the vapor of alkoxysilanes.[11]

There are a variety of schemes to obtain positive tone plasma-developable resists. Schellekens and Visser[12] studied a system based on photoinduced acid-catalyzed cross-linking of irradiated areas of poly(vinylphenol) and subsequent gas-phase silylation treatment. Since only the unirradiated areas were silylated, the irradiated regions were removed by O_2 RIE, giving a positive tone image. MacDonald and co-workers[13] have developed a positive tone plasma-developable resist based on an image-reversal process. This system employed the catalytic photogeneration of phenolic –OH groups in the film that reacted, in subsequent steps, with isocyanates that were delivered in the gas phase. The film was

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® Abstract published in *Advance ACS Abstracts,* March 1, 1995.

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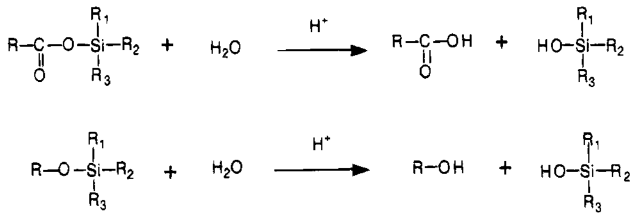
silylated after a flood irradiation. The carbamate regions of the film were more rapidly etched in an oxygen plasma, resulting in a positive tone image.

The polymers having silicon-containing side groups which can be removed upon irradiation can be used as oxygen-plasma-developable positive photoresists. The pioneering work for this purpose was done by Meyer and co-workers,[14] who have used a copolymer of methyl methacrylate and *p*-((trimethylsilyl)methyl)acetophenone oxime methacrylate. Upon irradiation with deep-UV light, the N−O bonds in the oxime ester linkage are cleaved, liberating silicon-containing species which can be removed by a thermal treatment. The silicon content is reduced by irradiation and subsequent baking, which gave positive tone images upon development with O_2 RIE. Ito and co-workers[15−17] have reported the acid-catalyzed depolymerization of polysilylphthalaldehyde, which provides all-dry O_2 RIE bilayer lithography through removal of silicon species from the exposed regions by a heating method.

In a recent communication,[18] we have reported the preliminary results concerning the photoinduced acid-catalyzed hydrolysis of silyl ester and silyl ether units in polymer films and subsequent removal of silicon species liberated in the films by the plasticization of the films using the vapor of organic solvents. In this paper we fully report the synthesis of the polymers, the removal of silicon-containing components from the irradiated areas of polymer films and the oxygen plasma etching properties of the polymer films which were irradiated and exposed in a subsequent step to the vapor of organic solvents at room temperature:



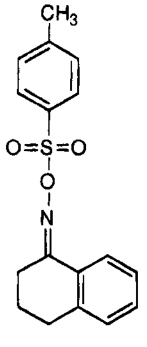
$$\mathrm{R{-}C(=O){-}O{-}Si(R_1)(R_3){-}R_2} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \mathrm{R{-}C(=O){-}OH} + \mathrm{HO{-}Si(R_1)(R_3){-}R_2}$$

$$\mathrm{R{-}O{-}Si(R_1)(R_3){-}R_2} + \mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \mathrm{R{-}OH} + \mathrm{HO{-}Si(R_1)(R_3){-}R_2}$$

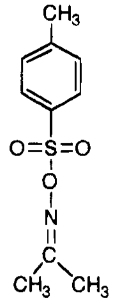
Silyl ethers and esters are known to be easily hydrolyzed in the presence of strong acid to form silanol.[19] In our approach the photochemically induced acid catalyzes the hydrolysis of silyl ester or ether units in polymer films. The treatment of the irradiated films with the vapor of organic solvents such as alcohols, acetone, or *n*-hexane enhanced both the acid-catalyzed hydrolysis of silyl ester or ether units in the films and the removal of the volatile silicon species formed in the irradiated films. The volatile silicon species generated in the irradiated areas of the films were completely removed by exposing the films to the vapor of organic solvents at room temperature and atmospheric pressure. This system has a potential as photoresists which can be dry-developed in an oxygen plasma to generate a positive tone image.

Experimental Section

Materials. *2-Propylideneamino p-toluenesulfonate (PTS)*: To a solution of acetoxime (1.61 g, 2 × 10^{-2} mol) in pyridine (22 mL) below 5 °C was added *p*-toluenesulfonyl chloride (4.2 g, 2.2 × 10^{-2} mol) portionwise over a period of 20 min. The reaction mixture was stirred at 5 °C for 3 h and poured with stirring into an ice-cold aqueous solution (130 mL) of 5% HCl. The reaction mixture was extracted with chloroform and the chloroform layer was dried over K_2CO_3. Evaporation of the chloroform under reduced pressure gave the crude product, which was recrystallized from a *n*-heptane−benzene (5:1, v/v) mixture; yield 76%, mp 85−86 °C. Anal. Calcd for $C_{10}H_{13}NO_3S$ (227.28): C, 52.85; H, 5.77; N, 6.16. Found: C, 52.92; H, 5.73; N, 6.09. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.9 (6H, s, CH_3), 2.4 (3H, s, CH_3), 7.3−7.9 ppm (4H, m, aryl).



NTS



PTS

The preparation of 1,2,3,4-tetrahydro-1-naphthylideneamino *p*-toluenesulfonate (NTS) has been reported elsewhere.[20]

tert-Butyldimethylsilyl methacrylate (BDMSMA): To a mixture of methacrylic acid (11 mL, 0.15 mol), hydroquinone (1.1 mg), imidazole (22 g, 0.32 mol), and *N,N*-dimethylformamide (80 mL) at room temperature was added *tert*-butyldimethylchlorosilane (24 g, 0.16 mol) in 50 mL of *N,N*-dimethylformamide portionwise over 30 min. The reaction mixture was stirred at 50 °C for 6 h and poured with stirring into 40 mL of aqueous NaCl solution (20 wt %). The reaction mixture was extracted with ethyl acetate and the ethyl acetate layer was dried over $MgSO_4$. After removal of the ethyl acetate under reduced pressure, the product was purified by distillation; yield 88%, bp 50−53 °C/5 mmHg. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.3 (6H, s, $Si{-}CH_3$), 1.0 (9H, s, $-C(CH_3)_3$), 1.9 (3H, s, $-CH_3$), 5.6−6.1 ppm (2H, d, $CH_2{=}$).

Trimethylsilyl methacrylate (TMSMA), 2-[(trimethylsilyl)oxy]ethyl methacrylate (TMSOEMA), styrene (St), benzyl methacrylate (BzMA), and methyl methacrylate (MMA) were of reagent grade and used after distillation.

Polymer Synthesis. *Poly(p-[(trimethylsilyl)oxy]styrene) (6)*: This polymer was prepared by modifying the method reported by Yamaoka and co-workers.[21] To a mixture of poly(*p*-hydroxystyrene) (Maruzene, $M_w = 9900$) (1.2 g, 1.0 × 10^{-2} mol), imidazole (2.0 g, 3.0 × 10^{-2} mol), and 1,4-dioxane (30 mL) at room temperature was added chlorotrimethylsilane (2.5 mL, 2.0 × 10^{-2} mol). The reaction mixture was stirred at 20 °C for 20 h and poured with stirring into 300 mL of ice-cold water. The precipitated polymer was separated by filtration and was dried in vacuo. The polymer was purified by dissolving in chloroform and precipitating with ethanol; yield 20%. The low yield is due to the repetition of the purification procedure. The complete silylation of poly(*p*-hydroxystyrene) was confirmed by comparing the ratio of proton signals due to $Si{-}CH_3$ and benzene ring measured by ^{1}H NMR spectroscopy (JEOL JNM-GX270). The glass transition temperature (T_g) of **6** was 56 °C.

The polymers containing Si (**1a−c**, **2−5**) were prepared by bulk copolymerization of corresponding monomers using azo-

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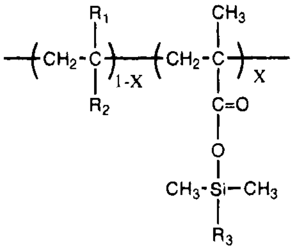
Table 1. Polymerization Conditions and Polymer Properties[a]

polymer	monomer (g) St	MMA	BzMA	TMSMA	BDMSMA	TMSOEMA	polymerization time (h)	yield (%)	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	T_g (°C)	X[c]
1a	3.12			1.58			11	23	7	1.5	98	0.29
1b	2.08			3.16			6	21	14	1.8	*b*	0.44
1c	1.04			4.74			6	18	18	2.2	*b*	0.61
2	1.56				3.0		13	35	10	1.6	97	0.53
3		1.70		2.69			2	50	31	2.2	84	0.50
4			2.11	2.21			2	50	52	2.2	*b*	0.50
5	1.56					3.03	10	32	13	1.6	48	0.43

[a] Polymerization was carried out with azobis(isobutyronitrile) (8.3×10^{-5} mol/L). [b] No distinct T_g was observed above room temperature. [c] Mole fraction of silyl ester or silyl ether units in the polymer. See Scheme 1.

Scheme 1. Structure of Polymers

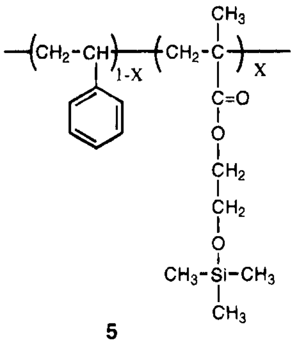


1a-c : R_1=H R_2=C_6H_5 R_3=CH_3

2 : R_1=H R_2=C_6H_5 R_3=$C(CH_3)_3$

3 : R_1=CH_3 R_2=$COOCH_3$ R_3=CH_3

4 : R_1=CH_3 R_2=$COOCH_2C_6H_5$ R_3=CH_3



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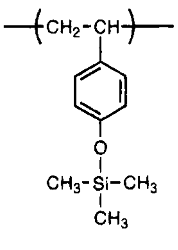

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Table 2. Characteristics of the Photoacid Generators

photoacid generator	T_m[a] (°C)	T_d[b] (°C)	abs max (nm)	$10^{-4}\,\epsilon$[c] (L/mol cm)	Φ[d]	photolysis degree (%)
NTS	98	149	256	1.51	0.29	17.3
PTS	85	118	227	0.046	0.094	8.2

[a] Melting point. [b] Decomposition temperature from DSC. [c] Molar extinction coefficient at 254 nm in acetonitrile. [d] Quantum yield for the photochemical formation of *p*-toluenesulfonic acid in PMMA film in air.

bisisobutyronitrile (AIBN) as the initiator at 55–60 °C. The polymers were stored in a refrigerator to prevent the spontaneous hydrolysis of silyl ester and ether units. The molecular weight of the polymers was determined by gel permeation chromatography (GPC) with polystyrene standards using a JASCO 880-PU with a column packed with polystyrene gel. Freshly distilled tetrahydrofuran was used as an eluent to minimize the hydrolysis of the Si-containing units. The fraction of Si-containing monomer units in the polymers was determined from ^{1}H NMR. Detailed polymerization conditions and polymer properties are shown in Table 1. The structures of the polymers used in this study are shown in Scheme 1.

Measurements. *Hydrolysis and removal of silicon species*: Polymer films were prepared on NaCl plates (diameter 2.5 cm, thickness 3 mm) by casting from chloroform solutions containing polymers and photoacid generators. The sample films were thoroughly dried under vacuum at room temperature. Although baking the films after casting was not carried out, the rates of the desilylation of the irradiated films were reproducible on repeated runs. The film thickness was usually 0.5–1.0 μm. Irradiation of the films was done with 254-nm light (1.62×10^{-9} einsteins/cm^2 s) from a low-pressure mercury lamp (Toshiba LB-11B, 5 W). The intensity of the incident light was measured with a chemical actinometer (potassium ferrioxalate).[22] The NaCl plate coated with the irradiated polymer film was placed at the center of a 500-mL cylindrical glass vessel with a septum inlet. Two milliliters of organic solvent was placed at the bottom of the vessel. The vessel was sealed and equilibrated for a given time at room temperature.

The hydrolysis of the silyl ester units in polymer films (**1a–c** and **2**) was monitored by following the decrease in absorbance at 1706 cm^{-1} due to ester C=O groups. The hydrolysis degree of the silyl ester units in the films of **3** and **4** was not determined by FT-IR because of the strong peaks around 1700 cm^{-1} due to methyl methacrylate or benzyl methacrylate units. The hydrolysis of the silyl ether units of **5** and **6** was followed by monitoring the decrease in the absorbances at 918 and 965 cm^{-1} due to the Si–O bonds, respectively. FT-IR spectra were taken on a JASCO FT-IR 7300. The degree of the silicon species removed from the irradiated films was determined by the decrease in the absorbance at 1253 cm^{-1} due to Si–CH_3 groups.

Quantum yield: The quantum yields (Φ) were obtained as follows: Sample films were prepared on a quartz plate (1×2 cm) by casting from dichloromethane solution of PMMA containing 40 wt % of NTS or PTS and drying under vacuum at room temperature for 1 h. A film was irradiated at room temperature in air with a low-pressure Hg lamp (0.7 mJ/cm^2 s). The quartz plate coated with the irradiated film was immersed in methanol (5 mL) and sonicated for 5 min. The methanol solution was filtered with a membrane filter (pore size 0.8 μm) and a known amount of it was subjected to analysis by high pressure liquid chromatography (HPLC) using a JASCO 880-PU. A column packed with silica gel coated with octadecylsilane was used. A water–methanol (3:7, v/v) mixture was used as an eluent. The Φ values for the formation of *p*-toluenesulfonic acid were determined as the number of moles of *p*-toluenesulfonic acid formed per einstein of 254-nm light absorbed by the photoacid generator.

Oxygen plasma etching: Oxygen plasma etching of the sample films 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 as follows: 20 W power (13.56 MHz), power density of 1.0 W/cm^2, and oxygen flow of 1 sccm at 125 mTorr. The thickness of the sample films was measured using a multiple-beam interferometer.

Results and Discussion

Photochemistry of the Photoacid Generators. Characteristics of the photoacid generators NTS and PTS are shown in Table 2. NTS showed an absorption maximum at 256 nm and a weak shoulder peak at about

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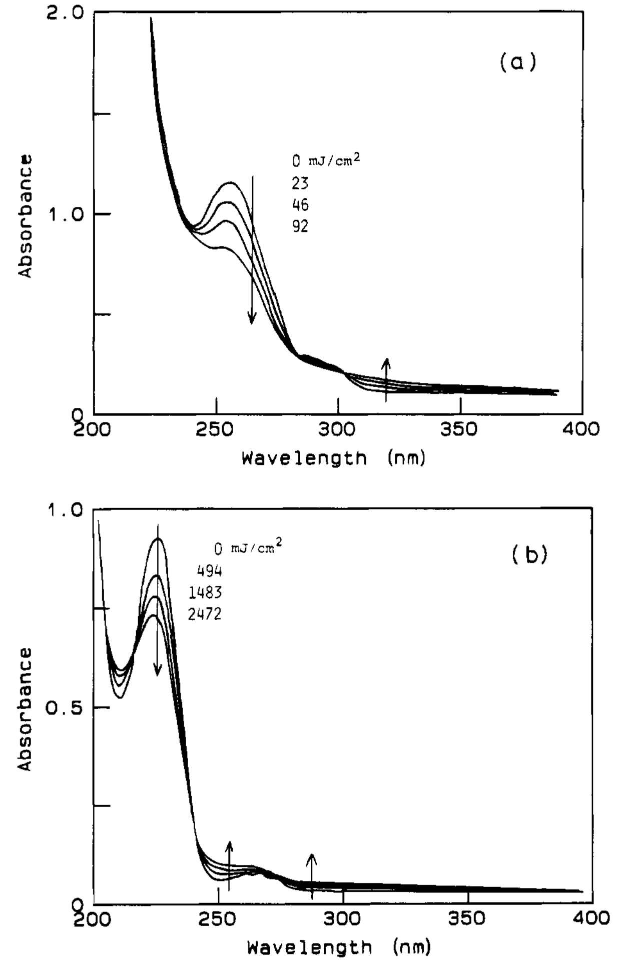
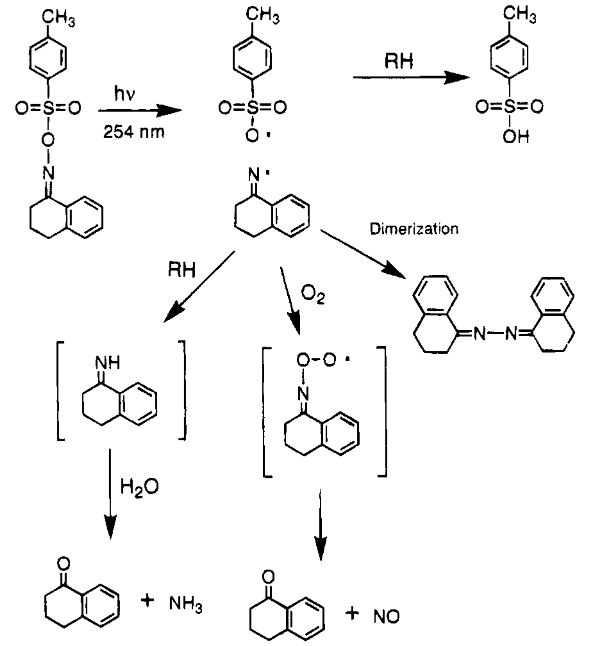


Figure 1. UV spectral changes of the film of **1b** containing a photoacid generator upon irradiation with 254-nm light. Photoacid generator: (a) 10 mol % of NTS and (b) 15 mol % of PTS. Film thickness: 0.8–0.9 μm.

Scheme 2. Mechanism for the Photolysis of NTS



300 nm. PTS showed an absorption maximum at 227 nm and a weak shoulder peak at about 260 nm. The molar extinction coefficients (ϵ) of NTS and PTS at 254 nm were 1.51 × 10^4 and 4.6 × 10^2 (L/mol cm). The thermal decomposition temperatures of NTS and PTS determined by differential scanning calorimetry (DSC) using a Rigaku DSC-8230 were 149 and 118 °C, respectively. Changes in the absorption spectrum upon irradiation at 254 nm of a thin film of **1b** containing 10 mol % of NTS or 15 mol % of PTS are shown in Figure 1. In the case of NTS the absorbance at 254 nm decreased with irradiation time, and an isosbestic point was observed at 305 nm. The slight increase in absorbance above 300 nm was due to the formation of tetraloneazine. When PTS was used as the photoacid generator, a similar change in the absorption spectrum was observed (Figure 1b). It has been reported that the UV irradiation cleaves the —O—N= bonds of imino sulfonate compounds.[23] Subsequent abstraction of hydrogen atoms from residual solvent in the polymer film or from polymer molecules leads to the formation of *p*-toluenesulfonic acid, ketones, and azines as shown in Scheme 2. For the photolysis of the photoacid generator in polymer film in air, the reaction of imino radicals with oxygen is dominant compared to their dimerization and hydrogen abstraction reactions. The quantum yields (Φ) for the photochemical formation of *p*-toluenesulfonic acid from NTS and PTS were 0.29 and 0.094, respectively, in PMMA film. The photolysis degrees for the photoacid generators were 8.2–17.3%. PTS showed an absorption maximum at 227 nm and a weak shoulder peak around 260 nm which is assigned to n–π^* transition. The low Φ value for PTS may be due to the n–π^* excitation of the chromophore upon photolysis with 254-nm light. In the case of NTS the π–π^* excitation (absorption maximum at 256 nn) was employed upon the photolysis with 254-nm light. The Φ value for NTS was comparable with the Φ values reported for 2,6-dinitrobenzyl esters of 4-substituted benzenesulfonic acid (Φ = 0.1–0.16)[24] and triphenylsulfonium hexafluoroantimonate (Φ = 0.26–0.4)[25] measured in thin films (≈1 μm) of PMMA or poly(4-[(*tert*-butoxycarbonyl)oxy]styrene).

Hydrolysis and Removal of Silicon Species. Silyl esters of carboxylic acids and silyl ethers of alcohols or phenols are known to be easily hydrolyzed in the presence of strong acid and water. Figure 2 shows changes in the FT-IR spectra of the films of **1b** and **6** before and after irradiation followed by the treatment with acetone vapor. The absorption peak at 1706 cm^{-1} for the film of **1b** containing NTS decreased with irradiation and a new peak appeared at 1696 cm^{-1}. The peak around 3300 cm^{-1} almost doubled. These findings suggest the formation of COOH groups by the hydrolysis of the silyl ester units. A similar change in FT-IR spectra of **1a**, **1c**, and **2** was observed. The hydrolysis degree of the silyl ester units was determined by the changes in the absorption peak at 1706 cm^{-1}. In the present system the water which was needed to accomplish the hydrolysis was supplied from the atmosphere. Since the hydrophobic polymer surface became hydrophilic due to the photochemical formation of *p*-toluenesulfonic acid, water sorption occurred at the

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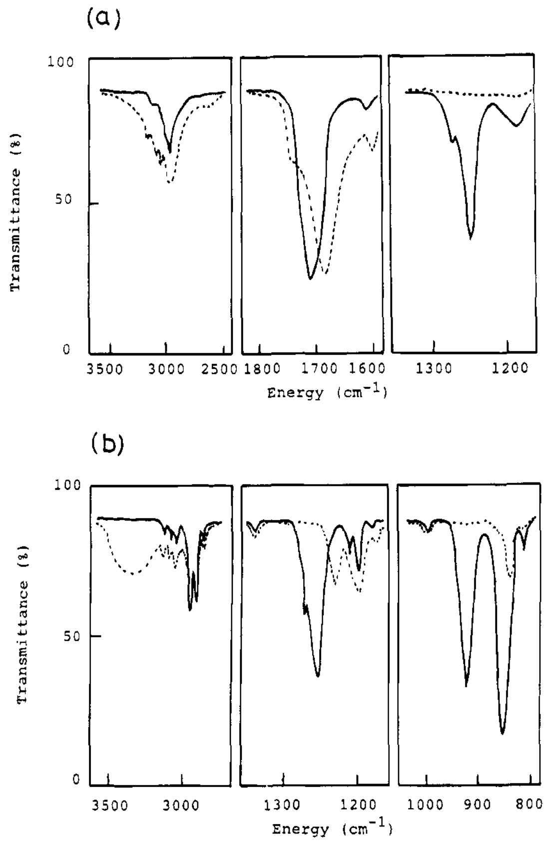

Figure 2. FT-IR spectra of the films of (a) **1b** and (b) **6** containing 10 mol % of NTS. Solid line: before irradiation. Dotted line: after irradiation followed by the acetone vapor treatment.

irradiated polymer surface. The hydrolysis degree of the silyl ester units in the films of **3** and **4** was not determined by FT-IR because of the strong peaks around 1700 cm^{-1} due to methyl methacrylate or benzyl methacrylate units. Upon irradiation of the film of **6** containing the photoacid generator, the absorption peak at 918 cm^{-1} due to Si$-$O simply decreased and a new peak appeared at 3320 cm^{-1} due to phenolic OH groups (Figure 2b). For the film of **5** containing the photoacid generator, the absorption peak at 965 cm^{-1} due to Si$-$O decreased upon irradiation. The hydrolysis degree of the silyl ether units in **5** and **6** was determined by the changes in absorption peak at 918 or 965 cm^{-1}. The amount of the silicon species remaining in the irradiated film was determined from the absorbance at 1253 cm^{-1} due to CH_3-Si groups.

To check the formation of hexamethyldisiloxane from the acid-catalyzed cleavage of the trimethylsilyl esters and ethers, a model experiment in the liquid state was carried out. The hydrolysis of trimethylsilyl methacrylate was accomplished in benzene solution containing small amounts of *p*-toluenesulfonic acid. The formation of hexamethyldisiloxane was confirmed by a gas chromatography using a Shimadzu GC-8A (retention time of hexamethyldisiloxane 3.35 min; column apiezon-L 10%; He flow 80 mL/min at 100 °C). Thus, if the trimethylsilanol liberated in the irradiated film can diffuse in the film, hexamethyldisiloxane can be formed in the film.

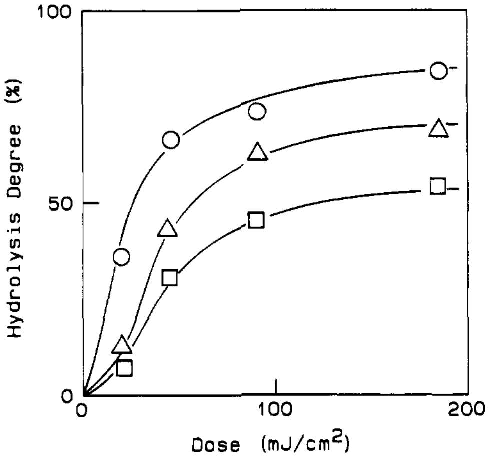

Figure 3. Effect of relative humidity during irradiation on hydrolysis of silyl ester units in the film of **1a** containing 10 mol % of NTS. Relative humidity: (○) 72, (△) 58, (□) 32%. Film thickness: 0.45 μm.

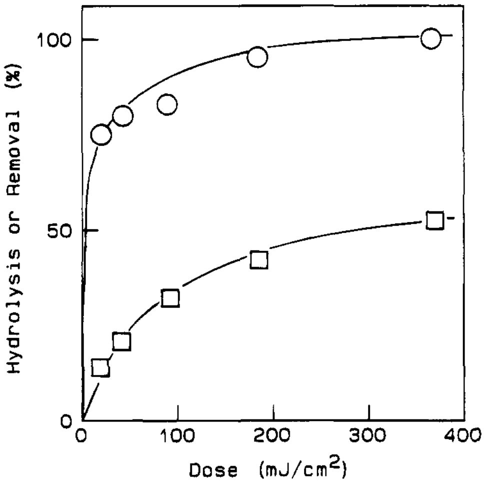

Figure 4. Effect of exposure dose on hydrolysis (○) and removal of silicon species (□) from the film of **1b** containing 10 mol % of NTS. Relative humidity: 58%. Film thickness: 0.45 μm.

Figure 3 shows the effect of relative humidity during irradiation on the hydrolysis of the film of **1a** containing 10 mol % of NTS. The hydrolysis degree of the silyl ester units in the film of **1a** increased with exposure dose and more gradually increased at high exposure dose. If compared at a constant exposure dose, the hydrolysis degree increased with relative humidity of the atmosphere during the irradiation. Water is essential for the acid-catalyzed hydrolysis of the silyl esters. Figure 4 shows the relationship between exposure dose and hydrolysis degree of the silyl ester units in the film of **1b** containing 10 mol % of NTS. This Figure also shows the relationship between exposure dose and fraction of silicon species removed from the film. The hydrolysis degree increased with exposure dose and reached 100% at an exposure of 360 mJ/cm^2. On the other hand, the fraction of silicon species removed from the film increased with exposure dose and reached 50% at 360 mJ/cm^2. Thus, 50% of the volatile silicon species formed by the photoinduced acid-catalyzed hydrolysis remained in the film. It was found that the silicon species formed in the film were completely removed by exposing the irradiated films to the vapor of organic solvents at room temperature. The volatile silicon species can be removed from the film as trimethylsilanol (bp 98$-$99 °C) and/or hexamethyldisiloxane (100.5 °C). The volatile silicon species in the film could not be completely removed by a simple vacuum treatment at room temperature. When the irradiated

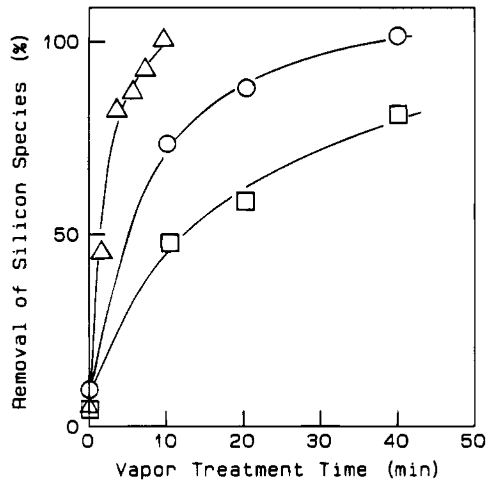

Figure 5. Effect of solvent vapor on the removal of silicon species from the irradiated **1b** film containing 10 mol % of NTS. Exposure dose: 27 mJ/cm^2. Film thickness: 0.45 μm. Solvent vapor: (△) acetone, (○) methanol, (□) *n*-hexane.

1a film containing 10 mol % of NTS was heated at 100 °C for 30 min, 97% of the silicon species could be removed from the irradiated film. However, the heat treatment at 100 °C for 30 min slightly induced a decomposition of the silyl ester units of the unirradiated film. Fifteen percent of the silicon species could be removed from the irradiated film by a heat treatment at 50 °C for 30 min.

The fraction of silicon species which escaped from the irradiated **1b** film was plotted in Figure 5 as a function of the period during which the sample film was exposed to the vapor of organic solvents such as methanol, acetone, and *n*-hexane. The degrees of hydrolysis of the silyl ester units in the irradiated **1b** film were 33–65%. The fraction of the silicon species removed from the film just after irradiation with a dose of 27 mJ/cm^2 was negligibly low, but it largely increased with vapor treatment time. The complete removal of the silicon species was accomplished by acetone vapor treatment for 10 min at 25 °C. Since the degree of hydrolysis of the trimethylsilyl ester units was 33–65% just after irradiation of the film, the vapor treatment enhanced the acid-catalyzed hydrolysis of the silyl ester units as well as the removal of the volatile silicon species from the film. The enhancement of hydrolysis of the silyl ester units and the fraction of silicon species removed from the film may be due to the plasticization of the film by the sorbed vapor of the organic solvents. When the vapor of alcohols was used, the efficiency for the removal of the silicon species from the irradiated films decreased in the order methanol > ethanol ≈ *n*-propanol > *n*-butanol. This means that the alcohol having high vapor pressure at room temperature is more effective. The thickness changes of the films by the treatment with organic vapors were negligibly small (<3%), which was checked by a multiple-beam interferometer.

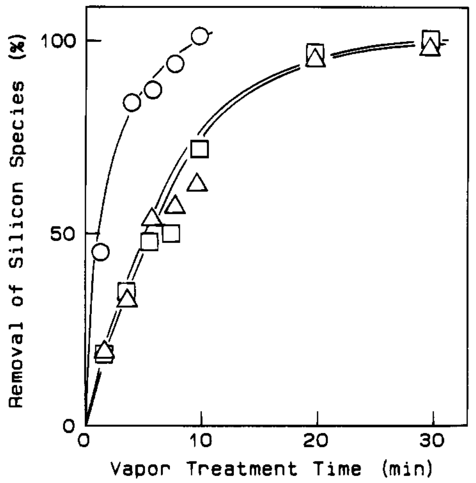

Figure 6. Effect of polymer structure on the rate of removal of silicon species. Sample films containing 10 mol % of NTS were irradiated (27 mJ/cm^2) and subsequently exposed to the vapor of acetone. Film thickness: 0.45 μm. Polymer: (○) **1b**, (□) **3**, (△) **4**.

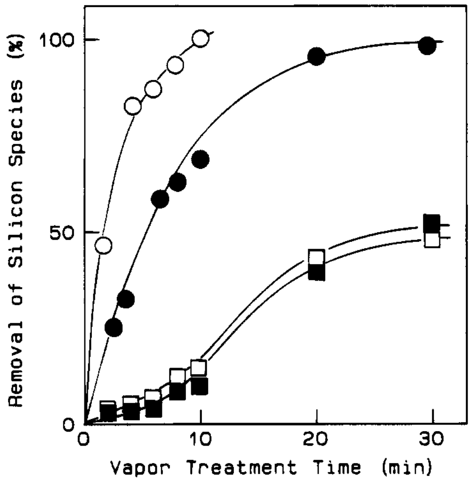

Figure 7. Effect of structures of silyl ester and silyl ether units in polymers on the rate of removal of silicon species. Film thickness: 0.45 μm. Sample films containing 10 mol % of NTS were irradiated (27 mJ/cm^2) and subsequently exposed to the vapor of acetone. Polymer: (○) **1b**, (□) **2**, (■) **5**, (●) **6**.

Figure 6 shows the fraction of the silicon species removed from the irradiated films of **1b**, **3**, and **4**. The content of trimethylsilyl methacrylate in the polymer was 44–50 mol %. The fraction of the silicon species removed from the irradiated film increased with the acetone vapor treatment time. The rate of removal of silicon species decreased in the order **1b** > **3** ≈ **4**. The ester C=O group of methyl methacrylate or benzyl methacrylate units which can interact with trimethylsilanol by forming hydrogen bond retarded the diffusion of the silanol in the film. Figure 7 shows the effect of structure of silyl ester or silyl ether units in polymers on the rate of removal of the silicon species from the irradiated films of **1b**, **2**, **5**, and **6**. The rate for the irradiated **1b** film was much higher than that for the irradiated **2** film. This may be due to the following facts: (i) trimethylsilyl ester of carboxylic acids can be hydrolyzed more rapidly than *tert*-butyldimethylsilyl ester of carboxylic acids and (ii) trimethylsilanol and hexamethyldisiloxane can diffuse faster than *tert*-butyldimethylsilanol and di-*tert*-butyltetramethyldisiloxane in the film. The rate of removal of silicon species from the irradiated **6** film was faster than that for the irradiated **5** film, though the hydrolysis rate for the trimethylsilyl ether units in the film of **5** was faster than that in the film of **6**. Thus, the slow rate of removal of silicon species from the irradiated **5** film may be due to the interaction between the trimethylsilanol and the methacrylic acid ester moieties in the film of **5** as described above.

The film thickness was observed to decrease upon removal of silicon species. The thickness loss was

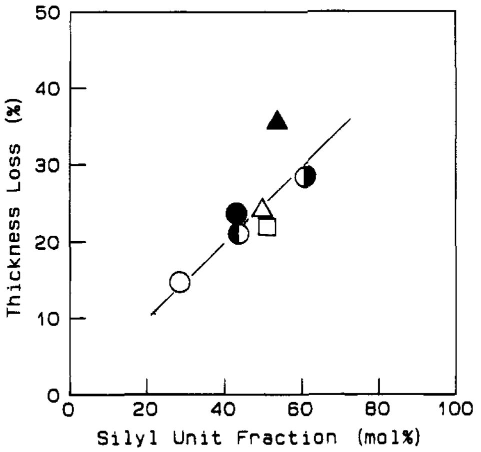

Figure 8. Relationship between thickness loss of films after 100% removal of the silicon species and fraction of the silyl ester or silyl ether units in polymers . Sample films containing 10 mol % of NTS were irradiated (430 mJ/cm^2) and subsequently exposed to the vapor of acetone for 30 min. Film thickness: 0.45 μm. Polymer: (○) **1a**, (◐) **1b**, (◑) **1c**, (▲) **2**, (△) **3**, (□) **4**, (●) **5**.

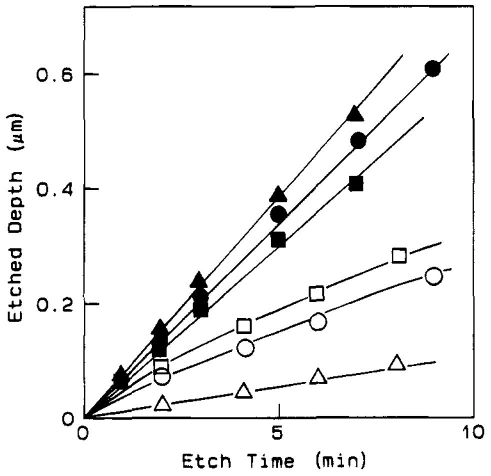

Figure 9. Plots of thickness loss versus etch time for the films of **1a–c** containing 10 mol % of NTS before (open symbol) and after (closed symbol) removal of the silicon species. Polymer: (□) **1a**, (○) **1b**, (△) **1c**.

measured by multiple-beam interferometry. Figure 8 shows the relationship between the thickness loss and fraction of the silyl ester or silyl ether units in the polymers. For the polymers having trimethylsilyl ester or trimethylsilyl ether moieties, the thickness loss was proportional to the mole fraction of the silyl units. The thickness loss for the film of **2** having a *tert*-butyldimethylsilyl moiety was larger than those for the polymers containing trimethylsilyl ester units because of the greater volume of the silyl group in the *tert*-butyl polymer.

Oxygen Plasma Etching. Figure 9 shows the thickness loss of **1a–c** films as a function of etch time using an oxygen plasma. The etch rates of the films of **1a**, **1b**, and **1c** were 36, 28, and 12 nm/min, respectively. Increased silyl ester content in polymers reduced the etch rate, while the etch rate increased after removal of silicon species. The etch rate for the **1c** film after removal of silicon species was higher than that for **1c** film by a factor of 7.2.

Figure 10 shows the etching rates of the **1b** film containing NTS or PTS before and after removal of silicon species. The rate of the **1b** film was not affected by the type of photoacid generator, NTS and PTS. The etched depth of the desilylated **1b** film containing PTS linearly increased until the etched thickness above 1 μm. When NTS was used as a photoacid generator, the etching rate of the desilylated **1b** film was strongly reduced after an 8 min etching. The initial rates were almost the same. Thus, the leveling off at longer etching times was assigned to the existence of trimethylsilyl ester units in the film, because NTS had a larger molar extinction coefficient (1.51 × 104 L/mol cm) at 254 nm than that (4.6 × 102 L/mol cm) of PTS. The depth to which the removal of silicon species occurs can be determined by the penetration depth of 254-nm light which induced the photolysis of the photoacid generator. The light penetrating depth depends upon the molar extinction coefficient of the photoacid generators at 254 nm. When PTS was used as a photoacid generator, it was possible to accomplish the removal of silicon species from the irradiated film more than 1 μm thick, but for NTS the maximum depth was $\leq$0.5 μm.

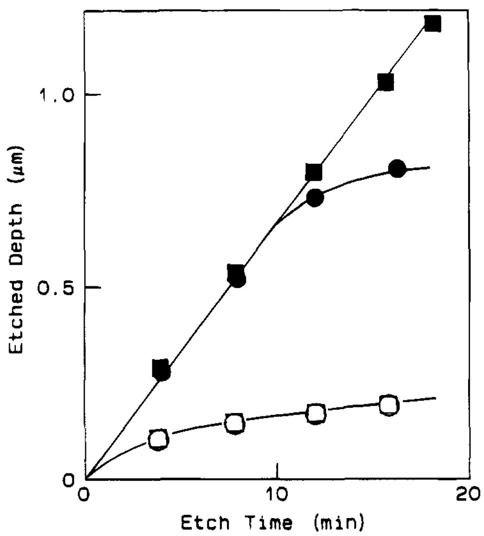

Figure 10. Plots of thickness loss versus etch time of the film of **1b** containing 10 mol % of NTS (○) or PTS (□). Open and closed symbols mean before and after removal of the silicon species from the film, respectively.

Conclusions

Polymers bearing silyl ester or silyl ether units were synthesized. When the polymer films containing photoacid generators were irradiated with 254-nm light, volatile silicon species were formed in the film by the photochemically induced acid-catalyzed hydrolysis of silyl ester or silyl ether units. It was found that the volatile silicon species in the film were completely removed by exposing the irradiated film to the vapor of organic solvents such as acetone, methanol, and *n*-hexane at room temperature and atmospheric pressure. The plasticization of the film by the sorption of the vapor of organic solvents enhanced the removal of the silicon species in the film. UV irradiation and subsequent treatment of the film with the vapor of organic solvents enhanced the rate of etching with an oxygen plasma.

Acknowledgment. This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science, and Culture, Japan (No. 06805084).

CM940358S